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

2nd Post-Combustion Capture Conference
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Gabriel Couchaux,
Alexandre Fontenay,
Virgil-Crépin Lissassi,
Danielle Barth,
Abdelaziz Faraj,
Théodorus de Bruin,
Javier Perez-Pellitero,
Julien Grandjean

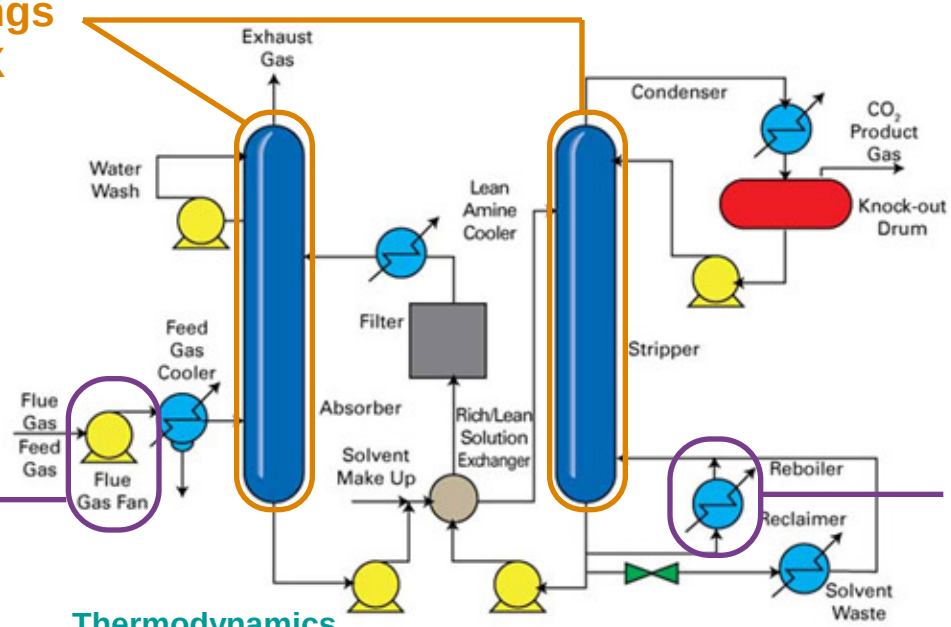
Outline

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

Context

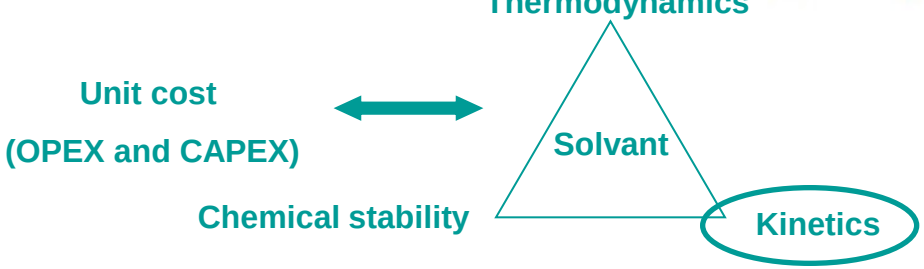
Post-combustion carbon capture

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

http://www.captureready.com/en/Channels/Research/showDetail2.asp?objID=298.
Raynal L., Bouillon P.A., Gomez A. and Broutin P., *Chem. Eng. J.* **2011**, 171, 742-752.
Raynal L., Gomez A., Caillat B. and Haroun Y., *Oil & Gas Sc. and Tech.* **2013**, DOI 10.2516/ogst/2012104.

Objectives

Choice of the optimal solvent

- **Tertiary amines**

$$CO_2(aq) + R_3N + H_2O \longleftrightarrow HCO_3^- + R_3\overset{+}{N}H$$

Moderate energy of regeneration

Low kinetics of reaction

- **Primary and secondary amines**

$$CO_2(aq) + 2R_2NH \longleftrightarrow R_2NCO_2^- + R_2\overset{+}{N}H_2$$

High energy of regeneration

Fast kinetics of reaction

Too many molecules to study all

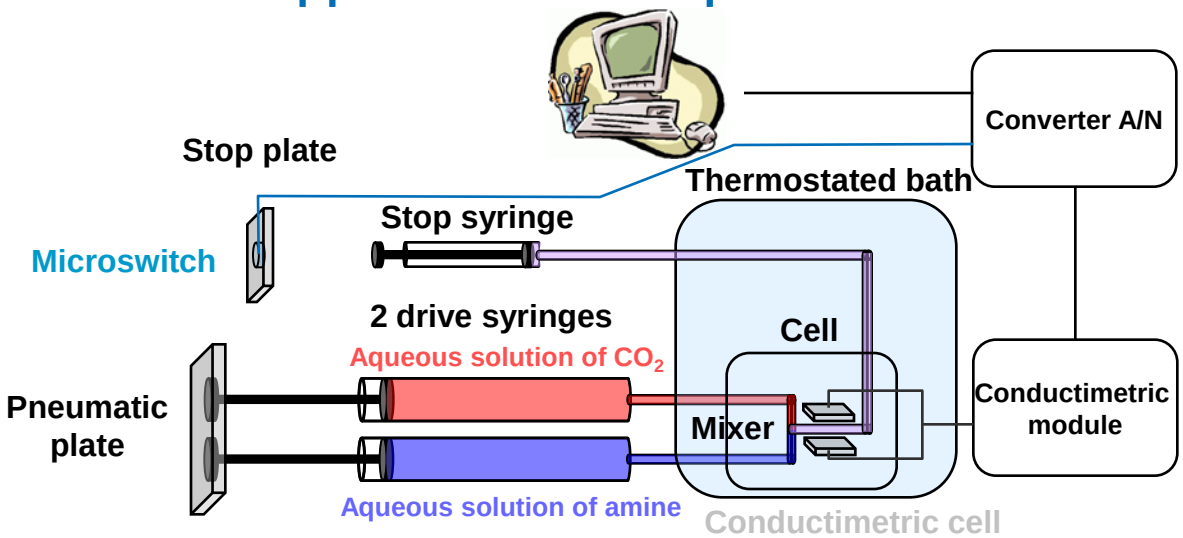
- **Study representative structures (25 °C)**
- **Understand influence of the structure on the kinetics**
- **Set up a predictive Q.S.P.R. model**

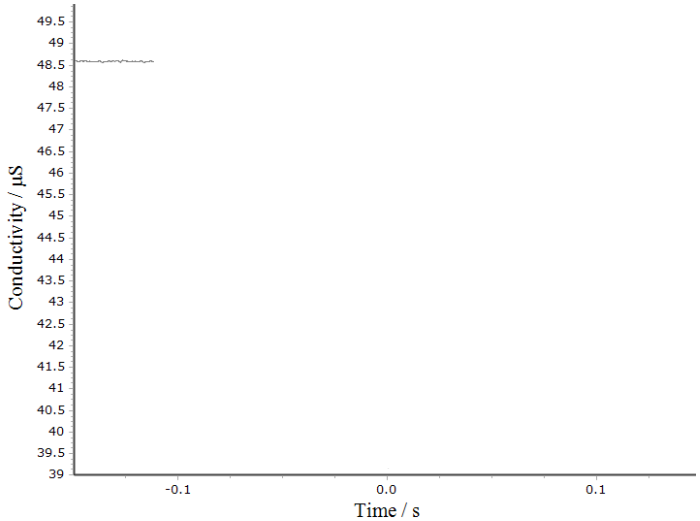
Methodology

Determination of apparent kinetic constants

- **Stopped-flow technique**

$2\ R_2NH + CO_2 \rightarrow R_2NH^+ + R_2NCO_2^-$





- **Extraction from raw data**
  - $[Am] \geq [CO_2] / 10 \rightarrow [Am] \approx$ constant
  - Reaction of CO_2 with HO^- and H_2O negligible
  - Optimization of conductimetric signal

