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# Kinetics of Carbon Dioxide with Amines. I. Stopped-Flow Studies in Aqueous Solutions. A Review

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**Résumé — Cinétique du dioxyde de carbone avec les amines – I. Étude par *stopped-flow* en solution aqueuse. Une revue** — Il est possible de trouver de nombreuses informations sur la cinétique de réaction amine-CO<sub>2</sub> dans la littérature. Toutefois, comme il existe plusieurs techniques expérimentales et plusieurs mécanismes réactionnels possibles, on observe parfois une grande dispersion des résultats expérimentaux avec diverses interprétations. Dans cet article, une méthode qui permet de comparer les constantes cinétiques obtenues par différents auteurs est proposée. D'abord nous présentons les différentes techniques expérimentales et justifions de comparer les données obtenues par la technique d'écoulement à flux bloqué. Ensuite nous représentons les données cinétiques des différentes amines étudiées dans la littérature à partir d'une dépendance en loi puissance en fonction de la concentration. Cette représentation illustre certaines relations structure-propriété et permet de confronter les données expérimentales aux différents mécanismes proposés. Les avantages et limites de chaque mécanisme sont discutés. Finalement nous justifions l'utilisation d'un modèle termoléculaire pour comparer les données obtenues par différents auteurs. Ce modèle conduit à l'observation d'un phénomène de compensation qui est un argument en faveur du mécanisme correspondant.

**Abstract — Kinetics of Carbon Dioxide with Amines. I. Stopped-Flow Studies in Aqueous Solutions. A Review** — It is possible to find plenty of information about kinetics of reaction between amine and carbone dioxide in the literature. However, there are several experimental techniques and several possible mechanisms which lead to observe sometimes high dispersion of experimental results with various interpretations. A method which enables to compare kinetic constant got by different authors is proposed in this work. First, we present experimental techniques and justify comparison of data obtained by stopped-flow technique. Then, we plot kinetic data for all amines studied in the literature by a power law dependency with the concentration. This representation illustrates some structure-activity relationships and enables to confront experimental results with the different mechanisms. Advantages and limits of each mechanism are discussed. Finally, we justify the choice of the termolecular model to compare data got by different authors. This model leads to a compensation effect which is an argument in favour of this mechanism.

## INTRODUCTION

Nowadays carbon dioxide (CO<sub>2</sub>) emissions represent over 76% of total emissions of greenhouse gases (Contribution of Working Groups *et al.*, 2008) in terms of CO<sub>2</sub> equivalent. These emissions are mainly due to production of electricity by combustion of fossil hydrocarbons. Amongst other solutions, Post-Combustion Capture (PCC) and storage of CO<sub>2</sub> seems to be an efficient way to reduce greenhouse gases emissions (de Coninck, 2010). Today, efficiency of several PCC processes has been demonstrated at large pilot-plant scale: KS-1 process (Mitsubishi), Chilled Ammonia process (Alstom), MEA based processes (IFPEN-Prosernat, Fluor), etc. Nevertheless, these processes have not been deployed intensively on power plants, mainly due to the cost associated to CO<sub>2</sub> capture with respect to penalties for CO<sub>2</sub> emissions.

Indeed, these processes suffer from a high energy consumption due to the low concentration of CO<sub>2</sub> in the flue gas, that represents the biggest part of the cost associated to CO<sub>2</sub> capture. Thus, in last years, amines with improved thermodynamic performances (Lecomte *et al.*, 2010) or advanced processes (Aleixo *et al.*, 2011; Raynal *et al.*, 2011) have been developed in order to address this issue. As the energy penalty is reduced, investment becomes more and more significant in the cost of CO<sub>2</sub> capture. Thus, more attention should be paid today on kinetics, in order to reduce the height of absorption column that is an important part of the investment. Indeed, the kinetics of the reaction between carbon dioxide and amine affects directly the height of the absorption column. For a given quantity of captured carbon dioxide, the absorption column will be shorter as the reaction is faster (van Loo *et al.*, 2007).

The kinetics of the reaction of CO<sub>2</sub> with different amines has been studied for nearly forty years. During this period methods used by authors have been improved on several aspects: better experimental tools, better mathematical method, more detailed mechanisms etc. On one hand, these improvements allow a better representation of the kinetics of amine-CO<sub>2</sub> system, and thus a better simulation of what happens in an absorption column. On the other hand, results available in the literature cannot be directly compared, because of discrepancies between equipments, experimental conditions and/or models used for data analysis. Thus, it is difficult to infer from these data a good understanding of the influence of the structure of the amine on the kinetics.

The present work describes an original approach which enables to compare data from different authors, in order to get an overview on kinetics of amine-CO<sub>2</sub> systems. First, we justify comparison of results from

different authors on different amines obtained with the stopped-flow technique. In fact, this technique covers a large range of reaction rates and is quite reproducible. Next, we choose to analyze kinetic data obtained by a monoexponential model which is the most widespread method to extract kinetic constant from stopped-flow experiments. Collected data are fitted by a power law dependency of first-order constant with concentration. Influence of *pKa* and steric hindrance on kinetic constants and order are observed and discussed with respect to the different mechanisms proposed in the literature. Nevertheless, we demonstrate that it is impossible to determine an univocal set of kinetic constant associated with the zwitterion mechanism. Single step termolecular mechanism is satisfactory to fit data with only two kinetic constants. A compensation effect is observed between preexponential factor and activation energy of these constants.

## 1 OVERVIEW OF EXPERIMENTAL TECHNIQUES

Experimental techniques for kinetic measurements on amine-CO<sub>2</sub> systems can be classified in two types of equipment at the laboratory scale: measurement of gas-liquid mass transfer rate on the one hand, and *in situ* measurements of reaction rate after rapid mixing of liquid phases on the other hand. Both types of techniques present advantages and drawbacks for data comparison and the establishment of a structure-activity relationship.

### 1.1 Mass-Transfer Techniques

Several kinds of gas-liquid reactors are dedicated to measure the kinetics of CO<sub>2</sub> absorption in amine solutions (Laurent *et al.*, 1975). Each of these equipments based on gas-liquid absorption measurement is characterized by a limited range of contact time or liquid mass transfer coefficient, and thus allows measurements in a given concentration range for appropriate formulations of amine. Since reaction rates of amines with CO<sub>2</sub> vary on several orders of magnitude, none of these equipments is adequate for accurate determination of kinetic parameters in the large experimental domain covered by the great variety of amines.

For example, a kinetics of absorption by a 30 wt% monoethanolamine solution will be studied on a wetted-wall column (Puxty *et al.*, 2010), whereas a 50 wt% methyldiethanolamine will be studied on a stirred vessel (Versteeg and van Swaaij, 1988b).

These techniques also imply the use of a mass-transfer model to analyze experimental data. This model takes

into account the thermodynamic equilibrium, the hydrodynamics of gas and liquid phase, physical solubility, diffusion of reactants and products in the liquid phase to fit measured mass transfer rate. In these conditions, estimation of kinetic constants greatly depends on the different hypotheses of the mass transfer model (Danckwerts, 1970; Laurent and Charpentier, 1974; Charpentier, 1981) which can provide additional source of dispersions on data.

For diethanolamine, which is commonly used in gas treatment, Rinker *et al.* (1996) show that dispersion between second order apparent kinetic constants found by different authors is higher than 50%.

### 1.2 Rapid Mixing Techniques

The most widely used of rapid mixing techniques for CO<sub>2</sub>-amine studies is the stopped-flow technique. In comparison with mass-transfer techniques, stopped-flow technique enables to determine kinetic constant usually ranged between about 0.01 and 1 000 s<sup>-1</sup>, the upper limit corresponding to the inverse of the mixing time which is close to 1 ms. It is then not suited to study kinetics of reaction of fast-reacting amines in industrial conditions. However, kinetic measurements with stopped-flow technique are free from gas-liquid mass transfer limitations. Signal can be directly related to the intrinsic reaction in the liquid phase which makes the method very reproducible. Rayer *et al.* (2011) show that the overall uncertainty on a these data are generally around 5%. Then this method is well fitted to draw quantitative structure activity relationship from the comparison of intrinsic kinetics of reaction of very different amines with CO<sub>2</sub>.

### 1.3 Scope of This Work

This review intends to compile experimental data obtained with the stopped-flow technique.

Different methods are available to treat raw data from this technique, which depend on detection type (conductimetry, spectrophotometry, etc.), mechanistic hypotheses and operating condition. For our purpose, we shall choose a common method to compare kinetic constants of amine studied by different authors.

## 2 DATA TREATMENT OF STOPPED-FLOW DATA

We distinguish two methods to derive kinetic parameters from stopped-flow data: numerical model on the one hand and analytical model on the other hand. We consider advantages and drawbacks of both methods to select the most adapted to our purpose.

### 2.1 Numerical Models

Numerical models take into account all chemical species with the reactions and thermodynamic equilibria in which they are involved. Kinetic parameters are optimized to reduce deviation between the model and experimental data. This kind of models is necessary when spectrophotometric detection is used to follow the reaction (Barth *et al.*, 1981, 1983, 1984, 1986) or if operating conditions like CO<sub>2</sub> loading is not compatible with an analytical solution of the model (Conway *et al.*, 2011, 2012; McCann *et al.*, 2009, 2011; Wang *et al.*, 2011; Xiang *et al.*, 2012).

