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* Corresponding author

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 carbon 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 (CO2) emissions represent over 76% of total emissions of greenhouse gases (Contribution of Working Groups et al., 2008) in terms of CO2 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 CO2 seems to be an efficient way to reduce greenhouse gases emissions (de Conineck, 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 CO2 capture with respect to penalties for CO2 emissions.

Indeed, these processes suffer from a high energy consumption due to the low concentration of CO2 in the flue gas, that represents the biggest part of the cost associated to CO2 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 CO2 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 CO2 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-CO2 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 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 monoeponential 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-CO2 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 CO2 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 CO2 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%, methylidioethanolamine 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 hydro-
dynamics of gas and liquid phase, physical solubility, dif-
fusion of reactants and products in the liquid phase to fit
measured mass transfer rate. In these conditions, estima-
tion of kinetic constants greatly depends on the different
hypotheses of the mass transfer model (Danckwerts,
1970; Laurent and Charpentier, 1974; Charpentier,
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
CO2-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⁻¹, 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 tech-
nique 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 reproduc-
able. Rayer et al. (2011) show that the overall uncertainty
on these data are generally around 5%. Then this
method is well fitted to draw quantitative structure activ-
ity relationship from the comparison of intrinsic kinetics
of reaction of very different amines with CO2.

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 (con-
ductimetry, 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 con-
sider 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 opti-
mized to reduce deviation between the model and exper-
imental data. This kind of models is necessary when
spectrophotometric detection is used to follow the reac-
tion (Barth et al., 1981, 1983, 1984, 1986) or if operating
conditions like CO2 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 solu-
tions.

2.2 Analytical Model

Analytical model is the most widespread approach for
stopped-flow studies on amine-CO2 reaction. This
approach considers a single, irreversible reaction with
amine in large excess, of first order with respect to
CO2. Generally, authors operate with a total concentra-
tion of amine at least ten times higher than the concen-
tration of carbon dioxide. In these conditions, the
variation of concentration of chemical species depends
on the pseudo first order kinetic constant k0 according
to a monoexponential variation. For conductivity
stopped flow measurements, the variation of concentra-
tions of ionic species is monitored by the change of con-
ductance in the solution. Conductance G (S) is the
inverse of the electric resistance R (Ω), A (S) is the ampli-
tude of the signal, k0 the pseudo first order kinetic con-
stant, t (s) is the time and C (S) is the value of the
conductance at the end of the observed reaction. Varia-
tion of conductance is then related to formation of amine
salts and to k0 according Equation (1) (Ali et al., 2000):

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

(1)

The pseudo first order kinetic constant k0 is defined as
shown by Equation (2). When it is measured in a large
excess of amine, k0 depends on the nature of the amine,
the concentration of amine and the temperature. For the
rest of the article, we decided to use k0 values because
they directly come from stopped-flow raw data which
are quite reproducible. Then, we limit our work to com-
pare first order kinetic constant obtained by this analyti-
cal method:

\[
r_{\text{CO}_2} = k_0 \cdot [\text{CO}_2]
\]  

(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 $k_{Am}$ and $n$ giving the same value of $k_0$ for concentration of amine of 100 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 g.mol$^{-1}$ and a density of 10$^3$ g.m$^{-3}$) in the operating range available by the stopped-flow technique:

$$k_0 = k_{Am} \cdot [Am]^n$$

(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 $pKa$. 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 $10^{-1}$ m$^3$.mol$^{-1}$.s$^{-1}$ and increase with the value of $pKa$ 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$_2$-CH$_2$-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 $pKa$ varies between 9.44 and 10.12 with an increasing steric hindrance around the nitrogen group. This variation of $pKa$ 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 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 $pKa$ 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$_2$ than tertiary amines having same $pKa$, 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>
<thead>
<tr>
<th>Name</th>
<th>Number</th>
<th>Chemical structure</th>
<th>Authors</th>
<th>Concentration range (mol.m(^{-3}))</th>
<th>Temperature range (°C)</th>
<th>pKa at 25°C</th>
<th>References</th>
</tr>
</thead>
</table>