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

Apparent kinetic constant

$$r_{CO_2} = k_0 \times [CO_2]$$

Methodology

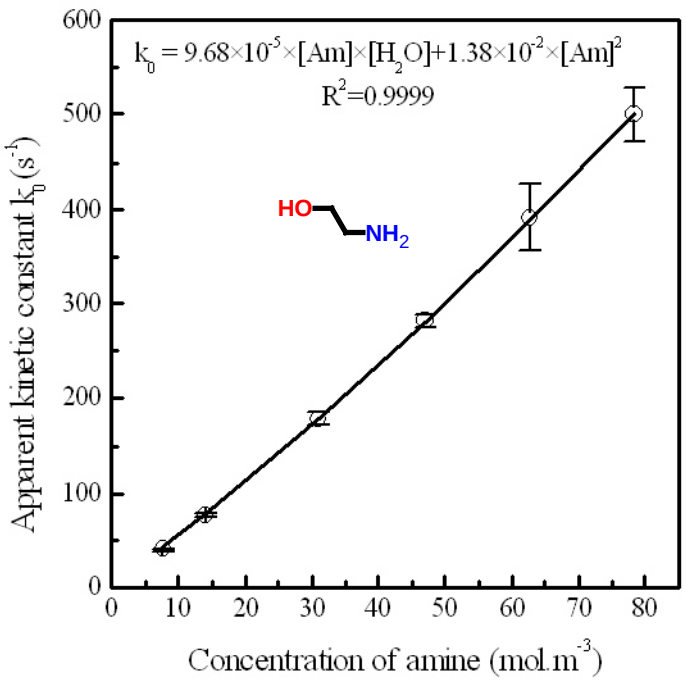
Determination of kinetic constants

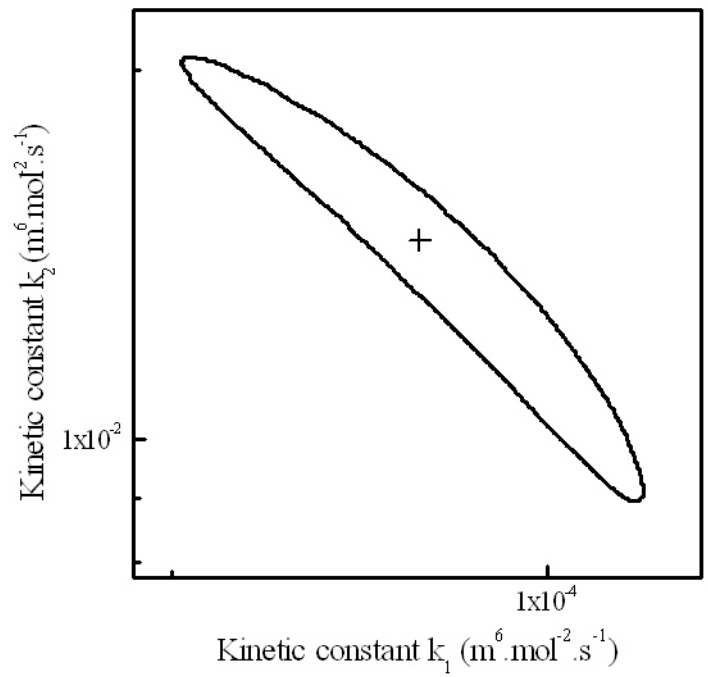
- **Semi-empirical model**

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

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

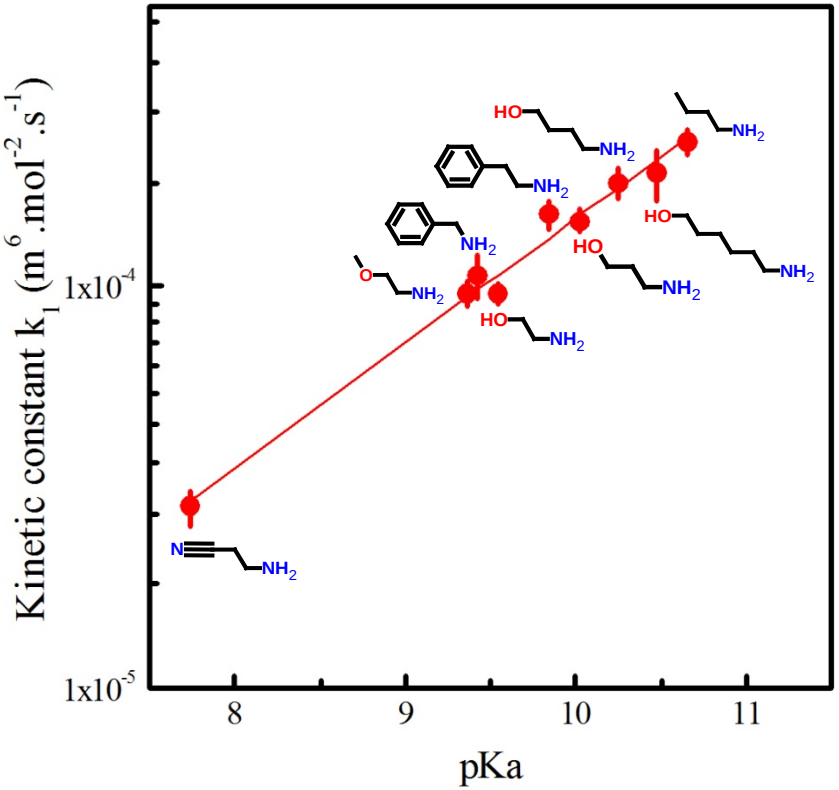
- **Extraction from raw data**

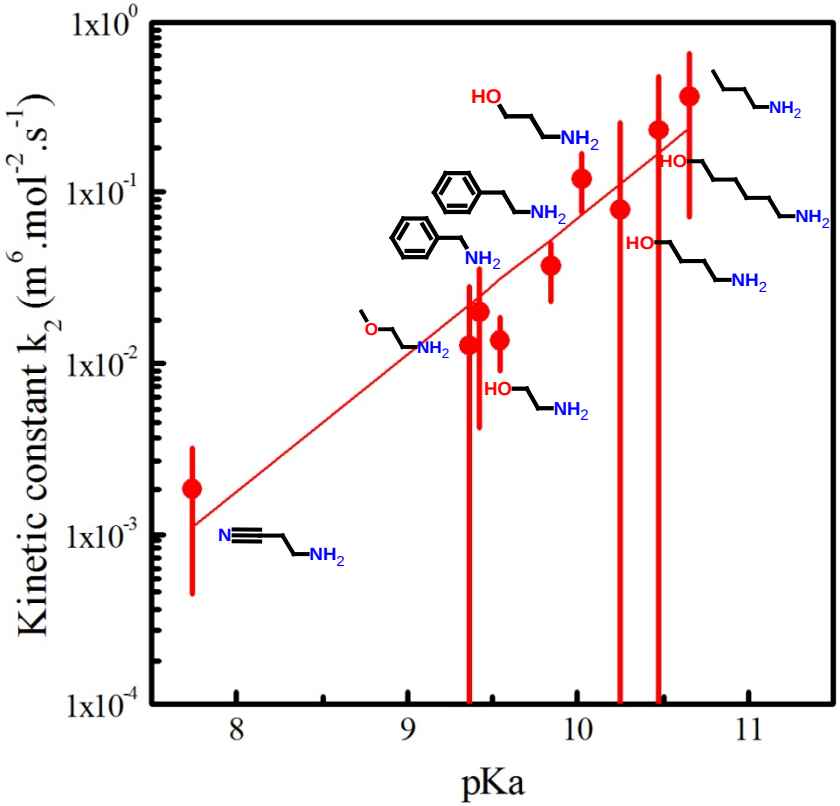




Experimental results

Primary amines (linear)

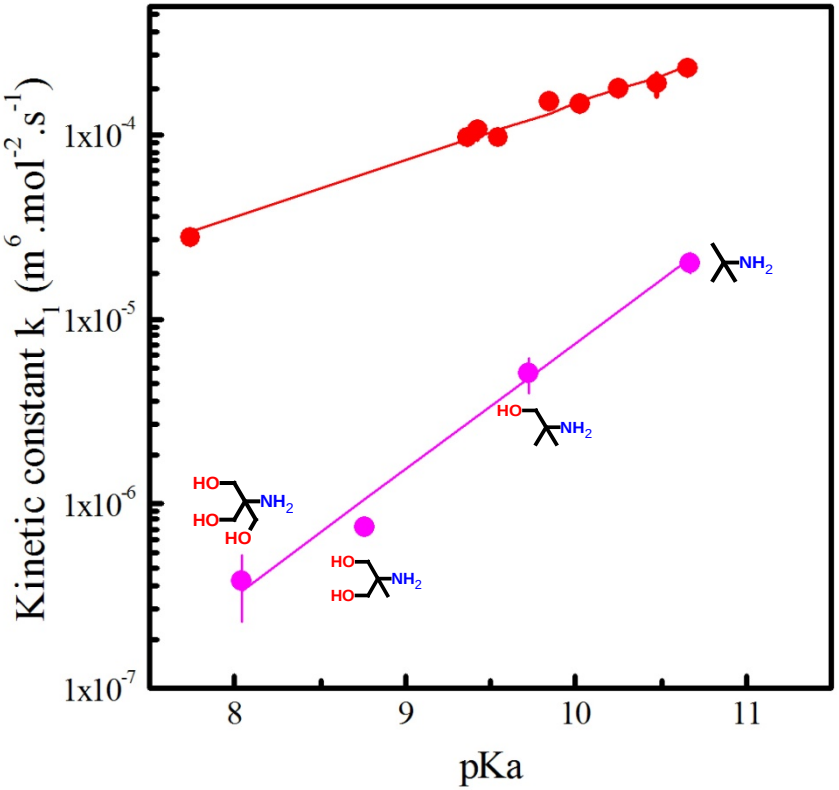


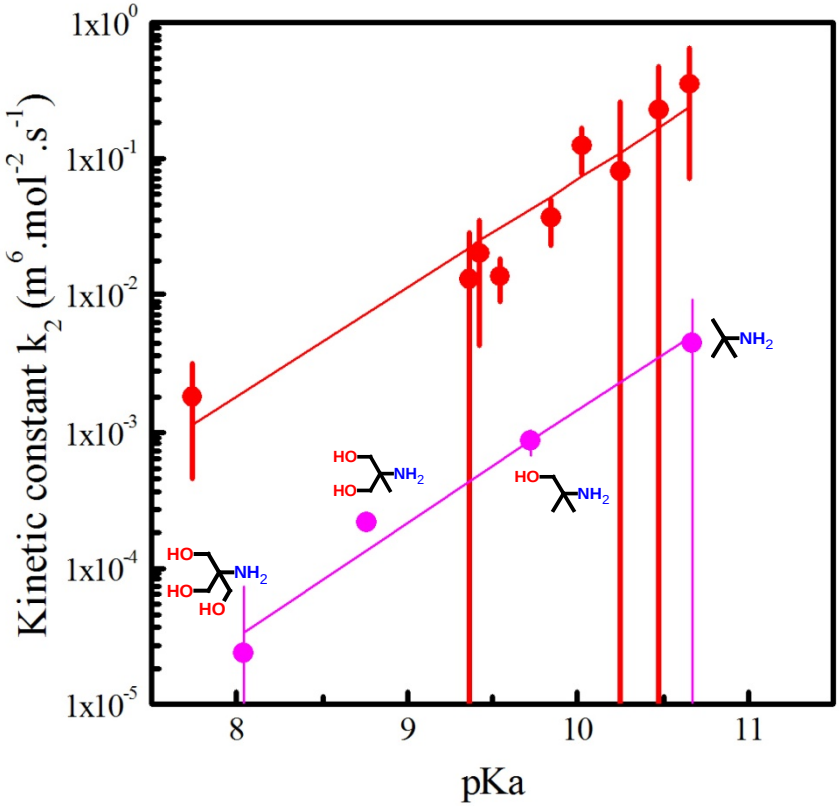


- Increase of kinetic constants k_1 & k_2 with increase of the pKa
- Different structures with the same properties (alkanol, benzyl and etheramines)