Although these methods are quite exhaustive, results on kinetic constants are still dependant on mechanistic hypotheses or thermodynamic model for non ideal solutions.

### 2.2 Analytical Model

Analytical model is the most widespread approach for stopped-flow studies on amine-CO<sub>2</sub> reaction. This approach considers a single, irreversible reaction with amine in large excess, of first order with respect to CO<sub>2</sub>. Generally, authors operate with a total concentration of amine at least ten times higher than the concentration of carbon dioxide. In these conditions, the variation of concentration of chemical species depends on the pseudo first order kinetic constant  $k_0$  according to a monoexponential variation. For conductivity stopped flow measurements, the variation of concentrations of ionic species is monitored by the change of conductance in the solution. Conductance  $G$  (S) is the inverse of the electric resistance  $R$  ( $\Omega$ ),  $A$  (S) is the amplitude of the signal,  $k_0$  the pseudo first order kinetic constant,  $t$  (s) is the time and  $C$  (S) is the value of the conductance at the end of the observed reaction. Variation of conductance is then related to formation of amine salts and to  $k_0$  according Equation (1) (Ali *et al.*, 2000):

$$\frac{1}{R(t)} = G(t) = -A \times \exp(-k_0 \times t) + C \quad (1)$$

The pseudo first order kinetic constant  $k_0$  is defined as shown by Equation (2). When it is measured in a large excess of amine,  $k_0$  depends on the nature of the amine, the concentration of amine and the temperature. For the rest of the article, we decided to use  $k_0$  values because they directly come from stopped-flow raw data which are quite reproducible. Then, we limit our work to compare first order kinetic constant obtained by this analytical method:

$$r_{\text{CO}_2} = k_0 \cdot [\text{CO}_2] \quad (2)$$

### 3 SYNTHESIS OF KINETIC DATA

#### 3.1 Representation of the Raw Data

All pseudo-first order constants  $k_0$  determined with a stopped-flow apparatus with a conductimetric detection and available in the literature have been compiled. The studied amines and the corresponding references are listed in Table 1. Some amines have been studied by different authors and, apart from two cases (Ali *et al.*, 2010) for molecule No. 8 (methylethanolamine), and (Crooks and Donnellan, 1989) for molecule No. 18 (diethanolamine), a discrepancy smaller than 25% between kinetic constants is observed. After elimination of the two latter references, we retain for each amine the study that covers the largest range of amine concentration and where data are available at 25°C. Corresponding references have been represented in bold in Table 1.

In order to analyze these raw data, without any mechanistic assumption, we determine the two parameters  $k_{Am}$  and  $n$  of the power law model given by Equation (3) by fitting variation of experimental pseudo first order constant  $k_0$  as a function of concentration for each amine.  $k_{Am}$  is an empirical kinetic constant and  $n$  is the apparent order of reaction with respect to amine. The average relative deviation between the experimental constants and this model over all data is 7.3%. For each amine, parameters  $k_{Am}$  and  $n$  are plotted in Figure 1. We also represent by continuous lines values of  $(k_{Am}, n)$  giving the same value of  $k_0$  for concentration of amine of  $100 \text{ mol.m}^{-3}$ . This concentration has been chosen because all studied amines can be evaluated at this concentration (1 wt% for molar weight of  $100 \text{ g.mol}^{-1}$  and a density of  $10^6 \text{ g.m}^{-3}$ ) in the operating range available by the stopped-flow technique:

$$k_0 = k_{Am} \cdot [Am]^n \quad (3)$$

#### 3.2 Analysis of the Raw Data

Values of  $k_{Am}$  and  $n$  plotted in Figure 1 are reported in Table 2 with the average relative deviation between the model and the experimental data. Apparent order  $n$  with respect to amine is between 0.6 and 2.0.

Most of tertiary amines, represented by triangles in Figure 1, have an apparent global order of reaction close to 1 with respect to amine. For molecules 5, 6 and 11, we observe an apparent order lower than 1. A linear fit (order = 1) will in fact lead to an intercept which is significantly different from zero, showing evidence of another reaction being preponderant in diluted solutions which shows increasing rate with  $pK_a$ . We can force order of these molecules at 1 as it is done by most of authors. From this point, we only consider values of

$k_{Am}$  obtained from fitting with  $n = 1$  for tertiary amines. Corresponding values of the empirical kinetics constant  $k_{Am}$  are between  $3 \times 10^{-3}$  and  $10^{-1} \text{ m}^3.\text{mol}^{-1}.\text{s}^{-1}$  and increase with the value of  $pK_a$  of the tertiary amine.

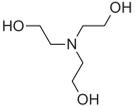
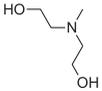
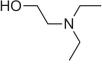
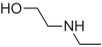
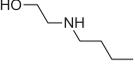
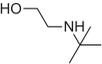
Primary and secondary amines, represented by circles have a global order of reaction included between 1 and 2 with respect to amine. Several observations can be drawn from these data.

Series of monoamines No. 7 to 11 correspond to ethanolamines R-NH-CH<sub>2</sub>-CH<sub>2</sub>-OH with R being with increasing number: hydrogen (7), methyl (8), ethyl (9), *n*-butyl (10) and tert-butyl (11). For this series of molecules, the  $pK_a$  varies between 9.44 and 10.12 with an increasing steric hindrance around the nitrogen group. This variation of  $pK_a$  and steric hindrance is correlated with significant variations of  $k_{Am}$  and  $n$ . It is very interesting to notice that the effect of hindrance around the amino group on the order  $n$  is not monotone: starting from 1.2 with MEA, it first increases up to a maximum around 2 for ethylethanolamine, and then decreases down to a value of 1 for tert-butylethanolamine. It is also possible to compare  $k_0$  for this amine at a concentration of  $100 \text{ mol.m}^{-3}$ : we see first an increase of the reaction rate from MEA to methylethanolamine, and an increasing negative effect of hindrance on  $k_0$  as the alkyl substituent of the secondary amine gets longer or more substituted, as  $k_0$  decreases by two orders of magnitude between methylethanolamine and tert-butylethanolamine.

Another result that needs to be pointed out, is the fact that all molecules having an amino group linked to a quaternary carbon (No. 11 to 14) have a value of order  $n$  less than 1.2. For these molecules, reaction rates figured by  $k_0$  are intermediate between tertiary amine on one hand and moderately hindered primary and secondary amines on the other hand. For example, tert-butylethanolamine (11), that can be fitted with  $n = 1$ , has a 2.3 time higher value of  $k_{Am}$  compared to the fastest tertiary amine (6). This difference is likely explained by the higher  $pK_a$  of tert-butylethanolamine. According to Ali *et al.* (2002), this amine fits the description given by Sartori and Savage (1983) of a severely sterically hindered amine. These authors have suggested that such amines are unable to form a carbamate and then behave as tertiary amine. If we now have a closer look on the series of molecules 12 to 14, which are all primary amine with an amino group linked to a quaternary carbon and exhibit an order  $n$  of 1.2, an increase of the  $pK_a$  tends to increase the value of  $k_{Am}$ , as it has been already pointed out with tertiary amine. However, these sterically hindered primary amines are faster to react with CO<sub>2</sub> than tertiary amines having same  $pK_a$ , as can be seen by comparing (6) with (12) ( $pK_a = 9.72-9.75$ ) or (13) with (5) ( $pK_a = 9.48-9.50$ ).

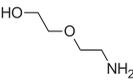
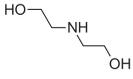
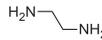
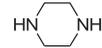
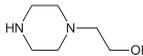
TABLE 1

Name, chemical structure, references of stopped-flow kinetic studies of amine-CO<sub>2</sub> reaction with conductimetric detection, concentration range, temperature range, *pKa* at 25 °C and references of *pKa* values. References selected for determination of (*k<sub>Am</sub>*, *n*) parameters at 25°C are indicated in bold

