Kinetics of Reaction between Primary and Secondary Amines and Carbon Dioxide in Water: a Structure-Property Study

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Outline

- Context
- Objectives
- Methodology
- Experimental results
- Quantitative Structure-Property Relationship (Q.S.P.R.)
- Conclusions and perspectives
Context

Post-combustion carbon capture

Columns and packings
30 to 50 % CAPEX

Solvent flow rate
5 to 10 % OPEX

Regeneration heat
50 to 60 % OPEX

Optimization = find the optimal solvent

Thermodynamics

Unit cost
(OPEX and CAPEX)

Chemical stability

Kinetics

Solvant


Objectives

Choice of the optimal solvent

- **Tertiary amines**
  \[
  \text{CO}_2(\text{aq}) + R_3\text{N} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + R_3\text{NH}^+
  \]

  - Moderate energy of regeneration
  - Low kinetics of reaction

- **Primary and secondary amines**
  \[
  \text{CO}_2(\text{aq}) + 2R_2\text{NH} \leftrightarrow 2R_2\text{NCO}_2^- + R_2\text{NH}_2^+
  \]

  - High energy of regeneration
  - Fast kinetics of reaction

Too many molecules to study all

- Study representative structures (25 °C)
- Understand influence of the structure on the kinetics
- Set up a predictive Q.S.P.R. model
Methodology

Determination of apparent kinetic constants

- **Stopped-flow technique**

- **Extraction from raw data**
  - \([\text{Am}] \geq \frac{[\text{CO}_2]}{10} \Rightarrow [\text{Am}] \approx \text{constant}\)
  - Reaction of \(\text{CO}_2\) with \(\text{HO}^-\) and \(\text{H}_2\text{O}\) negligible
  - Optimization of conductimetric signal

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

\[r_{\text{CO}_2} = k_0 \times [\text{CO}_2]\]
Methodology

Determination of kinetic constants

- **Semi-empirical model**

  \[ k_0 = k_1 \cdot [\text{Am}] \cdot [\text{H}_2\text{O}] + k_2 \cdot [\text{Am}]^2 \]

  Order 1 with respect to Am  
  Order 2 with respect to Am

- **Extraction from raw data**

  ![Graph showing kinetic constant vs. concentration of amine](image)
Experimental results

Primary amines (linear)

- Increase of kinetic constants $k_1$ & $k_2$ with increase of the pKa
- Different structures with the same properties (alkanol, benzyl and etheramines)
Experimental results

Primary amines (derivates from tert-butylamine)

- Increase of kinetic constants $k_1$ & $k_2$ with increase of the pKa
- Slower than linear primary amines (steric hindrance)
Experimental results

Primary amines (all studied)

- Methylamine faster than linear primary amines
- Effect of steric hindrance of moderately hindered primary amines
Experimental results

Acyclic secondary amines (linear)

- Increase of kinetic constants $k_1$ & $k_2$ with increase of the pKa
- Different structures with the same properties (alkanolamines/benzylamines)
Experimental results

Acyclic secondary amines

- $k_1$ linear secondary $< k_1$ linear primary ; $k_2$ linear primary $< k_2$ linear secondary
- In overall linear secondary amines more reactive than linear primary amines
Experimental results

Acyclic secondary amines (all studied)

- Dimethylamine faster than others linear secondary amines
- Diminution of kinetic constants with increase of steric hindrance (max for tert-butyl)
Experimental results

Cyclic secondary amines (non sterically hindered)

- Increase of kinetic constants $k_1$ & $k_2$ with increase of the pKa
Experimental results

Cyclic secondary amines

- Cyclic secondary amines more reactive than linear primary amines
Experimental results

Cyclic secondary amines

➢ Cyclic secondary amines more reactive than linear secondary amines
➢ Nucleophilicity: cyclic secondary > linear secondary > linear primary
Experimental results

Cyclic secondary amines (all studied)

- Diminution of kinetic constants $k_1$ & $k_2$ with steric hindrance
Q.S.P.R.

**Methodology: determination of molecular descriptors**

- **Molecule**
  - **Optimized structure**
    - Jaguar 7.9®
    - Quantum optimization
  - **Calculation of Van der Waals surface**
    - not shared with another atom
  - **Nitrogen accessible surface**
  - **Acid/base titration**
    - pKa (25 °C)

- **109 generic descriptors**
  - -11 with Jaguar 7.9®
  - -98 with Material Studio 5.5.3®

- **Hierarchical clustering methods**
  - 65 descriptors

**Graphs:**

- **Kinetic constant $k_1$ (m$^6$.mol$^{-2}$.s$^{-1}$)**
  - Log$_{10}(k_1) = 1.41 \times S_A^N - 13.60$
  - $R^2 = 0.88$

- **Kinetic constant $k_2$ (m$^6$.mol$^{-2}$.s$^{-1}$)**
  - Log$_{10}(k_2) = 1.66 \times S_A^N - 12.21$
  - $R^2 = 0.94$

**Equations:**

- $\log_{10}(k_1) = 1.41 \times S_A^N - 13.60$
- $\log_{10}(k_2) = 1.66 \times S_A^N - 12.21$
Q.S.P.R.