Experimental results

Primary amines (derivates from tert-butylamine)

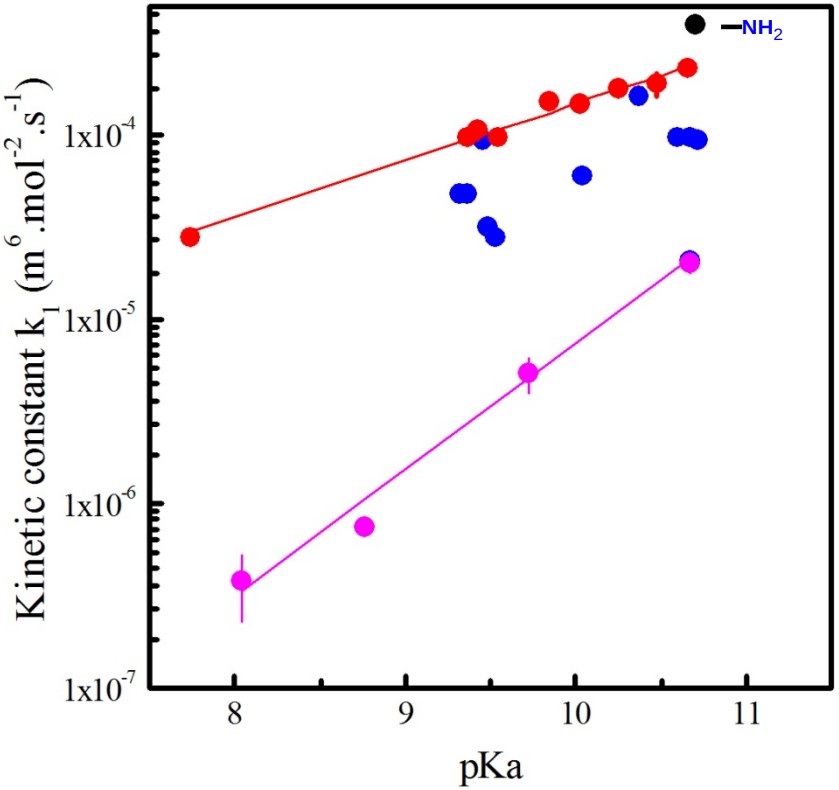


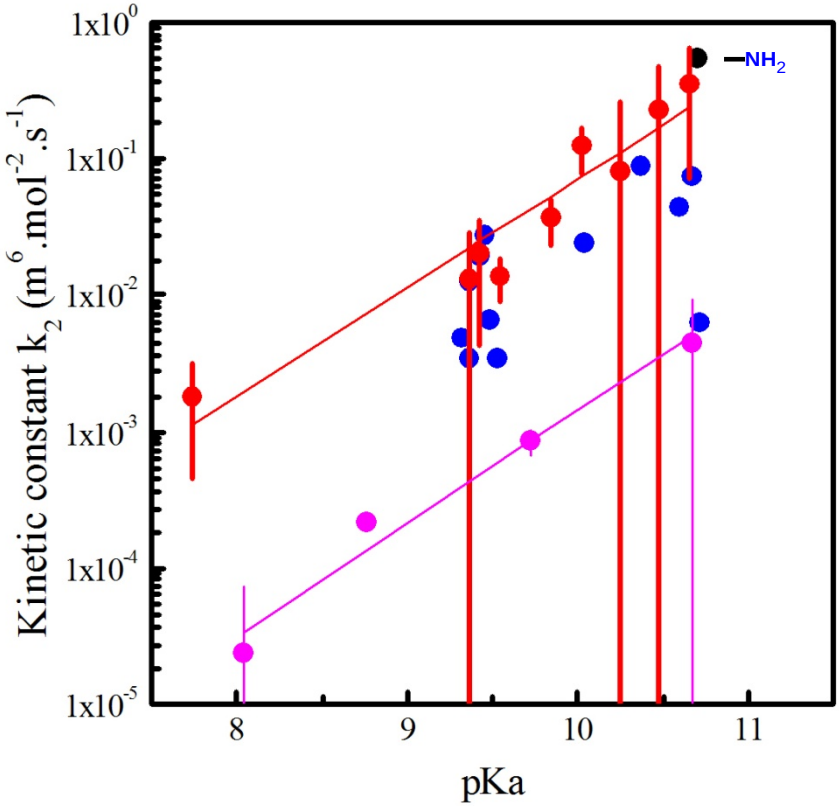


- Increase of kinetic constants k_1 & k_2 with increase of the pKa
- Slower than linear primary amines (steric hindrance)

Experimental results

Primary amines (all studied)

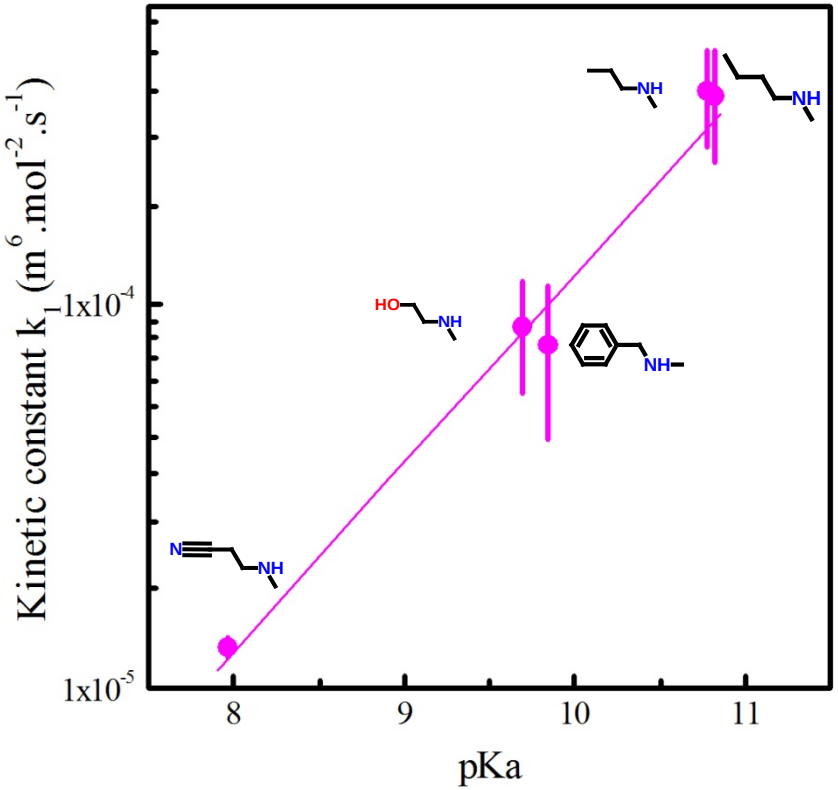


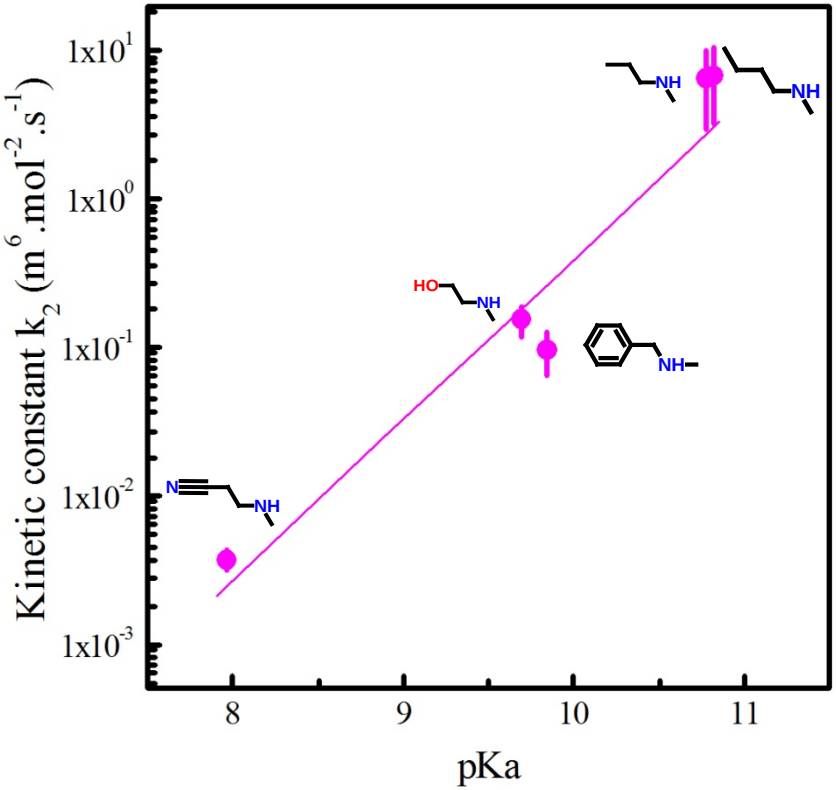


- Methylamine faster than linear primary amines
- Effect of steric hindrance of moderately hindered primary amines

Experimental results

Acyclic secondary amines (linear)