(continued)
<table>
<thead>
<tr>
<th>Name</th>
<th>Number</th>
<th>Chemical structure</th>
<th>Authors</th>
<th>Concentration range (mol.m⁻³)</th>
<th>Temperature range (°C)</th>
<th>pKα at 25°C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-amino-2-methylpropan-1,3-diol</td>
<td>13</td>
<td><img src="image1" alt="Chemical structure" /></td>
<td>Bouhamra et al. (1999)</td>
<td>25-1, 351</td>
<td>5-30</td>
<td>9.48</td>
<td>Chemicalize (2012b)</td>
</tr>
<tr>
<td>2-amino-2-hydroxymethyl-1,3-propanediol</td>
<td>14</td>
<td><img src="image2" alt="Chemical structure" /></td>
<td>Ume and Alper (2012)</td>
<td>500-2, 000</td>
<td>25</td>
<td>8.95</td>
<td>Chemicalize (2012d)</td>
</tr>
<tr>
<td>2-(2-aminoethoxy)ethanol</td>
<td>17</td>
<td><img src="image5" alt="Chemical structure" /></td>
<td>Alper (1990a)</td>
<td>12-206 (at 25°C)</td>
<td>5-25</td>
<td>9.46</td>
<td>da Silva and Svendsen (2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Li et al. (2007)</td>
<td>150-518</td>
<td>25-40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morpholine</td>
<td>19</td>
<td><img src="image7" alt="Chemical structure" /></td>
<td>Alper (1990a)</td>
<td>3-102 (at 25°C)</td>
<td>5-25</td>
<td>8.49</td>
<td>da Silva and Svendsen (2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rayer et al. (2011)</td>
<td>20-101</td>
<td>25-40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piperazine</td>
<td>21</td>
<td><img src="image9" alt="Chemical structure" /></td>
<td>Gordesli and Alper (2011)</td>
<td>10-100 (at 25°C)</td>
<td>5-25</td>
<td>9.71-5.41</td>
<td>Hamborg and Versteeg (2009)</td>
</tr>
<tr>
<td>Hydroxyethylpiperazine</td>
<td>22</td>
<td><img src="image10" alt="Chemical structure" /></td>
<td>Ume et al. (2012)</td>
<td>2.5-30</td>
<td>25</td>
<td>8.92-3.97</td>
<td>Hamborg and Versteeg (2009)</td>
</tr>
</tbody>
</table>
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 mol.m$^{-3}$/C0\text{H}_2\text{O}$ \times 10^{-2}$ s$^{-1}$). More recently Soli and Byrne (2002) determined the rate of this reaction (at 25°C $k'_{\text{H}_2\text{O}} = 3.06 \times 10^{-3}$ 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 hydroxide-CO$_2$ and amine-CO$_2$ reaction described below. The rate of reaction of carbon dioxide according to hydration mechanism is shown by Equation (6):

$$
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \xrightarrow{k'_{\text{H}_2\text{O}}} \text{H}_2\text{CO}_3
$$

In aqueous basic solution, carbon dioxide reacts with an hydroxide ion to form a bicarbonate ion (7).

$$
\text{H}_2\text{CO}_3 + \text{B} \xrightarrow{k_{\text{H}_2\text{CO}_3}} \text{H}_2\text{CO}_3^- + \text{BH}^+
$$

In aqueous basic solution, carbon dioxide reacts with an hydroxide ion to form a bicarbonate ion (7).

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 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 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°C $k_0 = 2.57 \times 10^2$ s$^{-1}$). More recently Soli and Byrne (2002) determined the rate of this reaction (at 25°C $k'_{\text{H}_2\text{O}} = 3.06 \times 10^{-2}$ 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 hydroxide-CO$_2$ and amine-CO$_2$ reaction described below. The rate of reaction of carbon dioxide according to hydration mechanism is shown by Equation (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 $k_{\text{H}_2\text{O}} = 8.32$ m$^3$.mol$^{-1}$.s$^{-1}$ at 25°C:

$$
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \xrightarrow{k_{\text{H}_2\text{O}}} \text{H}_2\text{CO}_3
$$