Name	Number	Chemical structure	Authors	Concentration range (mol.m <sup>-3</sup> )	Temperature range (°C)	<i>pKa</i> at 25°C	References
Triethanolamine	1		<b>Crooks and Donnellan (1990)</b>	<b>25-176</b>	<b>25</b>	7.76	da Silva and Svendsen (2007)
Methyldiethanolamine	2		<b>Crooks and Donnellan (1990)</b>	<b>25-176</b>	<b>25</b>	8.52	da Silva and Svendsen (2007)
Dimethylmonoethanolamine	3		<b>Henni et al. (2008)</b>	<b>303-986</b>	<b>25-40</b>	9.23	da Silva and Svendsen (2007)
3-Dimethylamino-1-propanol	4		<b>Kadiwala et al. (2012)</b>	<b>350-1 003</b>	<b>25-40</b>	9.54	Kadiwala et al. (2012)
1-Dimethylamino-2-propanol	5		<b>Kadiwala et al. (2012)</b>	<b>238-1 000</b>	<b>25-40</b>	9.50	Kadiwala et al. (2012)
Diethylmonoethanolamine	6		<b>Li et al. (2007)</b>	<b>197-997</b>	<b>25-40</b>	9.75	da Silva and Svendsen (2007)
Monoethanolamine	7		Crooks and Donnellan (1989) Alper (1990b) <b>Ali et al. (2002)</b>	20-59 28-52 (at 25°C) <b>5-36</b>	25 5-40 <b>25-40</b>	9.44	Hamborg and Versteeg (2009)
Methylethanolamine	8		<b>Ali et al. (2002)</b> <b>Ali et al. (2010)</b> Bavbek and Alper (1999)	<b>8-39</b> 20-69 25-50	<b>10-35</b> 25-40 30	9.85	Hamborg and Versteeg (2009)
Ethylethanolamine	9		<b>Li et al. (2007)</b> Bavbek and Alper (1999)	<b>28-82</b> 25-50	<b>25-40</b> 30	9.89	Chemicalize (2012a)
<i>n</i> -Butylethanolamine	10		<b>Ali et al. (2002)</b>	<b>20-98</b>	<b>10-35</b>	10.00	Chemicalize (2012b)
Tert-Butylethanolamine	11		<b>Ali et al. (2002)</b>	<b>17-63</b>	<b>10-35</b>	10.12	Littel et al., (1990b)
2-amino-2-methyl-1-propanol	12		<b>Alper (1990b)</b> Ali (2005)	<b>25-1 486</b> (at 25°C) 54-346	<b>5-25</b> 25-40	9.72	da Silva and Svendsen (2007)

(continued)

TABLE 1 (continued)

Name	Number	Chemical structure	Authors	Concentration range (mol.m <sup>-3</sup> )	Temperature range (°C)	pKa at 25°C	References
2-amino-2-methylpropan-1,3-diol	13		<a href="#">Bouhamra et al. (1999)</a>	<b>25-1 351</b> (at 25°C)	<b>5-30</b>	9.48	<a href="#">Chemicalize (2012b)</a>
2-amino-2-hydroxymethyl-1,3-propanediol	14		<a href="#">Ume and Alper (2012)</a>	<b>500-2 000</b>	<b>25</b>	8.95	<a href="#">Chemicalize (2012d)</a>
1-amino-2-propanol	15		<a href="#">Henni et al. (2008)</a> <a href="#">Bavbek and Alper (1999)</a>	<b>25-82</b> 25-50	<b>25-40</b> 30	9.46	<a href="#">da Silva and Svendsen (2007)</a>
3-amino-1-propanol	16		<a href="#">Henni et al. (2008)</a> <a href="#">Bavbek and Alper (1999)</a>	<b>27-61</b> 25-50	<b>25-40</b> 30	10.0	<a href="#">da Silva and Svendsen (2007)</a>
2-(2-aminoethoxy)ethanol	17		<a href="#">Alper (1990a)</a>	<b>12-206</b> (at 25°C)	<b>5-25</b>	9.46	<a href="#">da Silva and Svendsen (2007)</a>
Diethanolamine	18		<a href="#">Crooks and Donnellan (1989)</a> <a href="#">Ali (2004)</a> <a href="#">Li et al. (2007)</a>	100-1 016 <b>66-519</b> 150-518	25 <b>25-40</b> 25-40	8.96	<a href="#">da Silva and Svendsen (2007)</a>
Morpholine	19		<a href="#">Alper (1990a)</a> <a href="#">Ali et al. (2010)</a>	<b>3-102 (at 25°C)</b> 32-130	<b>5-25</b> 25-40	8.49	<a href="#">da Silva and Svendsen (2007)</a>
Ethylenediamine	20		<a href="#">Li et al. (2007)</a> <a href="#">Rayer et al. (2011)</a>	26-68 <b>20-101</b>	25-40 <b>25-40</b>	9.92	<a href="#">da Silva and Svendsen (2007)</a>
Piperazine	21		<a href="#">Gordesli and Alper (2011)</a>	<b>10-100 (at 25°C)</b>	<b>5-25</b>	9.71-5.41	<a href="#">Hamborg and Versteeg (2009)</a>
Hydroxyethylpiperazine	22		<a href="#">Ume et al. (2012)</a>	<b>2.5-30</b>	<b>25</b>	8.92-3.97	<a href="#">Hamborg and Versteeg (2009)</a>

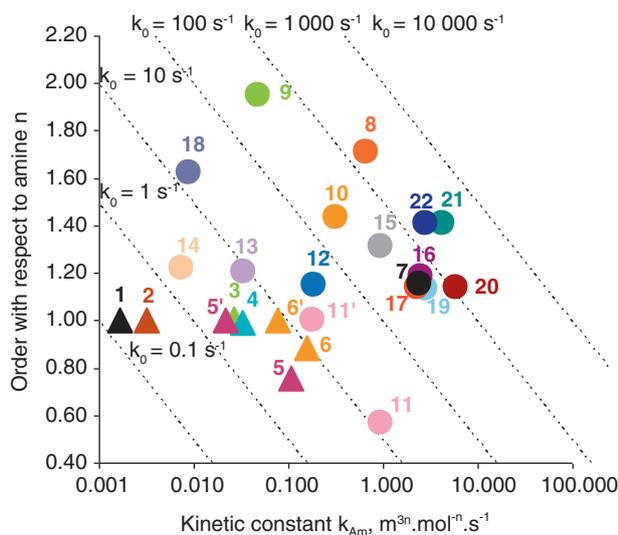


Figure 1

Values of  $k_{Am}$ ,  $n$  obtained from references in bold of Table 1. Plot of  $(k_{Am}, n)$  according to  $k_0 = k_{Am}[Am]^n$  for tertiary amines ( $\blacktriangle$ ), primary and secondary amines ( $\bullet$ ) listed in Table 1. Continuous lines represent values of  $(k_{Am}, n)$  giving the same value of  $k_0$  for  $[Am] = 100 \text{ mol.m}^{-3}$ . Setting  $n = 1$  for molecules 5, 6 and 11 gives 5', 6', 11'.

Finally, molecules 18 and 19 can be compared. These molecules are both secondary amines with the same number of carbon between nitrogen and the oxygen atoms. Linear diethanolamine (18) reacts 10 times more slowly than cyclic morpholine (19) at  $100 \text{ mol.m}^{-3}$  in spite of the fact that DEA is more basic.

Unfortunately, not enough multiamines have been tested in the literature to draw conclusions. We can just point out that molecule 20, 21 and 22 are the ones that exhibit the fastest kinetics.

Explanations of observed behaviors may be found in the different mechanisms proposed in the literature for tertiary amines on one hand, for primary and secondary amine on the other hand.

## 4 TERTIARY AMINES

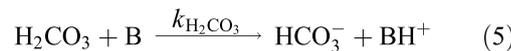
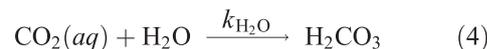
### 4.1 Mechanism Proposed in Literature

Absorption of  $\text{CO}_2$  in aqueous amine solutions implies two sets of reaction. The first set of reactions involves carbon dioxide with water or hydroxide ions and is common to all amines. The second set of reactions for tertiary amine is distinct from primary and secondary

amines, the latter forming carbamates. We limit here to reactions of  $\text{CO}_2$  with large excess of amine, without taking into account reversibility.

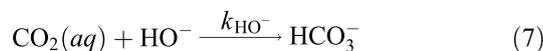
#### 4.1.1 Common Pathway

Carbon dioxide in presence of water is hydrated and forms carbonic acid (4). Carbonic acid reacts with a basic compound (B) present in solution (5). The base can be an amine, water or an hydroxide ion. Pinsent *et al.* (1956) showed first that reaction (4) is the limiting step and determined the pseudo-first-order associated rate constant (at  $25^\circ\text{C}$   $k'_{\text{H}_2\text{O}} = 2.57 \times 10^{-2} \text{ s}^{-1}$ ). More recently Soli and Byrne (2002) determined the rate of this reaction (at  $25^\circ\text{C}$   $k'_{\text{H}_2\text{O}} = 3.06 \times 10^{-2} \text{ s}^{-1}$ ). These values are not identical but have the same order of magnitude. They show that this reaction is very slow in front of hydroxyde- $\text{CO}_2$  and amine- $\text{CO}_2$  reaction described below. The rate of reaction of carbon dioxide according to hydration mechanism is shown by Equation (6):



$$r_{\text{CO}_2}^{\text{H}_2\text{O}} = \underbrace{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] \cdot [\text{CO}_2]}_{k'_{\text{H}_2\text{O}}} \quad (6)$$

In aqueous basic solution, carbon dioxide reacts with an hydroxide ion to form a bicarbonate ion (7). Rate of this reaction is given by kinetic law (8). The correlation determined by Pinsent *et al.* (1956) gives  $k_{\text{HO}^-} = 8.32 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  at  $25^\circ\text{C}$ :



$$r_{\text{CO}_2}^{\text{HO}^-} = k_{\text{HO}^-} \cdot [\text{CO}_2] \cdot [\text{HO}^-] \quad (8)$$