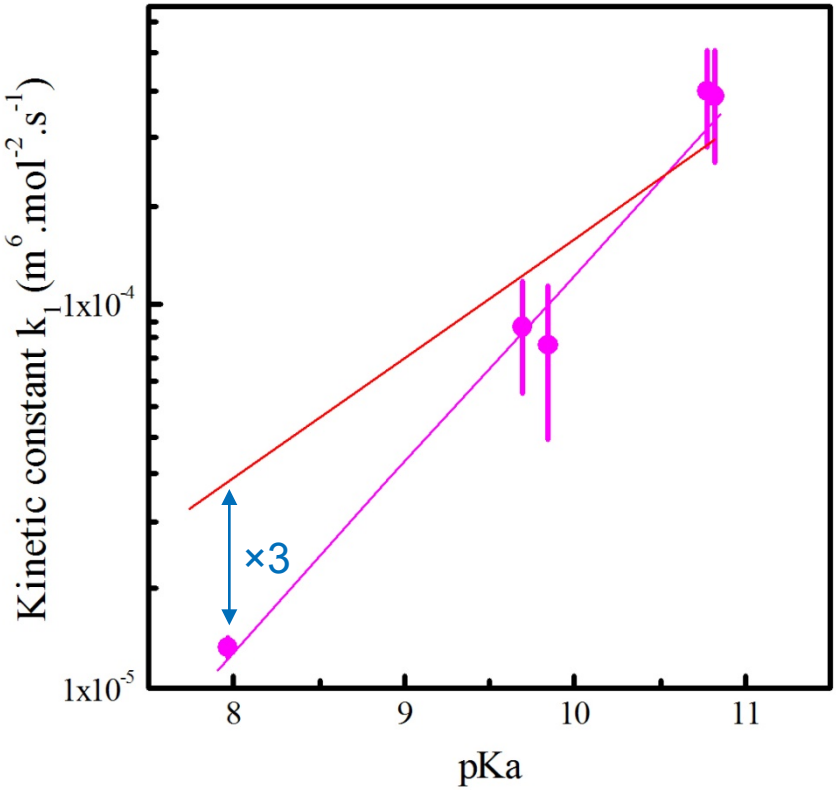


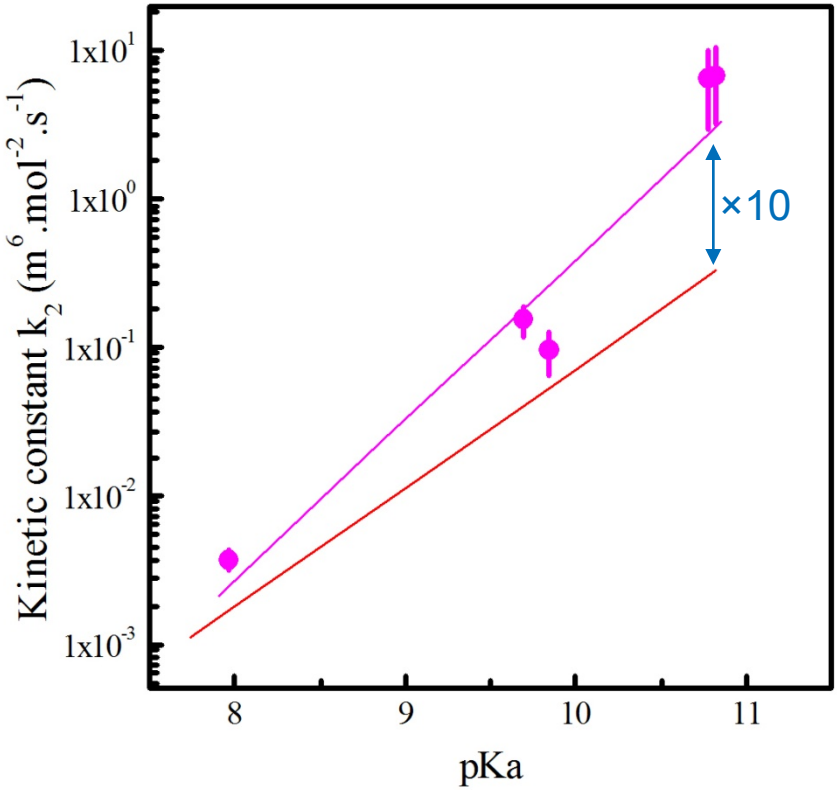


- Increase of kinetic constants k_1 & k_2 with increase of the pKa
- Different structures with the same properties (alkanolamines/benzylamines)

Experimental results

Acyclic secondary amines

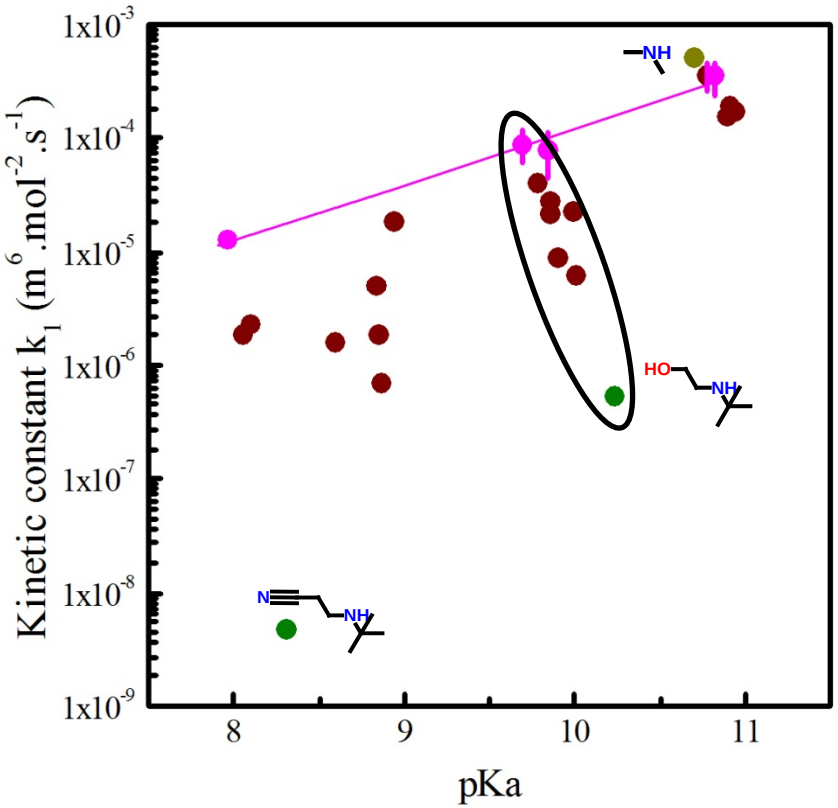


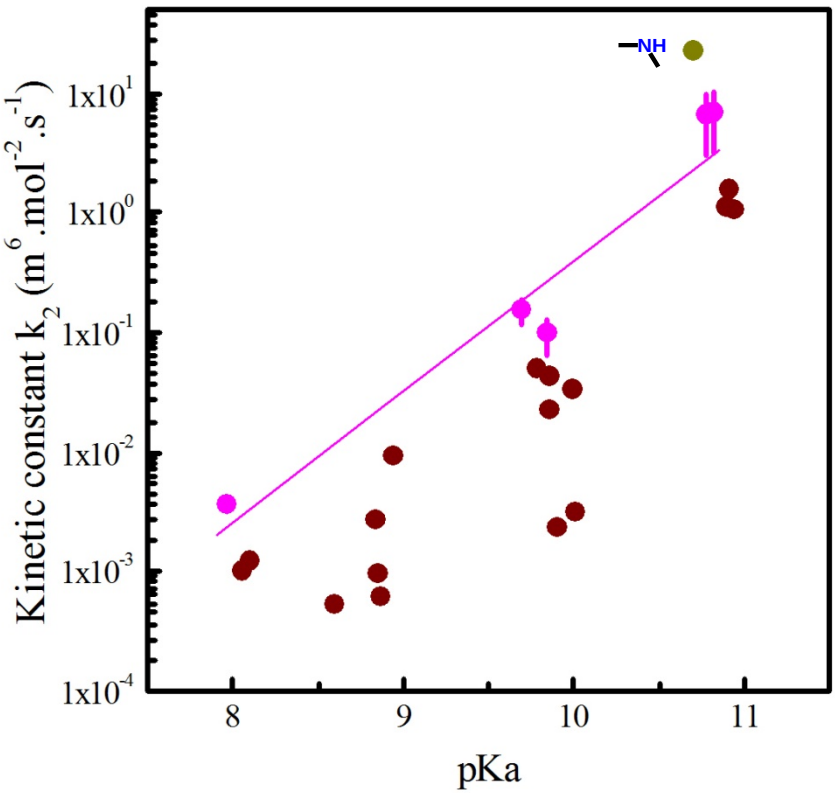


- k_1 linear secondary < k_1 linear primary ; k_2 linear primary < k_2 linear secondary
- In overall linear secondary amines more reactive than linear primary amines

Experimental results

Acyclic secondary amines (all studied)