Methodology: determination of the predictive relationship

\[ \hat{y} = b_0 + b_1 x_1 + b_2 x_2 + \cdots + b_j x_j \]

**Training**

- \( M \) models
  - \( \bullet \) training set
  - \( \Delta \) validation set
  - \( \square \) prediction set

**Prediction**

- \( \hat{y}_{\text{pred}} = \bar{b}_0 + \bar{b}_1 x_1 + \bar{b}_2 x_2 + \cdots + \bar{b}_j x_j \)

**Coefficient determination**

- \( W \) property = \( \log_{10}(k_i) \)
- \( b_0 \) = average of the intercepts (500 models)
- \( b_1 \) to \( b_j \) = average of the coefficients (500 models)
- \( x_1 \) to \( x_j \) = descriptors

**PLS-GLR regression**

**Validation**

- \( \text{RMSEP} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2} \)

- \( Q_{2.5} = 0.418 \)
- \( Q_{2.3} = 0.093 \)

**Estimation of the performance**

- Average relative absolute deviation (ARD)
  \[ \text{ARD} = 100 \times \frac{\sum_{i=1}^{n} |10^{y_i} - 10^{\hat{y}_{\text{pred}}}|}{n} \]
Q.S.P.R.

Results: modeling of kinetic constant $k_1$

Coefficients of normalized variables (main weight)

<table>
<thead>
<tr>
<th>Term</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKa x NAS</td>
<td>0.0623</td>
</tr>
<tr>
<td>(HOMOLUMOaq)$^2$</td>
<td>-0.0596</td>
</tr>
<tr>
<td>pKa</td>
<td>0.0481</td>
</tr>
<tr>
<td>NAS</td>
<td>0.0465</td>
</tr>
</tbody>
</table>

29 descriptors - order 2 - 123 terms

<table>
<thead>
<tr>
<th>Set</th>
<th>ARD ± $\sigma_{RD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Training &amp; validation</td>
<td>23.1 ± 20.3 %</td>
</tr>
<tr>
<td>Prediction</td>
<td>37.5 ± 42.2 %</td>
</tr>
</tbody>
</table>
Results: modeling of kinetic constant $k_2$

Coefficients of normalized variables (main weight)

<table>
<thead>
<tr>
<th>Term</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(HOMOLUMO_{aq})^2$</td>
<td>-0.0811</td>
</tr>
<tr>
<td>$(HOMOLUMO_{aq})$</td>
<td>0.0799</td>
</tr>
<tr>
<td>$(HOMOLUMO_{aq}) \times HOMO_{g}$</td>
<td>-0.079</td>
</tr>
<tr>
<td>$(HOMOLUMO_{aq}) \times MolDensity$</td>
<td>0.0744</td>
</tr>
<tr>
<td>$pKa \times MolDensity$</td>
<td>0.0668</td>
</tr>
</tbody>
</table>

16 descriptors - order 2 - 89 terms

<table>
<thead>
<tr>
<th>Set</th>
<th>ARD ± $\sigma_{RD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Training &amp; validation</td>
<td>117.7 ± 145.3 %</td>
</tr>
<tr>
<td>Prediction</td>
<td>23.3 ± 22.1 %</td>
</tr>
</tbody>
</table>
Q.S.P.R.

Results: comparison with experimental data

<table>
<thead>
<tr>
<th>Amine</th>
<th>pKα</th>
<th>RD on $k_1$</th>
<th>RD on $k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1103</td>
<td>10.67</td>
<td>11%</td>
<td>4%</td>
</tr>
<tr>
<td>1202</td>
<td>10.83</td>
<td>6%</td>
<td>31%</td>
</tr>
<tr>
<td>1222</td>
<td>9.86</td>
<td>13%</td>
<td>56%</td>
</tr>
<tr>
<td>1240</td>
<td>7.96</td>
<td>75%</td>
<td>1%</td>
</tr>
<tr>
<td>1129</td>
<td>8.04</td>
<td>102%</td>
<td>25%</td>
</tr>
</tbody>
</table>

Prediction of kinetic constants better for the faster molecules
Q.S.P.R.