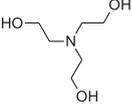
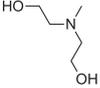
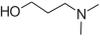
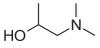
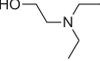
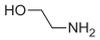
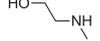
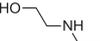
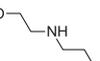
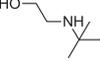
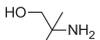
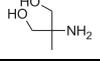
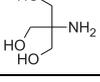
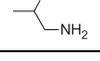
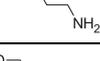
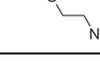
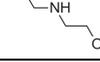
#### 4.1.2 Tertiary Amine Mechanisms

Donaldson and Nguyen (1980) show that tertiary amines ( $\text{R}_3\text{N}$ ) do not react directly with carbon dioxide. Tertiary amines are used as “pseudo-catalyst”. They accelerate the reaction of hydration of carbon dioxide. For this reason, this mechanism is called based-catalyzed hydration mechanism (9). Since concentration of water does not vary too much in kinetic studies and is in large excess, this reaction is generally considered to be first order with respect to amine concentration (10) with the pseudo-constant  $k'_{\text{R}_3\text{N}} = k_{\text{R}_3\text{N}} \cdot [\text{H}_2\text{O}]$  (Crooks and Donnellan, 1990):



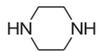
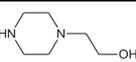
TABLE 2

Chemical structure, number, value of  $k_{Am}$  and  $n$  for selected data with average relative deviation between model and experimental data on concentration range specified in Table 1

Chemical structure	Number	$k_{Am}$ ( $m^3 \cdot mol^{-n} \cdot s^{-1}$ )	$n$	Average relative error (%)
	1	$1.66 \times 10^{-3}$	0.99	0.4
	2	$3.20 \times 10^{-3}$	0.99	3.3
	3	$2.64 \times 10^{-2}$	1.01	2.4
	4	$3.29 \times 10^{-2}$	0.99	12.1
	5	$1.06 \times 10^{-1}$	0.76	3.6
	5'	$2.17 \times 10^{-2}$	1.00	7.3
	6	$1.58 \times 10^{-1}$	0.89	3.3
	6'	$7.58 \times 10^{-2}$	1.00	5.9
	7	$2.42 \times 10^0$	1.16	5.4
	8	$6.54 \times 10^{-1}$	1.71	3.6
	9	$4.76 \times 10^{-2}$	1.95	7.9
	10	$3.17 \times 10^{-1}$	1.43	3.3
	11	$9.54 \times 10^{-1}$	0.57	12.6
	11'	$1.83 \times 10^{-1}$	1.00	20.6
	12	$1.84 \times 10^{-1}$	1.15	5.9
	13	$3.31 \times 10^{-2}$	1.21	8.3
	14	$7.54 \times 10^{-3}$	1.22	5.0
	15	$9.29 \times 10^{-1}$	1.31	3.7
	16	$2.15 \times 10^0$	1.18	2.1
	17	$2.25 \times 10^0$	1.14	7.6
	18	$8.96 \times 10^{-3}$	1.62	2.9
	19	$2.78 \times 10^0$	1.14	7.7

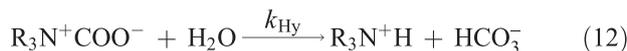
(continued)

TABLE 2 (continued)

Chemical structure	Number	$k_{Am}$ ( $m^{3n} \cdot mol^{-n} \cdot s^{-1}$ )	$n$	Average relative error (%)
	20	$5.95 \times 10^0$	1.14	5.5
	21	$4.30 \times 10^0$	1.41	7.2
	22	$2.84 \times 10^0$	1.41	30.9

$$r_{CO_2}^{R_3N} = \underbrace{k_{R_3N} \cdot [H_2O]}_{k'_{R_3N}} \cdot [CO_2] \cdot [R_3N] \quad (10)$$

A two-step mechanism was also suggested by Yu *et al.* (1985). Carbon dioxide reacts first with the amine to form a zwitterion (11). The zwitterion is then hydrolyzed by water to form ammonium ions and bicarbonate ions (12). As a very instable intermediate, the zwitterion is assumed at a steady state low concentration. With this assumption, reaction rate of  $CO_2$  is shown in Equation (13):



$$r_{CO_2}^{R_3N} = \frac{[R_3N] \cdot [CO_2]}{\frac{1}{k_{NA}} + \frac{1}{k_{Hy}^{H_2O}}} = k'_{R_3N} [R_3N] \cdot [CO_2] \quad (13)$$

$$\text{with } \frac{1}{k'_{R_3N}} = \frac{1}{k_{NA}} + \frac{1}{k_{Hy}^{H_2O}} \text{ and } k_{Hy}^{H_2O} = \frac{k_{NA} \cdot k_{Hy}^{H_2O} [H_2O]}{k_{-NA}}$$

In the case of tertiary amines, the overall rate of reaction of carbon dioxide (Eq. 14) corresponds to the sum of the contributions of three reaction paths (4 + 5), (7), and the reaction with the tertiary amine (9) or (11 + 12). Based-catalyzed hydration mechanism or zwitterion mechanism both yield to an order of reaction of one with respect to amine:

$$r_{CO_2}^{III} = r_{CO_2}^{H_2O} + r_{CO_2}^{HO^-} + r_{CO_2}^{R_3N} \quad (14)$$

## 4.2 Confrontation with Experimental Data

Based catalyzed hydration mechanism and zwitterion mechanism are both first order mechanisms with respect to amine. Both mechanisms can then explain experimental results of Figure 1, considering that reaction of  $CO_2$  with water and  $HO^-$  is neglected.

We focus our discussion on the six tertiary amines presented in Tables 1 and 2. In these tables, we indicate results of  $pKa$  at 25°C determined by da Silva and Svendsen (2007) and Kadiwala *et al.* (2012) for these

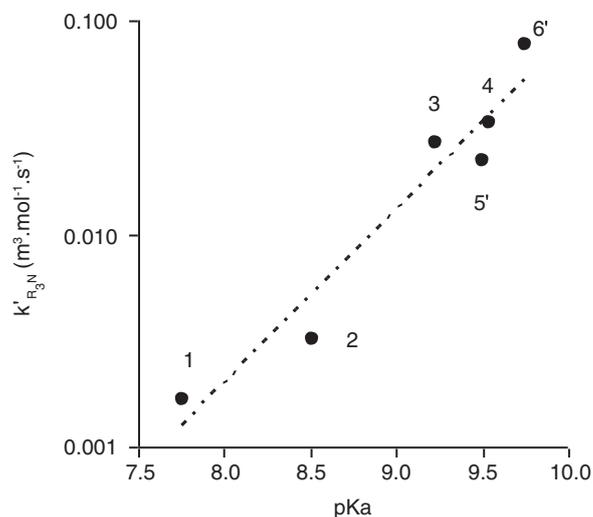


Figure 2

Kinetic constant  $k'_{R_3N}$  values versus  $pKa$ .

$$k'_{R_3N} = 6.22 \times 10^{-10} \cdot \exp(1.87 \times pKa) \text{ and } R^2 = 0.93.$$

amines. Since kinetics of tertiary amine- $CO_2$  shows a partial order of 1 with respect to amine,  $k_{Am}$  is identified to  $k'_{R_3N}$ .

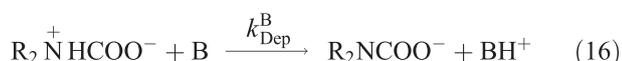
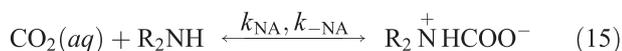
We plot in Figure 2 values of  $k'_{R_3N}$  as a function of  $pKa$ . We outline, as suggested by Littel *et al.* (1990a) that the logarithm of the second order kinetic constant of amine- $CO_2$  reaction shows a quasi linear variation with the of  $pKa$  of the amine according to a Brønsted relationship.

## 5 PRIMARY AND SECONDARY AMINES

### 5.1 Mechanisms Proposed in Literature

Primary and secondary amines generally react with  $CO_2$  to form carbamates. As we limit our discussion to reactions of  $CO_2$  with large excess of amine, we do not take into account inverse reactions or hydrolysis of carbamate to carbonates.