$\text{CO}_2(\text{aq}) + \text{HO}^- \xrightarrow{k_{\text{HO}^-}} \text{H}_2\text{CO}_3^-
$$

In aqueous basic solution, carbon dioxide reacts with an hydroxide ion to form a bicarbonate ion (7).

$$
\text{H}_2\text{CO}_3 + \text{B} \xrightarrow{k_{\text{H}_2\text{CO}_3}} \text{H}_2\text{CO}_3^- + \text{BH}^+
$$

4.1.2 Tertiary Amine Mechanisms

Donaldson and Nguyen (1980) show that tertiary amines (R$_3$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 $k'_{R_3N} = k_{R_3N} \cdot [\text{H}_2\text{O}]$ (Crooks and Donnellan, 1990):

$$
R_3\text{N} + \text{H}_2\text{O} + \text{CO}_2(\text{aq}) \xrightarrow{k_{R_3N}} \text{HCO}_3^- + R_3\text{NH}^+
$$

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$$
R_3\text{N} + \text{H}_2\text{O} + \text{CO}_2(\text{aq}) \xrightarrow{k_{R_3N}} \text{HCO}_3^- + R_3\text{NH}^+
$$
### Table 2

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

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Number</th>
<th>$k_{\text{Am}}$ (m$^3$·mol$^n$·s$^{-1}$)</th>
<th>$n$</th>
<th>Average relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="chemical structure" /></td>
<td>1</td>
<td>$1.66 \times 10^{-3}$</td>
<td>0.99</td>
<td>0.4</td>
</tr>
<tr>
<td><img src="image" alt="chemical structure" /></td>
<td>2</td>
<td>$3.20 \times 10^{-3}$</td>
<td>0.99</td>
<td>3.3</td>
</tr>
<tr>
<td><img src="image" alt="chemical structure" /></td>
<td>3</td>
<td>$2.64 \times 10^{-2}$</td>
<td>1.01</td>
<td>2.4</td>
</tr>
<tr>
<td><img src="image" alt="chemical structure" /></td>
<td>4</td>
<td>$3.29 \times 10^{-2}$</td>
<td>0.99</td>
<td>12.1</td>
</tr>
<tr>
<td><img src="image" alt="chemical structure" /></td>
<td>5</td>
<td>$1.06 \times 10^{-1}$</td>
<td>0.76</td>
<td>3.6</td>
</tr>
<tr>
<td><img src="image" alt="chemical structure" /></td>
<td>5'</td>
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</table>

(continued)
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 CO2 is shown in Equation (13):

\[
r_{CO_2} = \frac{k_{R_3N} [H_2O] [CO_2] [R_3N]}{k_{H_2O} + k_{CO_2}}
\]

With

\[
k_{H_2O} = \frac{1}{k_{NA}} + \frac{1}{k_{H_2O}^{R_3N}} \quad \text{and} \quad k_{H_2O}^{R_3N} = \frac{k_{Na} k_{H_2O}^{H_2O}}{k_{NA}}
\]

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:

\[
r_{III} = r_H^CO_2 + r_H^CO_2 + r_{R_3N}^{CO_2}
\]

### 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 CO2 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 amines. Since kinetics of tertiary amine-CO2 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-CO2 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 CO2 to form carbamates. As we limit our discussion to reactions of CO2 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, \( k_{\text{NA}} \) corresponds to the kinetic constant of the nucleophilic addition, \( k_{-\text{NA}} \) corresponds to the kinetic constant of the reverse reaction and \( k_{\text{Dep}}^{B} \) corresponds to the kinetic constant of the deprotonation of the zwitterion by a base B:

\[
\text{CO}_2(aq) + \text{R}_2\text{NH} \rightarrow \text{R}_2\text{NHCOO}^- + \text{BH}^+ + \text{H}_2\text{O} \quad (15)
\]