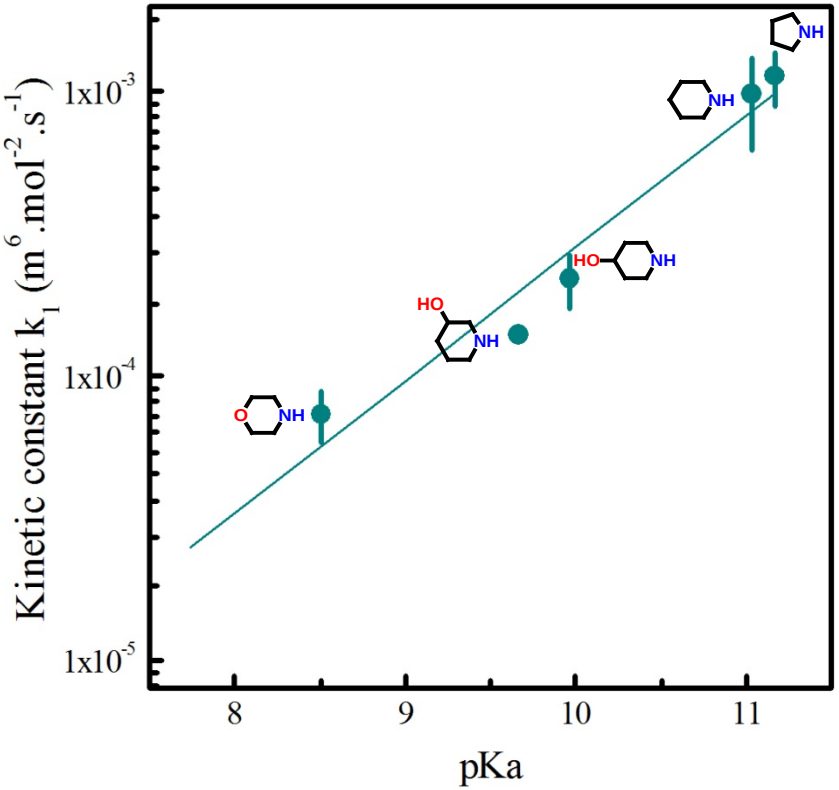


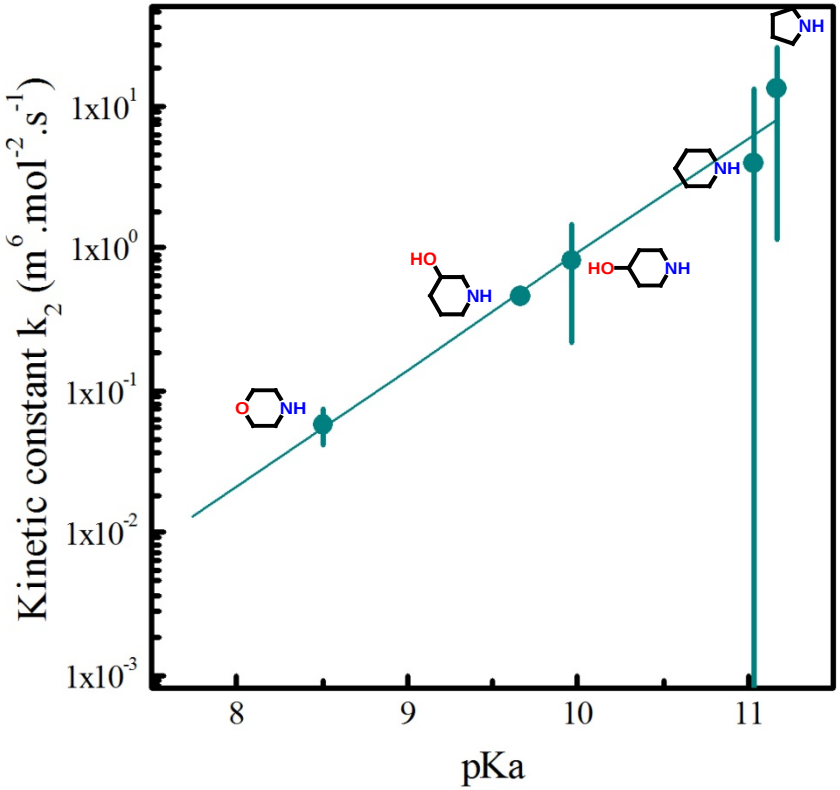


- Dimethylamine faster than others linear secondary amines
- Diminution of kinetic constants with increase of steric hindrance (max for tert-butyl)

Experimental results

Cyclic secondary amines (non sterically hindered)