The two-step mechanism proceeding through the formation of a zwitterion as an intermediate has been suggested for the first time by Caplow (1968) and reintroduced by Danckwerts (1979). In the first step, amine reacts with carbon dioxide and forms a zwitterion (15). Then zwitterion is deprotonated by a base B (16). In these equations,  $k_{NA}$  corresponds to the kinetic constant of the nucleophilic addition,  $k_{-NA}$  corresponds to the kinetic constant of the reverse reaction and  $k_{Dep}^B$  corresponds to the kinetic constant of the deprotonation of the zwitterion by a base B:



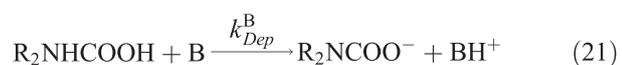
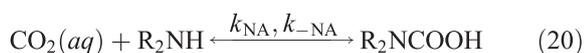
Versteeg and van Swaaij (1988a) have shown that deprotonation reaction with hydroxide ion as a base is insignificant for unloaded solution. Only amine and water have to be considered as bases for deprotonation of the zwitterion. The rate of the reaction of  $\text{CO}_2$  with amine is then given by Equation (17), assuming zwitterion concentration at quasi steady state (Danckwerts, 1979). We simplify this equation as shown by Equation (18) and with  $k_{Dep}^{\text{R}_2\text{NH}}$  and  $k_{Dep}^{\text{H}_2\text{O}}$  defined in Equation (19):

$$r_{\text{CO}_2}^{\text{R}_2\text{NH}} = \frac{[\text{R}_2\text{NH}] \cdot [\text{CO}_2]}{\frac{1}{k_{NA}} + \frac{k_{-NA}}{k_{NA}(k_{Dep}^{\text{R}_2\text{NH}} \cdot [\text{R}_2\text{NH}] + k_{Dep}^{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}])}} \quad (17)$$

$$r_{\text{CO}_2}^{\text{R}_2\text{NH}} = \frac{[\text{R}_2\text{NH}] \cdot [\text{CO}_2]}{\frac{1}{k_{NA}} + \frac{1}{k_{Dep}^{\text{R}_2\text{NH}} \cdot [\text{R}_2\text{NH}] + k_{Dep}^{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}]}} \quad (18)$$

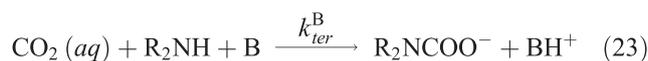
$$k_{Dep}^{\text{R}_2\text{NH}} = \frac{k_{NA} \cdot k_{Dep}^{\text{R}_2\text{NH}}}{k_{-NA}}; \quad k_{Dep}^{\text{H}_2\text{O}} = \frac{k_{NA} \cdot k_{Dep}^{\text{H}_2\text{O}}}{k_{-NA}} \quad (19)$$

Recently McCann *et al.* (2009) proposed a mechanism which is close to the zwitterion model. According to them, the reaction between carbon dioxide and amine forms a carbamic acid (20). Carbamic acid is a more stable tautomeric form of the zwitterion according to NMR measurements. Then carbamic acid is deprotonated instantaneously by a base (21). Reaction rate according to this carbamic acid mechanism is given by Equation (22) which has the same expression as the limit case of zwitterion model when nucleophilic addition is the rate-limiting step:



$$r_{\text{CO}_2}^{\text{R}_2\text{NH}} = k_{NA} \cdot [\text{R}_2\text{NH}] \cdot [\text{CO}_2] \quad (22)$$

Another mechanism which considers that carbon dioxide, amine and base react simultaneously, has been suggested by Crooks and Donnellan (1989). This termolecular mechanism (23) corresponds to a limiting case of the zwitterion mechanism where the limiting step is deprotonation. This mechanism has been recently supported by molecular modelisation (da Silva and Svendsen, 2004). In this work, da Silva and Svendsen (2004) show that energetic levels are in favour of a one step mechanism. In this equation,  $k_{ter}^B$  corresponds to the third order kinetic constant of the termolecular mechanism. By analogy with the zwitterion mechanism, termolecular reaction with hydroxide ions is insignificant. The reaction rate according to this termolecular mechanism is given by Equation (24). Third order kinetic constants  $k_{ter}^{\text{H}_2\text{O}}$  and  $k_{ter}^{\text{R}_2\text{NH}}$  correspond to the reaction of  $\text{CO}_2$  with respectively one molecule of amine and one molecule of water and two molecules of amine. The overall rate of carbon dioxide reaction for a primary or secondary amine is then given in Equation (25):



$$r_{\text{CO}_2}^{\text{R}_2\text{NH}} = k_{ter}^{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}] \cdot [\text{R}_2\text{NH}] \cdot [\text{CO}_2] + k_{ter}^{\text{R}_2\text{NH}} [\text{R}_2\text{NH}]^2 \cdot [\text{CO}_2] \quad (24)$$

$$r_{\text{CO}_2}^{I/II} = r_{\text{CO}_2}^{\text{H}_2\text{O}} + r_{\text{CO}_2}^{\text{HO}^-} + r_{\text{CO}_2}^{\text{R}_2\text{NH}} \quad (25)$$

## 5.2 Confrontation of Mechanisms with Experimental Data

The series of ethanolamines 7, 8, 9, 10 and 11 with increasing molecular weight and hindrance of substituting group on nitrogen, respectively hydrogen, methyl, ethyl, *n*-butyl and tert-butyl is represented by Figure 3. These molecules are in a *pKa* range between 9.44 for monoethanolamine (7) (Hamborg and Versteeg, 2009) and 10.12 for *t*-butyl-ethanolamine (11) (Littel *et al.*, 1990b) at 25°C. Values of *pKa* and *Taft* constants which give an indication of steric hindrance have been indicated in Table 3. Evolution of apparent order *n* with these parameters is a first trial for the three different mechanisms.

### 5.2.1 Carbamic Acid Mechanism

McCann *et al.* (2009) use the mechanism of carbamic acid to explain kinetics of monoethanolamine in loaded solution. Although it is convenient to account for first

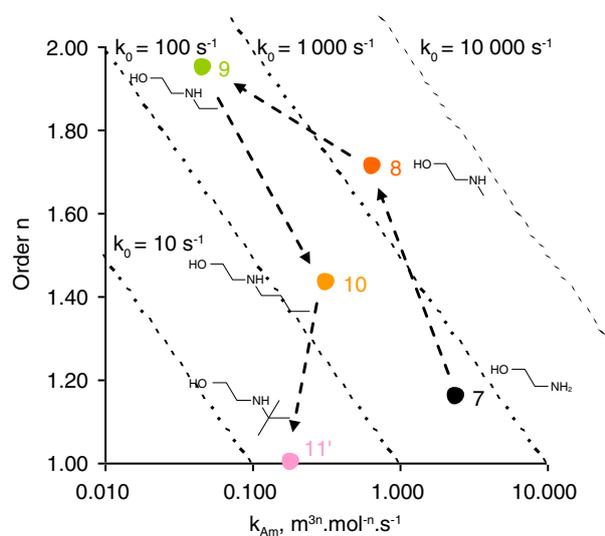


Figure 3

Values of  $(k_{Am}, n)$  ethanolamines (No. 7, 8, 9, 10 and 11) at 25°C. We indicate iso- $k_0$  lines for a concentration of amine of  $100 \text{ mol.m}^{-3}$ .

order kinetics with respect to amine, it can not be generalized to orders larger than 1.

### 5.2.2 Zwitterion Mechanism

For monoethanolamine (7), apparent order with respect to amine  $n$  is close to 1, which matches either with the nucleophilic addition or the deprotonation by water as the limiting step of the carbamate formation. Iida and Sato (2012) suggest that nucleophilic addition of zwitterion mechanism is the rate-limiting step. However, Kumar *et al.* (2003) assume that deprotonation by water is the limiting step at low concentration of amine. Since monoethanolamine is not sterically hindered, it seems

yet difficult to consider a deprotonation as a limiting step. Indeed, deprotonations reactions, which are acid-base reactions, are generally easier than nucleophilic addition, hydration or hydrolysis reaction. For example, at 25°C the rate constant of the reaction between oxonium ions and hydroxide ions in water is equal to  $1.4 \times 10^{11} \text{ dm}^3.\text{mol}^{-1}.\text{s}^{-1}$  (Atkins and de Paula, 2006).

With a methyl group on the nitrogen, methylethanolamine (8) is slightly more basic and moderately hindered. Apparent order  $n$  is close to 1.7. Consistently with the discussion on the monoethanolamine, this intermediate order for methylethanolamine (8) can be explained by a competition between nucleophilic addition step and deprotonation of zwitterion by the amine. With an ethyl group as a substituent (9), apparent order  $n$  is almost 2 consistent with a deprotonation of the zwitterion by the amine as the rate limiting step in the studied range of concentration.

With a  $n$ -butyl substituent to the nitrogen atom (10),  $n$  is close to 1.4 with a value of  $k_0$  10 times less than methylethanolamine (8) at the same concentration of  $100 \text{ mol.m}^{-3}$ . Two hypotheses can support this result. We either have a competition between nucleophilic addition step and deprotonation by amine or a competition between deprotonation by water and deprotonation by amine.

Further increase of steric hindrance for molecule 11 leads to an apparent order of 1. Instead of deprotonation, zwitterion reacts directly with water to form bicarbonate. It is yet not possible to assess which step is rate-limiting in this case. This mechanism has also been suggested by Yu *et al.* (1985) for tertiary amine as an alternative to the base-catalyzed hydration mechanism. Indeed, this molecule follows the Brønsted relationship observed in Figure 2 and then behaves as tertiary amines.

It comes out that the zwitterion mechanism can explain apparent orders between 1 and 2 observed for primary and secondary amine which are consistent with steric hindrance of the nitrogen. However, in most cases,

TABLE 3  
Values of  $pK_a$  at 25°C and  $Taft$  constants for the series of molecule No. 7 to 11 (Taft (1976)).

Number	Chemical structure	$pK_a$	References	$Taft$ constant
7	Hydrogene	9.44	Hamborg and Versteeg (2009)	0
8	Methyl	9.85	Hamborg and Versteeg (2009)	-1.24
9	Ethyl	9.89	Chemicalize (2012a)	-1.31
10	$n$ -Butyl	10.00	Chemicalize (2012b)	-1.63
11	Tert-butyl	10.12	Littel <i>et al.</i> (1990b)	-2.78

uncertainty remains on the respective contribution of the two steps of the reaction.