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 \( k_{\text{Dep}}^{\text{R}_{2}\text{NH}} \) and \( k_{\text{Dep}}^{\text{H}_2\text{O}} \) defined in Equation (19):

\[
\frac{\text{R}_2\text{NH}}{r_{\text{CO}_2}} = \frac{[\text{R}_2\text{NH}][\text{CO}_2]}{\frac{1}{k_{-\text{NA}}} + \frac{k_{\text{NA}}}{k_{-\text{NA}}} + \frac{k_{\text{Dep}}^{\text{R}_{2}\text{NH}}}{k_{\text{Dep}}^{\text{R}_{2}\text{NH}}}[\text{R}_2\text{NH}][\text{CO}_2]} \quad (17)
\]

\[
\frac{\text{R}_2\text{NH}}{r_{\text{CO}_2}} = \frac{[\text{R}_2\text{NH}][\text{CO}_2]}{\frac{1}{k_{-\text{NA}}} + \frac{k_{\text{Dep}}^{\text{R}_{2}\text{NH}}}{k_{\text{Dep}}^{\text{R}_{2}\text{NH}}}[\text{R}_2\text{NH}][\text{CO}_2]} \quad (18)
\]

\[
\frac{k_{\text{Dep}}^{\text{R}_{2}\text{NH}}}{k_{\text{Dep}}^{\text{H}_2\text{O}}} = \frac{1}{k_{\text{Dep}}^{\text{R}_{2}\text{NH}}}[\text{R}_2\text{NH}] + \frac{k_{\text{Dep}}^{\text{H}_2\text{O}}}{k_{\text{Dep}}^{\text{R}_{2}\text{NH}}}[\text{R}_2\text{NH}] + \frac{k_{\text{Dep}}^{\text{H}_2\text{O}}}{k_{\text{Dep}}^{\text{R}_{2}\text{NH}}}[\text{H}_2\text{O}] \quad (19)
\]

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:

\[
\text{CO}_2(aq) + \text{R}_2\text{NH} \rightarrow \text{R}_2\text{NCOO}^- + \text{BH}^+ \quad (20)
\]

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, \( k_{\text{Dep}}^{\text{R}_{2}\text{NH}} \) 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 \( k_{\text{Dep}}^{\text{H}_2\text{O}} \) and \( k_{\text{Dep}}^{\text{R}_{2}\text{NH}} \) 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):

\[
r_{\text{CO}_2}^{\text{R}_{2}\text{NH}} = k_{\text{Dep}}^{\text{R}_{2}\text{NH}} [\text{R}_2\text{NH}][\text{CO}_2] \quad (23)
\]

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

\[
r_{\text{CO}_2}^{\text{H}_2\text{O}} = r_{\text{CO}_2}^{\text{H}_2\text{O}} + r_{\text{CO}_2}^{\text{R}_{2}\text{NH}} \quad (25)
\]

### 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 \( pK_a \) 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 \( pK_a \) 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
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 $1.4 \times 10^{11} \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ (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 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,
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 \( \text{CO}_2 \) by a single step termolecular mechanism involving amine, water, and \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) with amine and water is negligible in front of one step reaction of \( \text{CO}_2 \) 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 1486 mol.m\(^{-3}\), correlated with variation of water concentration between 55 431 and 48 197 mol.m\(^{-3}\) according to the Equation (26)

\[
[H_2O] = \frac{\rho_w - [Am] \times M_{Am}}{M_w} \tag{26}
\]

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 \( k_{\text{NA}} \), \( k_{\text{Dep}}^{\text{R2NH}} \), and \( k_{\text{Dep}}^{\text{H2O}} \), 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\(^\text{®}\) the response surface of \( k_{\text{NA}} \), \( k_{\text{Dep}}^{\text{R2NH}} \), and \( k_{\text{Dep}}^{\text{H2O}} \) 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 \( 10^{-5} \) and \( 10^5 \) using 200 points for each constant on a logarithmic scale. Red points which appear in Figure 4, correspond to values of \( k_{\text{NA}} \), \( k_{\text{Dep}}^{\text{R2NH}} \) and \( k_{\text{Dep}}^{\text{H2O}} \) 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 \( \text{CO}_2 \). In this case, the response surface of those parameters giving an average relative deviation below 1\% stretches between \( 10^{1.3} \) and \( 10^{2.8} \text{ m}^3\text{mol}^{-1}\text{s}^{-1} \) for \( k_{\text{NA}} \), between \( 10^{-1.6} \) and \( 10^{0.4} \text{ m}^6\text{mol}^{-2}\text{s}^{-1} \) for \( k_{\text{Dep}}^{\text{R2NH}} \) and between \( 10^{-4.1} \) and \( 10^{-3.1} \text{ m}^6\text{mol}^{-2}\text{s}^{-1} \) for \( k_{\text{Dep}}^{\text{H2O}} \).