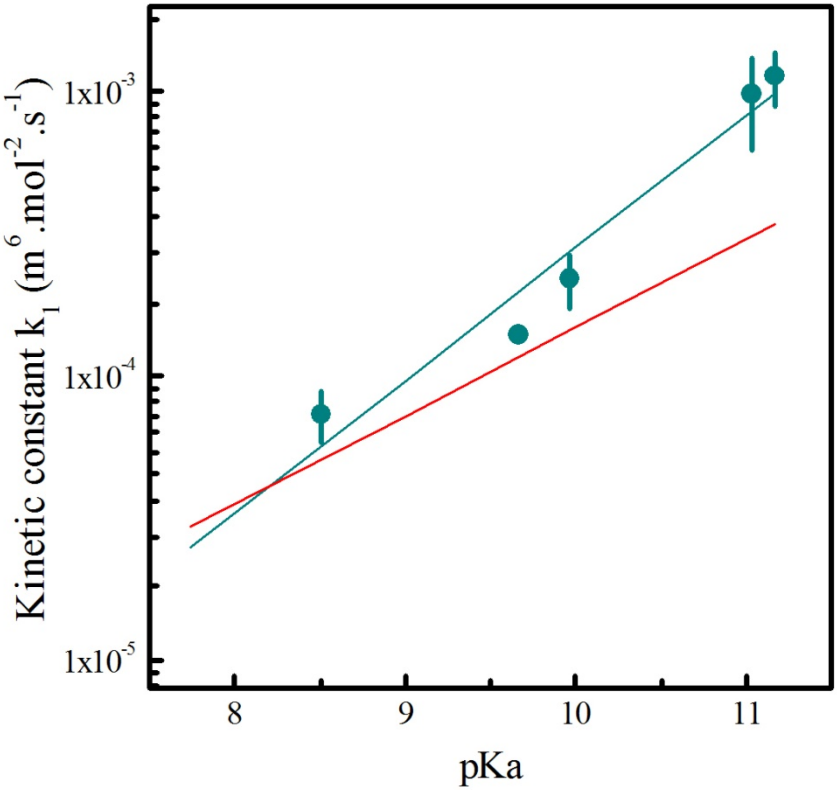


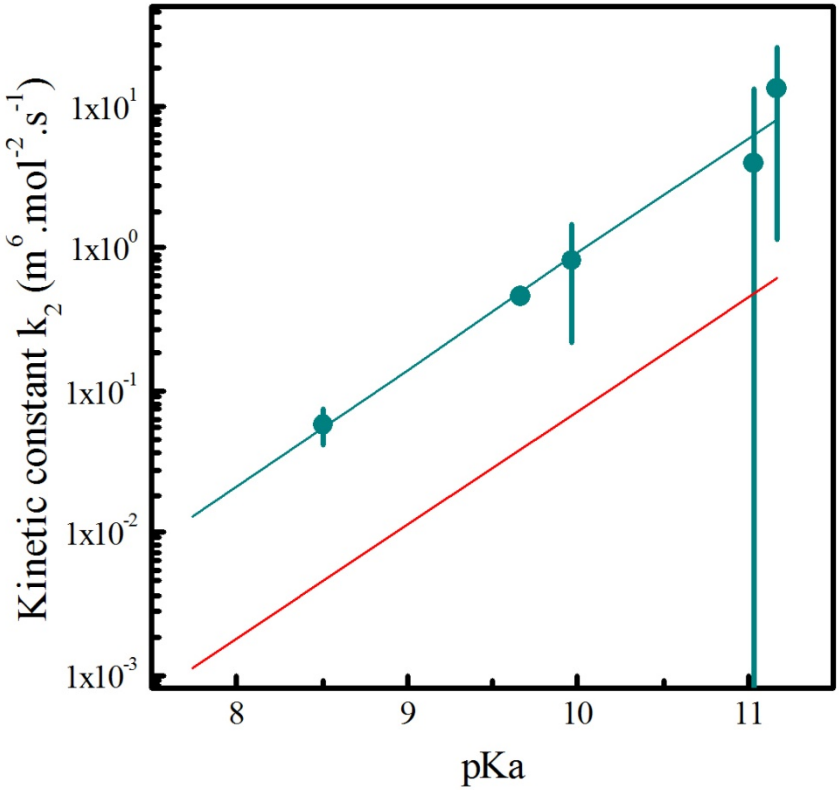


➢ Increase of kinetic constants k_1 & k_2 with increase of the pKa

Experimental results

Cyclic secondary amines

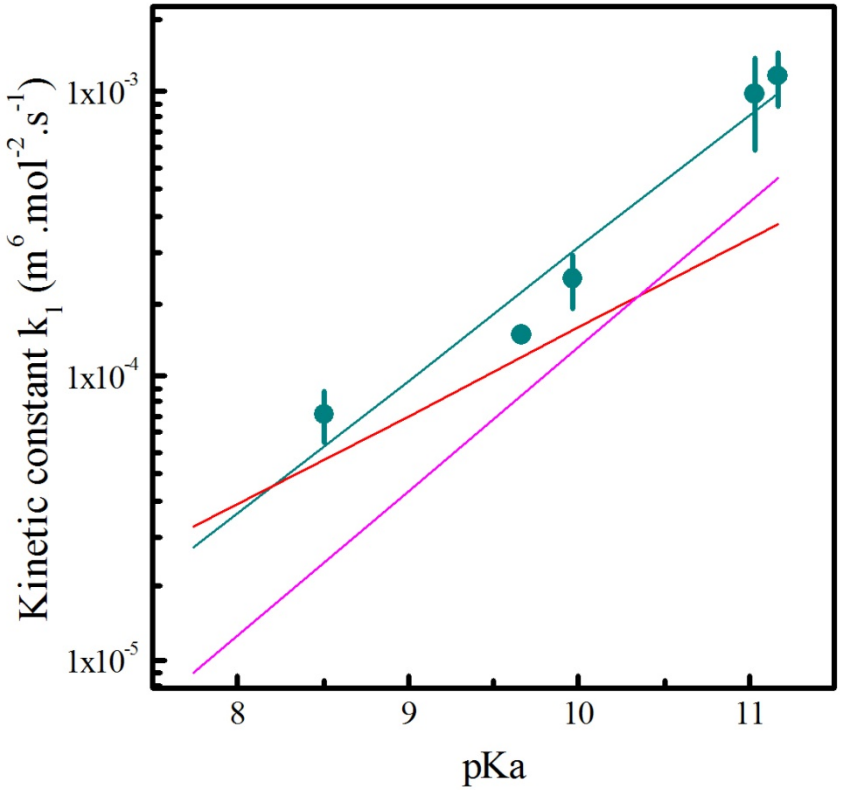


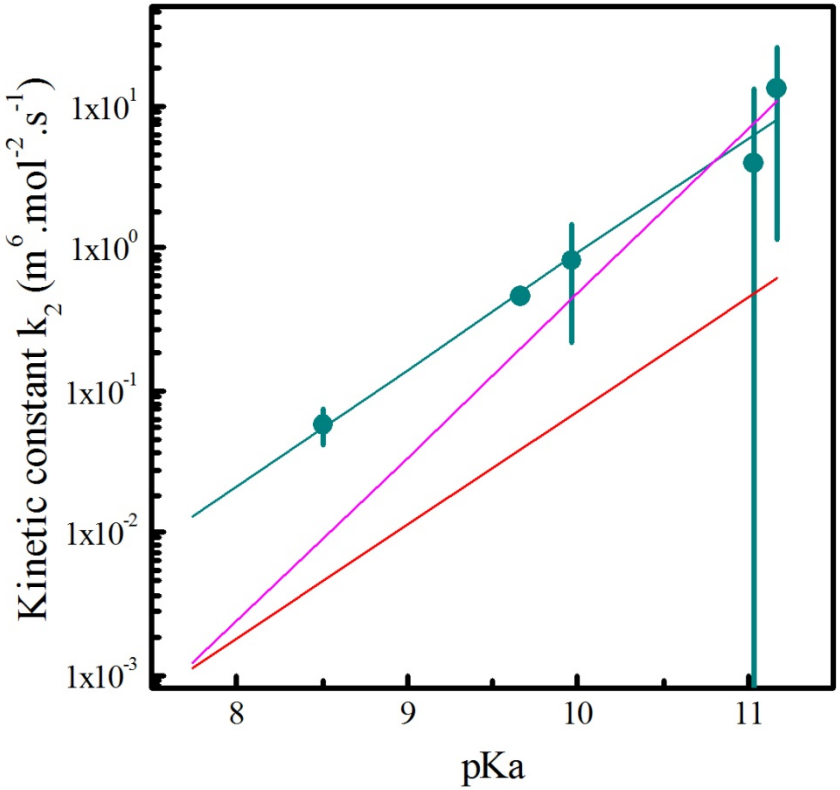


- Cyclic secondary amines more reactive than linear primary amines

Experimental results

Cyclic secondary amines

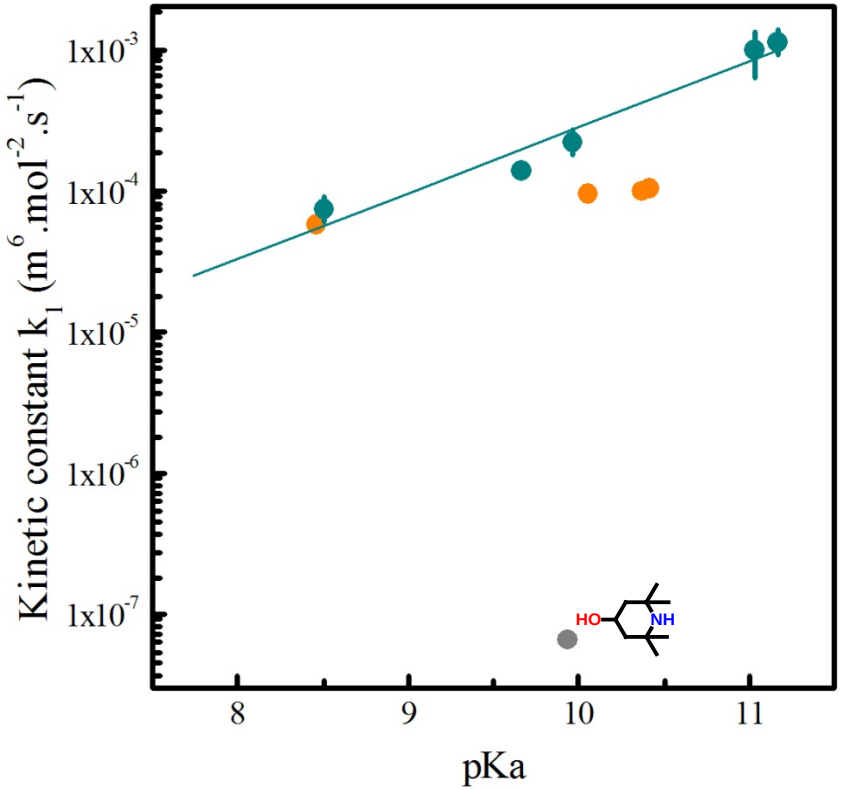


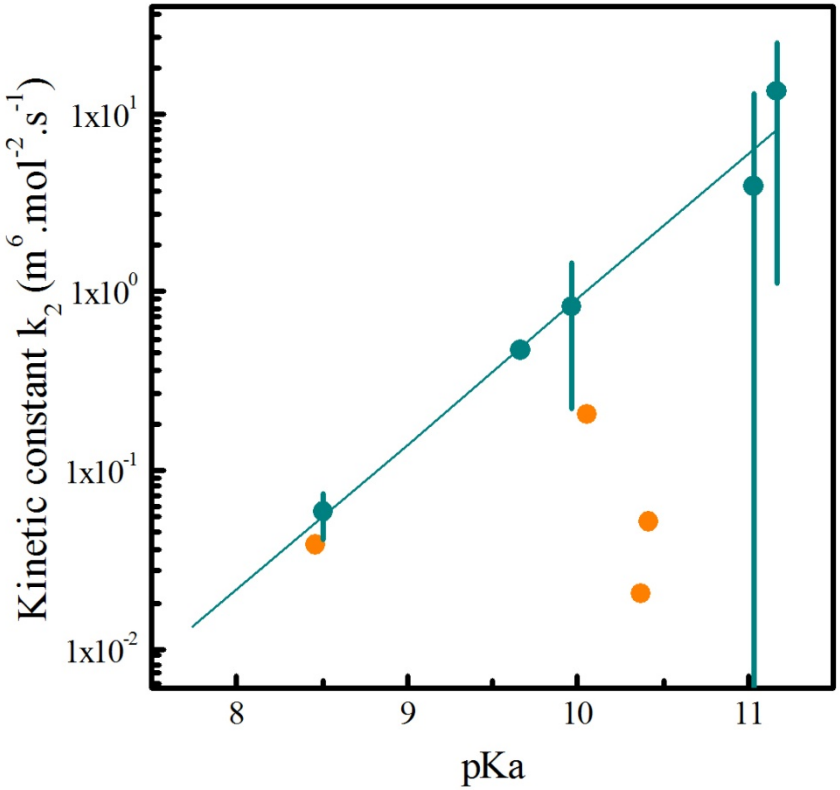


- Cyclic secondary amines more reactive than linear secondary amines
- Nucleophilicity: cyclic secondary > linear secondary > linear primary

Experimental results

Cyclic secondary amines (all studied)





➢ Diminution of kinetic constants k_1 & k_2 with steric hindrance

Q.S.P.R.

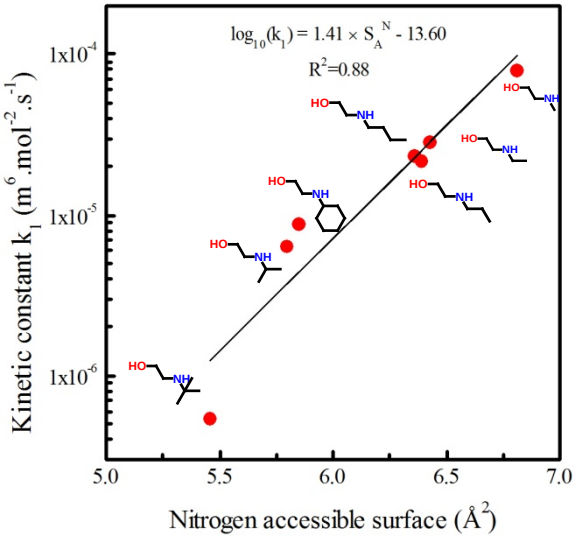
Methodology: determination of molecular descriptors

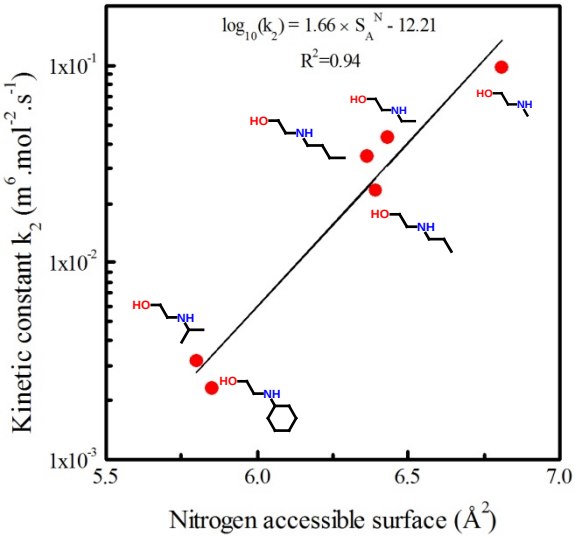
Molecule

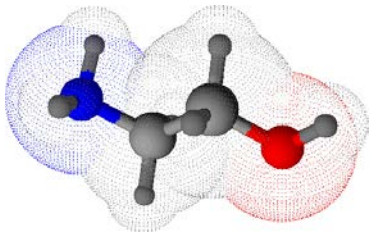
→ **Optimized structure**
Jaguar 7.9®
Quantum optimization
→ **109 generic descriptors**
-11 with Jaguar 7.9®
-98 with Material Studio 5.5.3®
→ Hierarchical clustering methods → **65 descriptors**

→ Acid/base titration → **pKa (25 °C)**

→ **Optimized structure**
Material Studio 5.5.3®
Lennard-Jones potential
→ Calculation of Van der Waals surface not shared with another atom → **Nitrogen accessible surface**

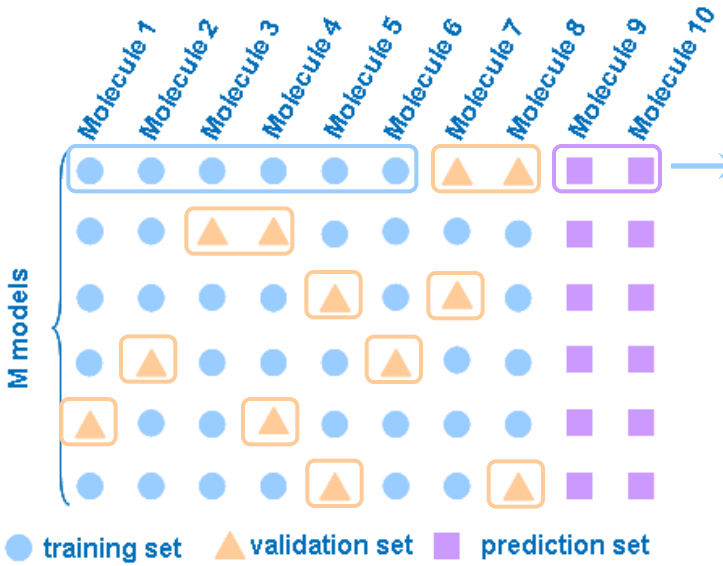






Q.S.P.R.