### 5.2.3 Termolecular Mechanism

Crooks and Donnellan (1989) explain reaction of monoethanolamine (7) with CO<sub>2</sub> by a single step termolecular mechanism involving amine, water and CO<sub>2</sub> where nucleophilic addition and deprotonation represent one single energy barrier. This hypothesis has been supported by *ab initio* calculations of da Silva and Svendsen (2004).

According to termolecular mechanism, the apparent order of 1.7 for methylethanolamine (8) is explained by a competition between reaction of CO<sub>2</sub> with amine and water (order 1) and with two molecules of amine (order 2).

For ethylethanolamine (9), order of 2 means that the one step reaction of CO<sub>2</sub> with amine and water is negligible in front of one step reaction of CO<sub>2</sub> with two molecules of amine.

Apparent order of 1.4 for *n*-butyl-ethanolamine (10) is explained by the competition between the two single step termolecular reactions as for methylethanolamine (8).

Order 1 for tert-butylethanolamine (11), which does not form carbamate, can be explained by the base-catalyzed hydration mechanism of tertiary amine, which can be seen as an extension of termolecular mechanism for tertiary amine and severely hindered secondary amines.

To conclude with this series of primary and secondary amines, one-step termolecular or zwitterion mechanisms both explain experimental orders of reaction. One-step termolecular mechanism leads to the same kinetic law as the zwitterion mechanism where the deprotonation step is rate limiting.

On a practical point of view, the choice of one or the other mechanism should be driven by the ability of the model to fit experimental data of  $k_0$  on the studied concentration range and to determine all its kinetic constants.

### 5.3 Indetermination of the Zwitterion Model

For primary and secondary amines, the set of experimental data does not allow to extract the three kinetic constants of the zwitterion model. This indetermination is due to the small variation of concentration of water.

For example in the case of 2-amino-2-methyl-1-propanol studied by Alper (1990b), the concentration of amine varies between 25 and 1 486 mol.m<sup>-3</sup>, correlated with variation of water concentration between 55 431 and 48 197 mol.m<sup>-3</sup> according to the Equation (26)

where  $\rho_w$  is the density of water,  $M_{Am}$  is the molecular weight of amine and  $M_w$  is the molecular weight of water:

$$[\text{H}_2\text{O}] = \frac{\rho_w - [\text{Am}] \times M_{Am}}{M_w} \quad (26)$$

As the concentration of amine varies more than 60 times, the concentration of water varies only by 15 percent. In order to discriminate contributions of  $k_{NA}$ ,  $k_{Dep}^{R_2NH}$  and  $k_{Dep}^{H_2O}$ , both concentrations of water and amine should vary significantly. Since it is not the case, several sets of kinetic constants can fit variation of  $k_0$  with amine concentration. This is illustrated by the case of piperazine for which experimental results obtained by Rayer *et al.* (2011) at 30°C are given in Table 4.

With these data we calculate with Maple<sup>®</sup> the response surface of  $k_{NA}$ ,  $k_{Dep}^{R_2NH}$  and  $k_{Dep}^{H_2O}$  yielding to an average relative deviation below 1% between the model and experimental values of  $k_0$ . This response surface has been obtained for values of constant between 10<sup>-5</sup> and 10<sup>5</sup> using 200 points for each constant on a logarithmic scale. Red points which appear in Figure 4, correspond to values of  $k_{NA}$ ,  $k_{Dep}^{R_2NH}$  and  $k_{Dep}^{H_2O}$  that give a prediction of  $k_0$  with an average relative deviation from the experimental data lower than 1%.

From this calculation, it is impossible to minimize the average relative deviation giving a single set of kinetic parameters able to represent the reaction of piperazine with CO<sub>2</sub>. In this case, the response surface of those parameters giving an average relative deviation below 1% stretches between 10<sup>1.3</sup> and 10<sup>2.8</sup> m<sup>3</sup>.mol<sup>-1</sup>.s<sup>-1</sup> for  $k_{NA}$ , between 10<sup>-1.6</sup> and 10<sup>0.4</sup> m<sup>6</sup>.mol<sup>-2</sup>.s<sup>-1</sup> for  $k_{Dep}^{R_2NH}$  and between 10<sup>-4.1</sup> and 10<sup>-3.1</sup> m<sup>6</sup>.mol<sup>-2</sup>.s<sup>-1</sup> for  $k_{Dep}^{H_2O}$ .

In this surface, we identify two areas. The first with low value of  $k_{NA}$  (10<sup>1.3</sup> m<sup>3</sup>.mol<sup>-1</sup>.s<sup>-1</sup>) and high value of  $k_{Dep}^{R_2NH}$  (10<sup>0.4</sup> m<sup>6</sup>.mol<sup>-2</sup>.s<sup>-1</sup>) corresponds to the

TABLE 4  
Experimental data of  $k_0$  for piperazine determined by Rayer *et al.* (2011) at 30°C

[PZ] (mol.m <sup>-3</sup> )	[H <sub>2</sub> O] (mol.m <sup>-3</sup> )	$k_0$ (s <sup>-1</sup> )
20	55 460	341
31	55 409	533
40	55 365	711
52	55 308	939
60	55 270	1 100
80	55 174	1 497
100	55 077	1 910

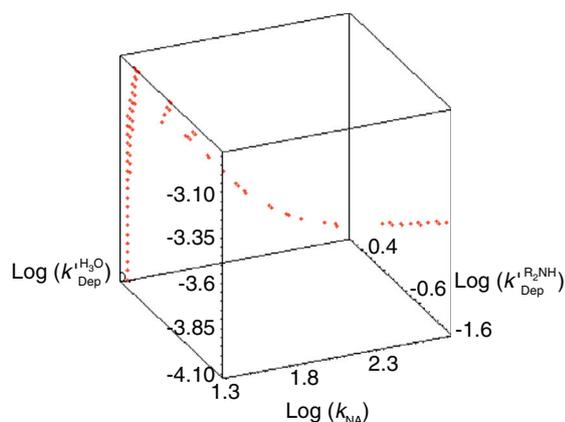


Figure 4

Response surface for average relative error below 1% for  $k_0$  modelled with zwitterion mechanism for piperazine at 30°C (Rayer *et al.*, 2011). Variation between  $10^{1.3}$  and  $10^{2.8}$   $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  for  $k_{\text{NA}}$ , between  $10^{-1.6}$  and  $10^{0.4}$   $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$  for  $k_{\text{Dep}}^{\text{R}_2\text{NH}}$  and between  $10^{-4.1}$  and  $10^{-3.1}$   $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$  for  $k_{\text{Dep}}^{\text{H}_2\text{O}}$ .

nucleophilic addition limiting step. In this area, value variation of  $k_{\text{Dep}}^{\text{H}_2\text{O}}$  by a factor of 10 is not sensitive on the result. The second one with an intermediate value of  $k_{\text{Dep}}^{\text{H}_2\text{O}}$  ( $10^{-3.5}$   $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ ) and a low value of  $k_{\text{Dep}}^{\text{R}_2\text{NH}}$  ( $10^{-1.6}$   $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ ) corresponds to the deprotonation by water limiting step. In this area, variation of  $k_{\text{NA}}$  by a factor close to 10 has no impact on  $k_0$ .

Finally, it is impossible to determine what is the limiting step of the zwitterion mechanism. We reach the same conclusion for 2-amino-2-methyl-1-propanol with  $n = 1$  (Alper, 1990b). In the case of a study of an amine with  $n = 2$ , (ethylethanolamine (Li *et al.*, 2007)), kinetic constant  $k_{\text{Dep}}^{\text{R}_2\text{NH}}$  can be determined but other constants are insensitive as they are first order kinetic constant according to the amine concentration.

In overall, it is mathematically impossible to determine a unique set of kinetic constants related to the zwitterion model which would be characteristic of a given amine.

#### 5.4 Mathematical Expression of the Termolecular Mechanism

With apparent order  $n$  between one and two, all data can be fitted by the termolecular mechanism given by Equation (27). For practical reasons, we replace  $k_{\text{ter}}^{\text{H}_2\text{O}}$  by  $k_1$  and  $k_{\text{ter}}^{\text{R}_2\text{NH}}$  by  $k_2$  and obtain Equation (28). Unlike the variety of interpretations associated to the zwitterion model, the fitting of  $k_0$  with the termolecular model

yields to one single set of ( $k_1$ ;  $k_2$ ) parameters to characterize each amine, independently of its structure and functionality (primary, secondary or tertiary):

$$k_0 = k_{\text{ter}}^{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}] \cdot [\text{R}_2\text{NH}] + k_{\text{ter}}^{\text{R}_2\text{NH}} [\text{R}_2\text{NH}]^2 \quad (27)$$

$$k_0 = k_1 \cdot [\text{H}_2\text{O}] \cdot [\text{R}_2\text{NH}] + k_2 \cdot [\text{R}_2\text{NH}]^2 \quad (28)$$

## 6 COMPENSATION EFFECT

Based on experimental data collected in Table 1, we determine parameters  $k_1$  and  $k_2$  of the Equation (28). Values of  $k_1$  and  $k_2$  at different temperatures are reported in Table 5 with average relative error between model and experimental values of  $k_0$ . Deprotonation by amine is not considered ( $k_2 = 0$ ) for amines with  $n = 1$  (molecule 3, 4, 5, 6, 11) and deprotonation by water is not considered ( $k_1 = 0$ ) for amines with  $n = 2$  (molecule 9).