Results: calculation of apparent kinetic constant $k_0$

<table>
<thead>
<tr>
<th>Set</th>
<th>ARD ± $\sigma_{RD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Training &amp; validation</td>
<td>39.2 ± 45.7 %</td>
</tr>
<tr>
<td>Prediction</td>
<td>39.9 ± 28.4 %</td>
</tr>
</tbody>
</table>

QSPR fits all molecules with an ARD of 40% → same order of magnitude than reproducibility → error of 20% for absorption rate
Conclusions and perspectives

**Conclusions**
- Kinetic study of 59 primary and secondary monoamines at 25°C
- Identification of effects of the structure (pKa, +I effect, steric hindrance) on $k_1$ & $k_2$
- Development of a new descriptor of steric hindrance: nitrogen accessible surface
- Set up of a predictive Q.S.P.R. model: fit experimental data ± 40%

**Perspectives**
- Study of multi-amines
- Comparison behavior mono/multi-amines
- Prediction of kinetic performance of new solvents
Thank you for your attention!
Takk for oppmerksomheten!
Appendices

Mechanisms

All cases
Base = HO-, Amine, H2O

H2O, R3N \[\text{HCO}_3^-, \text{R}_3\text{NH}^+\]

\[k_{R3N}\]

R3N \[R3N^+\text{COO}^-\]

H2O \[k_{H2O}\]

CO2 (aq) \[k_{Dep}\]

Base \[= \text{HCO}_3^- + \text{BaseH}^+\]

Limiting step

8,32 m³.mol⁻¹.s⁻¹ at 25 °C

8,32 m³.mol⁻¹.s⁻¹ at 25 °C

Zwitterion

Tertiary amines R₃N

H₂O, R₃N \[\text{HCO}_3^-, \text{R}_3\text{NH}^+\]

\[k_{R3N}\]

R₃N \[R3N^+\text{COO}^-\]

H₂O \[k_{H2O}\]

CO₂ \[k_{Dep}\]

Based-catalyzed mechanism

Zwitterion

Amines primaires et secondaires R₂NH

R₂NH \[R₂N^+\text{HCOO}^-\]

H₂O \[k_{H2O}\]

R₂N⁺H₂ + R₂NCOO⁻ \[k_{Dep}\]

Zwitterion

Carbamic acid

R₂NH \[R₂N⁺\text{H₂COO}^-\]

H₂O \[k_{H2O}\]

R₂NH, R₂NH \[k_{Dep}\]

Termolecular

8,32 m³.mol⁻¹.s⁻¹ at 25 °C

8,32 m³.mol⁻¹.s⁻¹ at 25 °C

\[k_{H2O}\]

R₂NH \[R₂N⁺\text{COO}^-\]

H₂O \[k_{Dep}\]

R₂NH, R₂NH \[k_{Dep}\]

R₂NH, H₂O \[k_{Dep}\]

\[8,32 \text{ m}^3\text{.mol}^{-1}\text{.s}^{-1} \text{ at } 25^\circ\text{C}\]

\[r_{\text{CO}_2} = k_{\text{Dep}} \cdot [H_2\text{O}] \cdot [\text{R}_2\text{NH}] \cdot [\text{CO}_2] \cdot [R_3\text{N}] \]

\[r_{\text{CO}_2} = k_{\text{Dep}} \cdot [H_2\text{O}] \cdot [\text{R}_2\text{NH}] \cdot [\text{CO}_2] \cdot [R_3\text{N}] \]

\[r_{\text{CO}_2} = k_{\text{Dep}} \cdot [H_2\text{O}] \cdot [\text{R}_2\text{NH}] \cdot [\text{CO}_2] \cdot [R_3\text{N}] \]

\[r_{\text{CO}_2} = k_{\text{Dep}} \cdot [H_2\text{O}] \cdot [\text{R}_2\text{NH}] \cdot [\text{CO}_2] \cdot [R_3\text{N}] \]


Département catalyse et séparation – Etablissement d’une relation structure propriété pour la cinétique de réaction amine-CO₂ – 26 avril 2012
Appendices
Appendices

- **Methylamine**
  - Linear primary amines
  - Moderately hindered primary amines
  - Severally hindered primary amines

- **Dimethylamine**
  - Linear acyclic secondary amines
  - Moderately hindered acyclic secondary amines
  - Severally hindered acyclic secondary amines

- **Non sterically hindered cyclic secondary amines**
  - Moderately hindered cyclic secondary amines
  - Severally hindered cyclic secondary amines

- **Cyclic secondary amines**

- **Acyclic secondary amines**

- **Primary amines**
Appendices

Steric hindrance

pKa

Linear

Moderately hindered
Appendices

Linear methylamines

Steric hindrance

 moderated hindered

pKa

10.5

8.5
Appendices

Steric hindrance

Unhindered

Moderately hindered

Severely hindered

pKa

11

9