Methodology: determination of the predictive relationship



Training (1 model)

$$\hat{y} = b_0 + b_1 \times x_1 + b_2 \times x_2 + \cdots + b_j \times x_j$$

Coefficients obtained by PLS-GLR regression

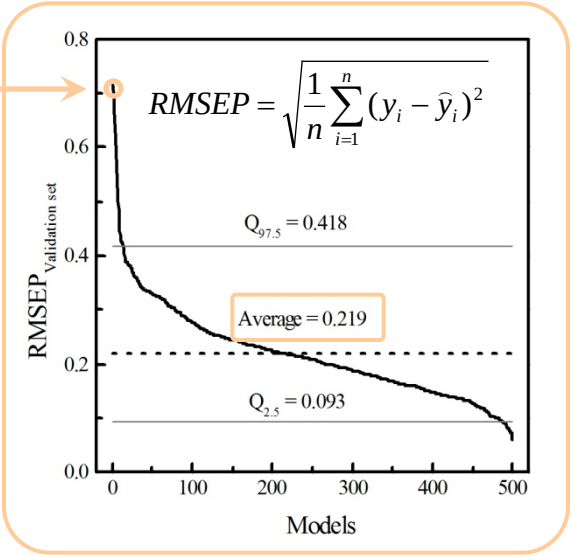
w property = $\log_{10}(k_i)$

b_0: intercept

b_1 to b_j: coefficients

x_1 to x_j: descriptors

Validation



500 models, 75 % training

Prediction

$$\hat{y}_{pred} = \bar{b}_0 + \bar{b}_1 \times x_1 + \bar{b}_2 \times x_2 + \cdots + \bar{b}_j \times x_j$$

w_{pred}: property of the predicted molecule

$\bar{b}_0$: average of the intercepts

$\bar{b}_1$ to $\bar{b}_j$: average of the coefficients

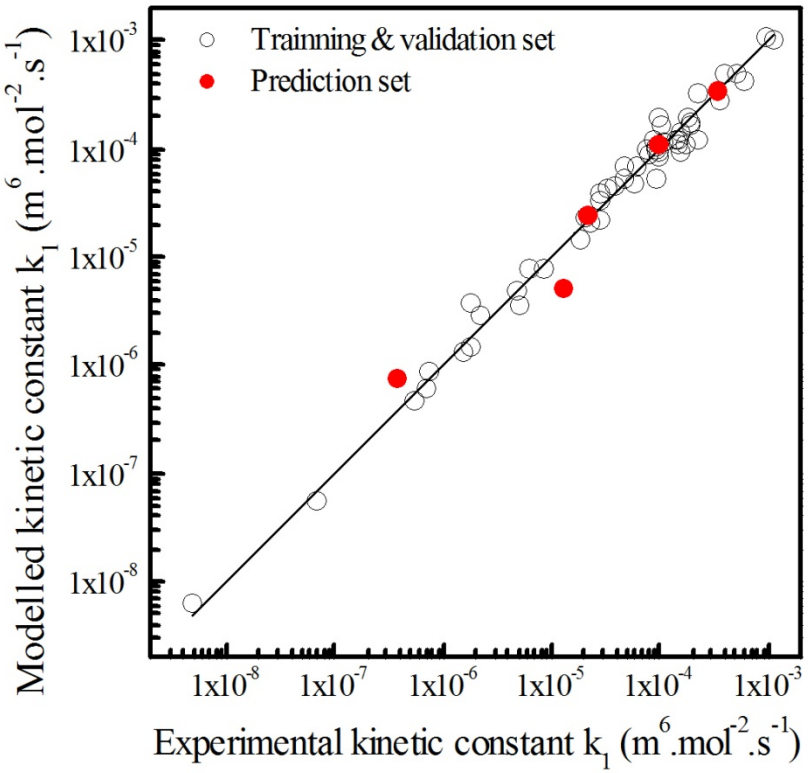
x_1 to x_j: descriptors

Estimation of the performance

Average relative error: $ARD = 100 \times \frac{\sum_{i=1}^{n} \frac{\left|10^{y_i^{exp}} - 10^{\bar{y}_{Hi}^{pred}}\right|}{10^{y_i}}}{n}$

Q.S.P.R.

Results: modeling of kinetic constant k_1



29 descriptors – order 2 – 123 terms

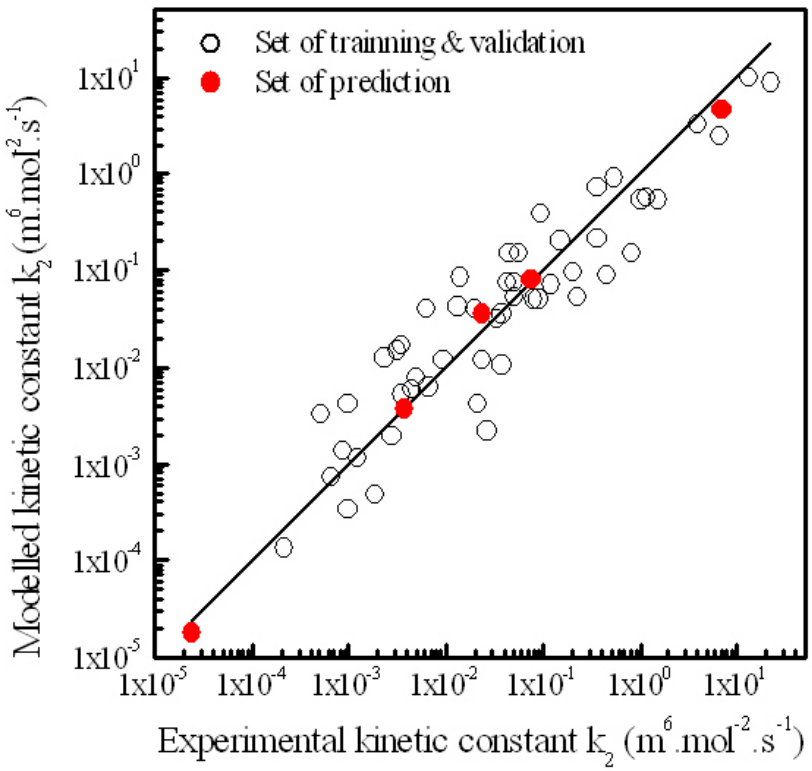
Coeffficients of normalized variables (main weight)

Term	Coefficient
pKa x NAS	0.0623
$(HOMOLUMOaq)^2$	-0.0596
pKa	0.0481
NAS	0.0465

Set	ARD ± σ_{RD}
Training & validation	23.1 ± 20.3 %
Prediction	37.5 ± 42.2 %

Q.S.P.R.

Results: modeling of kinetic constant k_2



16 descriptors – order 2 – 89 terms

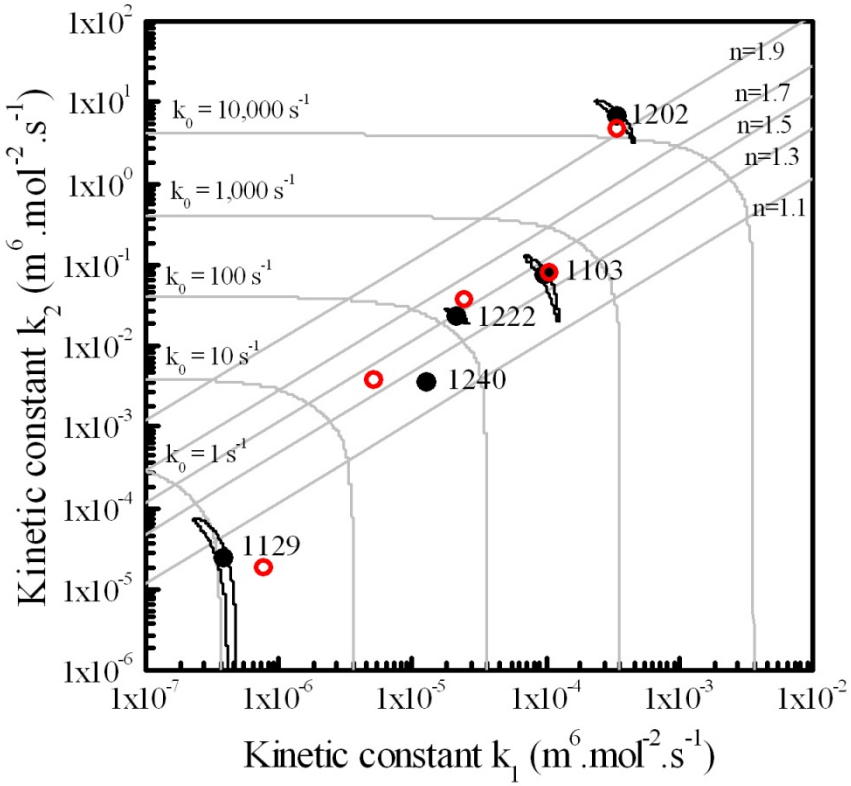
Coeffficients of normalized variables (main weight)

Term	Coefficient
$(HOMOLUMOaq)^2$	-0.0811
(HOMOLUMOaq)	0.0799
(HOMOLUMOaq)x HOMOg	-0.079
(HOMOLUMOaq)x MolDensity	0.0744
pKa x MolDensity	0.0668

Set	ARD ± σ_{RD}
Training & validation	117.7 ± 145.3 %
Prediction	23.3 ± 22.1 %

Q.S.P.R.