Then, we determine parameters of Arrhenius law for  $k_1$ ,  $k_2$  constants given by Equation (29) and (30). Figures 5 and 6 show the activation energy  $E_a$  of each kinetic constant  $k_1$  and  $k_2$  versus  $\ln(A)$ . For both constants, we can draw a linear relationship between activation energy and reaction frequency factor  $A$  as shown in Equation (31).

$$k_1 = A_1 \cdot \exp\left(\frac{-E_{a1}}{RT}\right) \quad (29)$$

$$k_2 = A_2 \cdot \exp\left(\frac{-E_{a2}}{RT}\right) \quad (30)$$

$$E_{ai} = b \cdot \ln A_i + c \quad (31)$$

This correlation has been described in the literature as a compensation effect. According to Liu and Guo (2001), this phenomenon appears in several fields of chemistry (adsorption, chromatography, substitution reaction, proton transfer, etc.). According to Liu and Guo (2001), there are two main explanations to this phenomenon.

### 6.1 Statistical Compensation Effect

In the temperature range of the stopped-flow experiments, the neperian logarithm of the kinetic constant ( $\ln k_1$  and  $\ln k_2$ ) and the value of  $1/T$  have a limited variation which can account for uncertainty on the independent determination of preexponential factor and energy of activation. This indetermination can be a first explanation for the apparent compensation effect generally

TABLE 5  
 Number, value of  $k_1$  and  $k_2$  and average relative deviation between termolecular model and experimental values of  $k_0$   
 from literature data specified in Table 1

Number	Temperature (°C)	$k_1$ ( $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ )	$k_2$ ( $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ )	Average relative error (%)
3	25	$5.27 \times 10^{-7}$	-	2.5
	30	$7.49 \times 10^{-7}$	-	2.2
	35	$1.03 \times 10^{-6}$	-	3.7
	40	$1.47 \times 10^{-6}$	-	3.7
4	25	$6.01 \times 10^{-7}$	-	12.0
	30	$1.06 \times 10^{-6}$	-	11.3
	35	$1.74 \times 10^{-6}$	-	6.1
	40	$2.64 \times 10^{-6}$	-	7.6
5	25	$4.22 \times 10^{-7}$	-	5.8
	30	$6.19 \times 10^{-7}$	-	7.6
	35	$9.54 \times 10^{-7}$	-	4.7
	40	$1.40 \times 10^{-6}$	-	5.6
6	25	$1.48 \times 10^{-6}$	-	3.7
	30	$2.10 \times 10^{-6}$	-	6.1
	35	$3.03 \times 10^{-6}$	-	5.8
	40	$4.17 \times 10^{-6}$	-	5.6
7	25	$5.31 \times 10^{-5}$	$3.60 \times 10^{-2}$	4.6
	30	$6.92 \times 10^{-5}$	$4.09 \times 10^{-2}$	1.3
	35	$9.39 \times 10^{-5}$	$4.22 \times 10^{-2}$	3.9
	40	$1.33 \times 10^{-4}$	$3.86 \times 10^{-2}$	3.2
8	10	$2.33 \times 10^{-5}$	$5.11 \times 10^{-2}$	18.5
	15	$2.99 \times 10^{-5}$	$7.26 \times 10^{-2}$	11.9
	25	$2.40 \times 10^{-5}$	$1.98 \times 10^{-1}$	3.1
	35	$3.36 \times 10^{-5}$	$2.74 \times 10^{-1}$	5.5
9	25	-	$3.75 \times 10^{-2}$	7.3
	30	-	$4.43 \times 10^{-2}$	6.0
	35	-	$5.35 \times 10^{-2}$	3.5
	40	-	$6.40 \times 10^{-2}$	2.5
10	10	$2.49 \times 10^{-6}$	$1.18 \times 10^{-2}$	9.7
	15	$5.13 \times 10^{-6}$	$1.58 \times 10^{-2}$	3.6
	25	$1.93 \times 10^{-5}$	$1.28 \times 10^{-2}$	6.8
	35	$3.20 \times 10^{-5}$	$1.32 \times 10^{-2}$	4.2

(continued)

TABLE 5 (continued)

Number	Temperature (°C)	$k_1$ ( $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ )	$k_2$ ( $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ )	Average relative error (%)
11	5	$6.73 \times 10^{-7}$	-	17.8
	15	$1.19 \times 10^{-6}$	-	17.5
	25	$3.31 \times 10^{-6}$	-	22.3
	35	$6.99 \times 10^{-6}$	-	22.6
12	5	$1.59 \times 10^{-6}$	$5.29 \times 10^{-5}$	7.9
	15	$3.56 \times 10^{-6}$	$1.04 \times 10^{-4}$	12.4
	25	$7.22 \times 10^{-6}$	$1.48 \times 10^{-4}$	10.1
14	15	$1.63 \times 10^{-7}$	$1.00 \times 10^{-5}$	13.8
	25	$4.37 \times 10^{-7}$	$1.15 \times 10^{-5}$	7.3
	30	$5.29 \times 10^{-7}$	$1.44 \times 10^{-5}$	4.1
15	25	$3.73 \times 10^{-5}$	$2.10 \times 10^{-2}$	3.3
	30	$4.61 \times 10^{-5}$	$2.56 \times 10^{-2}$	2.7
	35	$5.50 \times 10^{-5}$	$3.38 \times 10^{-2}$	3.2
	40	$5.72 \times 10^{-5}$	$4.92 \times 10^{-2}$	4.2
16	25	$7.35 \times 10^{-5}$	$2.17 \times 10^{-2}$	2.0
	30	$9.69 \times 10^{-5}$	$3.27 \times 10^{-2}$	2.1
	35	$1.09 \times 10^{-4}$	$6.78 \times 10^{-2}$	2.0
	40	$1.40 \times 10^{-4}$	$9.26 \times 10^{-2}$	2.5
17	5	$2.28 \times 10^{-5}$	$7.93 \times 10^{-4}$	7.5
	15	$4.00 \times 10^{-5}$	$3.08 \times 10^{-3}$	10.9
	25	$7.79 \times 10^{-5}$	$1.03 \times 10^{-3}$	9.1
18	25	$1.89 \times 10^{-6}$	$6.72 \times 10^{-4}$	6.7
	30	$2.89 \times 10^{-6}$	$7.77 \times 10^{-4}$	7.3
	35	$2.62 \times 10^{-6}$	$1.01 \times 10^{-3}$	6.7
	40	$4.27 \times 10^{-6}$	$1.01 \times 10^{-3}$	6.3
19	5	$2.97 \times 10^{-5}$	$7.23 \times 10^{-3}$	7.6
	10	$4.13 \times 10^{-5}$	$7.03 \times 10^{-3}$	4.7
	15	$3.79 \times 10^{-5}$	$2.05 \times 10^{-2}$	21.5
	25	$6.23 \times 10^{-5}$	$2.09 \times 10^{-2}$	3.5
20	5	$2.06 \times 10^{-5}$	$2.55 \times 10^{-2}$	5.2
	15	$1.52 \times 10^{-4}$	$7.15 \times 10^{-2}$	3.1
	25	$2.53 \times 10^{-4}$	$1.39 \times 10^{-1}$	14.8

(continued)

TABLE 5 (continued)

Number	Temperature (°C)	$k_1$ ( $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ )	$k_2$ ( $\text{m}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ )	Average relative error (%)
21	25	$1.70 \times 10^{-4}$	$1.62 \times 10^{-2}$	6.5
	30	$2.24 \times 10^{-4}$	$1.56 \times 10^{-2}$	5.5
	35	$2.64 \times 10^{-4}$	$4.19 \times 10^{-2}$	3.7
	40	$3.03 \times 10^{-4}$	$1.16 \times 10^{-1}$	2.9

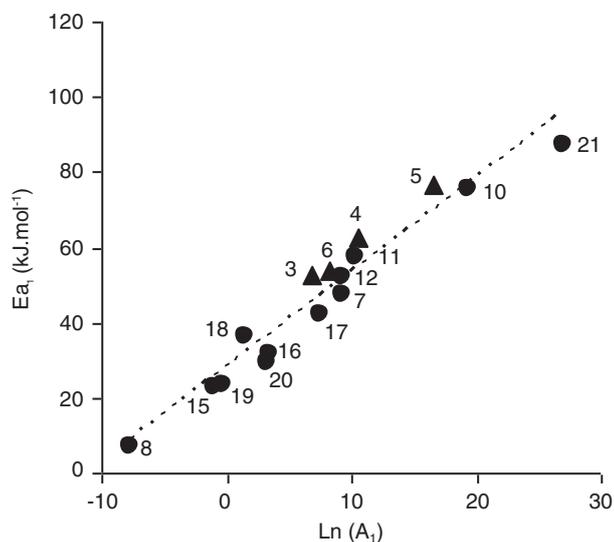


Figure 5

Relation between Arrhenius parameters for  $k_1$ .  
 $E_{a1} = 2.52 \times \ln(A_1) + 27.84$  and  $R^2 = 0.94$ .