In this surface, we identify two areas. The first with low value of \( k_{\text{NA}} \) (\( 10^{1.3} \text{ m}^3\text{mol}^{-1}\text{s}^{-1} \)) and high value of \( k_{\text{Dep}}^{\text{R2NH}} \) (\( 10^{0.4} \text{ m}^6\text{mol}^{-2}\text{s}^{-1} \)) corresponds to the

<table>
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nucleophilic addition limiting step. In this area, value variation of $k_{Dep}^{R^2NH}$ by a factor of 10 is not sensitive on the result. The second one with an intermediate value of $k_{Dep}^{H_2O}$ (10$^{-3.5}$ m$^3$.mol$^{-1}$.s$^{-1}$) and a low value of $k_{Dep}^{R^2NH}$ (10$^{-1.6}$ m$^6$.mol$^{-2}$.s$^{-1}$) for $k_{Dep}^{R^2NH}$ and between 10$^{-4.1}$ and 10$^{-3.1}$ m$^6$.mol$^{-2}$.s$^{-1}$ for $k_{Dep}^{H_2O}$.

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 $k_{Dep}^{R^2NH}$ 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 $k_{ter}^{H_2O}$ by $k_1$ and $k_{ter}^{R^2NH}$ 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):

$$k_0 = k_{ter}^{H_2O} . [H_2O] . [R_2NH] + k_{ter}^{R^2NH} [R_2NH]^2$$

(27)

$$k_0 = k_1 . [H_2O] . [R_2NH] + k_2 . [R_2NH]^2$$

(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($A_i$). For both constants, we can draw a linear relationship between activation energy and reaction frequency factor $A$ as shown in Equation (31).

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

(29)

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

(30)

$$E_{a1} = b . \ln A_i + c$$

(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.
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<th>$k_2$ (m³·mol⁻²·s⁻¹)</th>
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(continued)
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 \( b \) is the vector of parameters \((\ln(A), E_a)\), \( b \) is the estimation of \((\ln(A), E_a)\) represented by the center of the ellipse, \( C \) is the covariance matrix between parameters, \((p + 1) = 2\) is the number of parameters, \( s^2 \) is the residual variance, \( F_{x,p;/(n-p-1)} \) corresponds to the F-distribution value with a confidence level of \((1-\alpha)\%\) and \( n \) is the number of data points used to estimate \( b \).

\[
(b - \hat{b})' C (b - \hat{b}) \leq (p + 1).s^2.F_{x,p;/(n-p-1)} \tag{32}
\]

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.

### TABLE 5 (continued)

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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 $\Delta^1 H$ 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, $\Delta^1 S$ is the activation entropy and $c_0^{\Delta n^i}$ is the unitary concentration (1 000 mol.m\(^{-3}\)) with (1-$\Delta n^i$) which is the molecularity of the process (which is 3). Values of activation enthalpy and entropy are given in Table 6:

\[
E_a = \Delta^1 H - RT \tag{33}
\]

\[
A = \exp(1) \times \frac{k_B T}{h} \times \exp\left(\frac{\Delta^1 S}{R}c_0^{\Delta n^i}\right) \tag{34}
\]

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\(_2\) 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.

**TABLE 6**

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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$_2$. 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.

REFERENCES


Chemicalize (2012a) http://www.chemicalize.org/structure/#!mol=CCNCCO&source=calculate

Chemicalize (2012b) http://www.chemicalize.org/structure/#!mol=CCCCNCCO&source=calculate

Chemicalize (2012c) http://www.chemicalize.org/structure/#!mol=2-amino-2-methylpropan-1%2C3-diol&source=fp

Chemicalize (2012d) http://www.chemicalize.org/structure/#!mol=2-amino-2-hydroxymethyl-1%2C3-propanediol&source=calculate