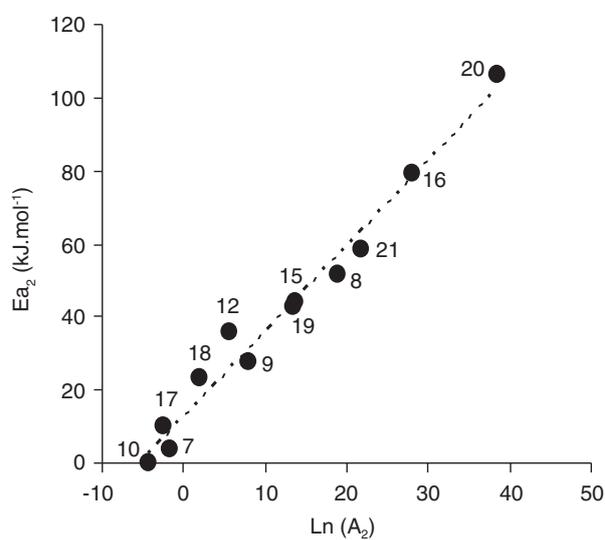


Figure 6

Relation between Arrhenius parameters for  $k_2$ .  
 $E_{a2} = 2.33 \times \ln(A_2) + 12.73$  and  $R^2 = 0.98$ .

called the statistical compensation effect. This phenomena is well described by [Barrie \(2012\)](#).

We determine for each molecule the confidence ellipse area in order to evaluate the impact of statistical compensation effect on our parameters. The expression of the confidence ellipse area is given by Equation (32) where  $\mathbf{b}$  is the vector of parameters ( $\ln(A); E_a$ ),  $\hat{\mathbf{b}}$  is the estimation of ( $\ln(A); E_a$ ) represented by the center of the ellipse,  $\mathbf{C}$  is the covariance matrix between parameters,  $(p+1) = 2$  is the number of parameters,  $s^2$  is the residual variance,  $F_{\alpha;p;(n-p-1)}$  corresponds to the  $F$ -distribution value with a confidence level of  $(1-\alpha)\%$  and  $n$  is the number of data points used to estimate  $\mathbf{b}$ .

$$(\mathbf{b} - \hat{\mathbf{b}})' \mathbf{C} (\mathbf{b} - \hat{\mathbf{b}}) \leq (p+1) \cdot s^2 \cdot F_{\alpha;p;(n-p-1)} \quad (32)$$

We represent in [Figure 7](#) the activation energy  $E_a$  versus  $\ln(A)$  for kinetic constant  $k_1$ . Indeed, this first

order kinetic constant has the greatest sensitivity on  $k_0$  for most of the molecules which are generally close to  $n = 1$ . We limit our representation to molecules which are less impacted by statistical indetermination. The plot has been realized with the function ellipse of the  $R$  software with a 95% confidence level.

[Figure 7](#) confirms a correlation between activation energy and reaction preexponential factor  $A$  even with ellipse confidence area. Moreover the position of the molecule in this figure is clearly dependent on the reactivity of the molecule characterized by the degree of substitution and steric hindrance of the amine function. In fact, ethylenediamine which is the most reactive molecule has the lowest value of activation energy and preexponential factor. On the other side, a tertiary amine (3-dimethylaminopropanolamine) has the highest value of activation energy and preexponential factor.

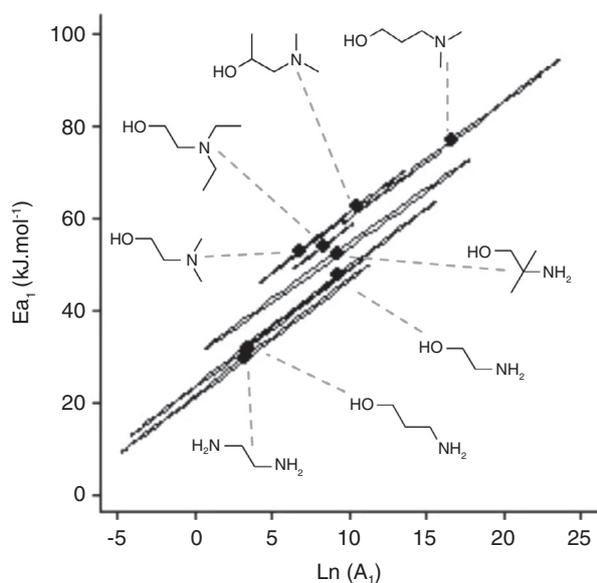


Figure 7  
Relation between Arrhenius parameters for  $k_1$ .

TABLE 6

Corresponding number, structure, value of activation enthalpy and activation entropy determined according to transition state theory for amines of Figure 7

Number	Structure	$\Delta^\ddagger H$ (kJ.mol <sup>-1</sup> )	$\Delta^\ddagger S$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )
4	<chem>HO-CH2-CH2-N(CH3)2</chem>	74	-18
5	<chem>HO-CH2-CH(CH3)-N(CH3)2</chem>	60	-68
6	<chem>HO-CH2-CH2-CH2-N(CH3)2</chem>	51	-87
3	<chem>HO-CH2-CH2-N(CH3)2</chem>	50	-99
12	<chem>HO-CH2-CH(CH3)-NH2</chem>	50	-79
7	<chem>HO-CH2-CH2-NH2</chem>	45	-78
16	<chem>HO-CH2-CH2-CH2-NH2</chem>	29	-128
20	<chem>H2N-CH2-CH2-NH2</chem>	27	-128

## 6.2 Physical Compensation Effect

The compensation effect could also have a physical explanation. According to the transition state theory, activation energy can be related with activation enthalpy and preexponential factor with activation entropy according to Equation (33) and Equation (34) (Scacchi *et al.*, 1996), where  $\Delta^\ddagger H$  is the activation enthalpy,  $R$  is the gas constant,  $T$  the temperature (here, we set at 298.15 K),  $k_B$  is the Boltzmann constant,  $h$  is the Planck constant,  $\Delta^\ddagger S$  is the activation entropy and  $c_0^{\Delta n^\ddagger}$  is the unitary concentration (1 000 mol.m<sup>-3</sup>) with  $(1-\Delta n^\ddagger)$  which is the molecularity of the process (which is 3). Values of activation enthalpy and entropy are given in Table 6:

$$E_a = \Delta^\ddagger H - RT \quad (33)$$

$$A = \exp(1) \times \frac{k_B T}{h} \times \exp\left(\frac{\Delta^\ddagger S}{R}\right) c_0^{\Delta n^\ddagger} \quad (34)$$

For all molecules, values of activation entropy are negative. This variation of entropy, which reflects a reduction of molecular disorder, is due to the formation of two ions formed from three molecules (amine, water and carbon dioxide) in the transition state (Crooks and Donnellan, 1988). We notice that for linear primary amines 20 and 16, the reduction of molecular disorder is more important than for tertiary amines 4 and 5.

At the same time the enthalpy of activation is less important for primary amines than for tertiary amines.

In fact, primary amines have a higher reactivity with carbon dioxide in agreement with the lowest values of enthalpy. This higher reactivity is correlated with a larger reduction of entropy associated with carbamate formation. A smaller reduction of entropy in the case of carbonate formation for tertiary amine, specially for molecule 4 may also come from a smaller association of the reactant molecules in the transient state. In fact, hydrogen bonding between the water molecule associated to the amine function and the hydroxyl group of the amine should be weaker in the case of molecule 4 (propanolamine) than for ethanolamines.

In summary, a low activation enthalpy tends to be compensated by a large negative activation entropy correlated with strong association of water, CO<sub>2</sub> and amine in the transient state. This compensation phenomenon which partially explains the apparent relationship between activation energy and preexponential factor of  $k_1$  and  $k_2$  is certainly a new argument in favor of the termolecular mechanism.

## CONCLUSION

Literature teems with experimental data about kinetic between amines and carbon dioxide. In this work, we have suggested a method in order to compare data from different authors.

We compare the apparent first order constants  $k_0$  obtained from simple exponential fit of stopped flow data, as this technique is proven to be reproducible and adapted to study a large variety of amines.

Compilation of all data is represented in a 2D-plot of an empirical kinetic law with a power dependency of  $k_0$  with the concentration. From this representation, structure-activity relationships are drawn for tertiary amines and primary or secondary amines with varying degree of steric hindrance. These data are also confronted with mechanisms proposed in the literature. Both termolecular and zwitterion mechanism are consistent to explain the reaction rates of all amines with CO<sub>2</sub>. However, it is generally impossible to know which step is rate-limiting in the zwitterion mechanism and to determine the three kinetic constants in the case where the two steps would contribute to the reaction rate.

The termolecular mechanism has the advantage to characterize each amine by only two kinetic constants which can be univocally derived from experimental data at different concentrations. With this model, a compensation effect between activation energy and preexponential factor has been observed which is a supplementary indication in favor of this mechanism.

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