Results: comparison with experimental data

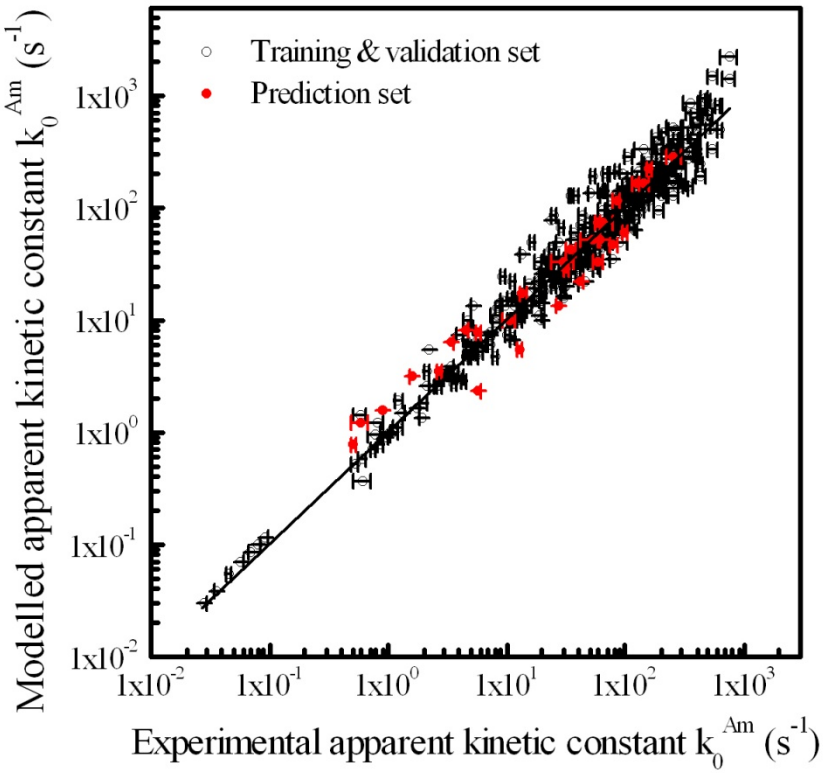


Amine	pKa	RD on k_1	RD on k_2
1103	10.67	11%	4%
1202	10.83	6%	31%
1222	9.86	13%	56%
1240	7.96	75%	1%
1129	8.04	102%	25%

Prediction of kinetic constants better for the faster molecules

Q.S.P.R.

Results: calculation of apparent kinetic constant k_0



Set	ARD ± σ_{RD}
Training & validation	39.2 ± 45.7 %
Prediction	39.9 ± 28.4 %

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, H_2O

[1] Limiting step

$H_2CO_3 \xrightarrow{H_2O} HCO_3^- + BaseH^+$ (k_{H_2O})

$$r_{CO_2}^{H_2O} = \underbrace{k_{H_2O}}_{k'_{H_2O}} .[H_2O].[CO_2]$$

k'_{H_2O} = 2,6.10^{-2} s^{-1} at 25 °C

[1] $CO_2 \xrightarrow{HO^-} HCO_3^-$ (k_{HO^-})

$$r_{CO_2}^{HO^-} = \underbrace{k_{HO^-}}_{8,32\ m^3.mol^{-1}.s^{-1}\ \text{at}\ 25\ °C} .[CO_2].[HO^-]$$

$CO_{2\,(aq)}$

Tertiary amines R_3N

$H_2O, R_3N \xrightarrow{k_{R_3N}} HCO_3^-, R_3NH^+$ [2]

$$r_{CO_2}^{R_3N} = \underbrace{k_{R_3N}}_{k'_{R_3N}} .[H_2O].[CO_2].[R_3N]$$

Based-catalyzed mechanism

$R_3N \xrightarrow{k_{AN},\, k_{-AN}} R_3N^+COO^- \xrightarrow{H_2O} HCO_3^-, R_3NH^+$ [2] ($k_{Dep}^{H_2O}$)

$$r_{CO_2}^{R_3N} = \frac{[R_3N].[CO_2]}{\frac{1}{k_{AN}} + \frac{1}{k'^{H_2O}_{Dep}.[H_2O]}}$$

Zwitterion

Amines primaires et secondaires R_2NH

$R_2NH \xrightarrow{k_{AN},\, k_{-AN}} R_2N^+HCO^-$

$R_2N^+HCO^- \xrightarrow{H_2O} H_3O^+ + R_2NCOO^-$ ($k_{Dep}^{H_2O}$) [2]

$R_2N^+HCO^- \xrightarrow{R_2NH} R_2N^+H_2 + R_2NCOO^-$ [3] ($k_{Dep}^{R_2NH}$)

Zwitterion

$$r_{CO_2}^{R_2NH} = \frac{[R_2NH].[CO_2]}{\frac{1}{k_{AN}} + \frac{1}{k'^{R_2NH}_{Dep}.[R_2NH] + k'^{H_2O}_{Dep}.[H_2O]}}$$

$R_2NH \xrightarrow{k_{AN}} R_2NCOOH$ instantaneous

$R_2NH, H_2O \xrightarrow{k_{Dep}^{H_2O}} R_2NH, R_2NH$ [2] ($k_{Dep}^{R_2NH}$)

Carbamic acid

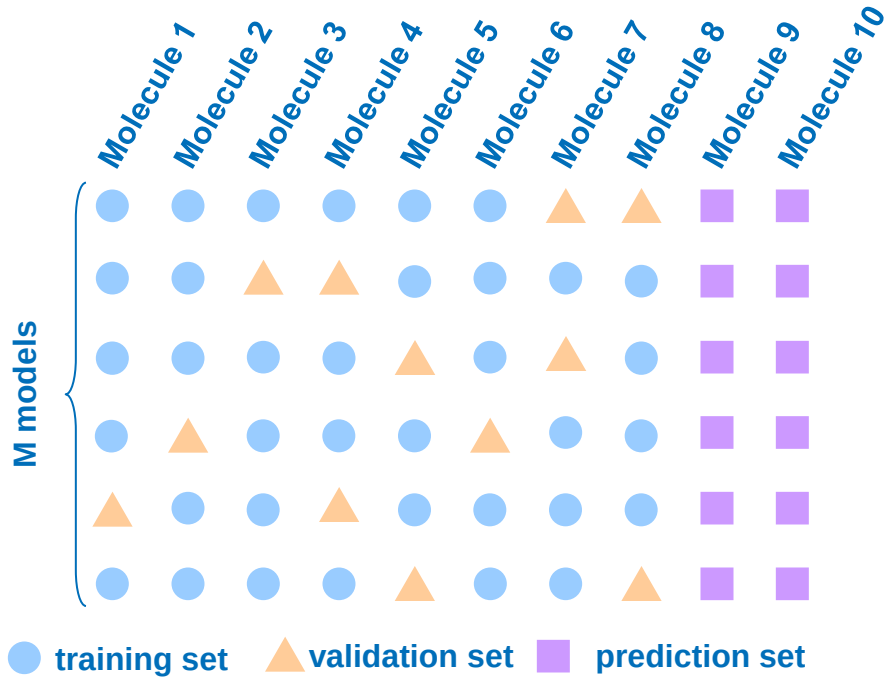
$$r_{CO_2}^{R_2NH} = k_{AN}.[CO_2].[R_2NH]$$

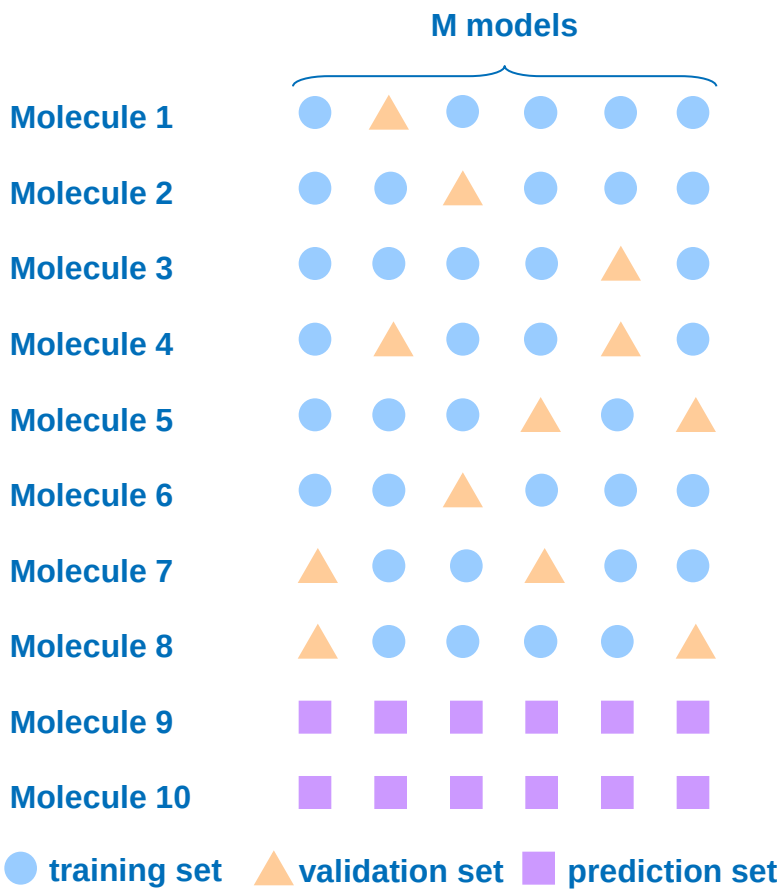
Termolecular

$$r_{CO_2}^{ter} = k_{Dep}^{H_2O}.[H_2O][R_2NH].[CO_2] + k_{Dep}^{R_2NH}[R_2NH]^2.[CO_2]$$

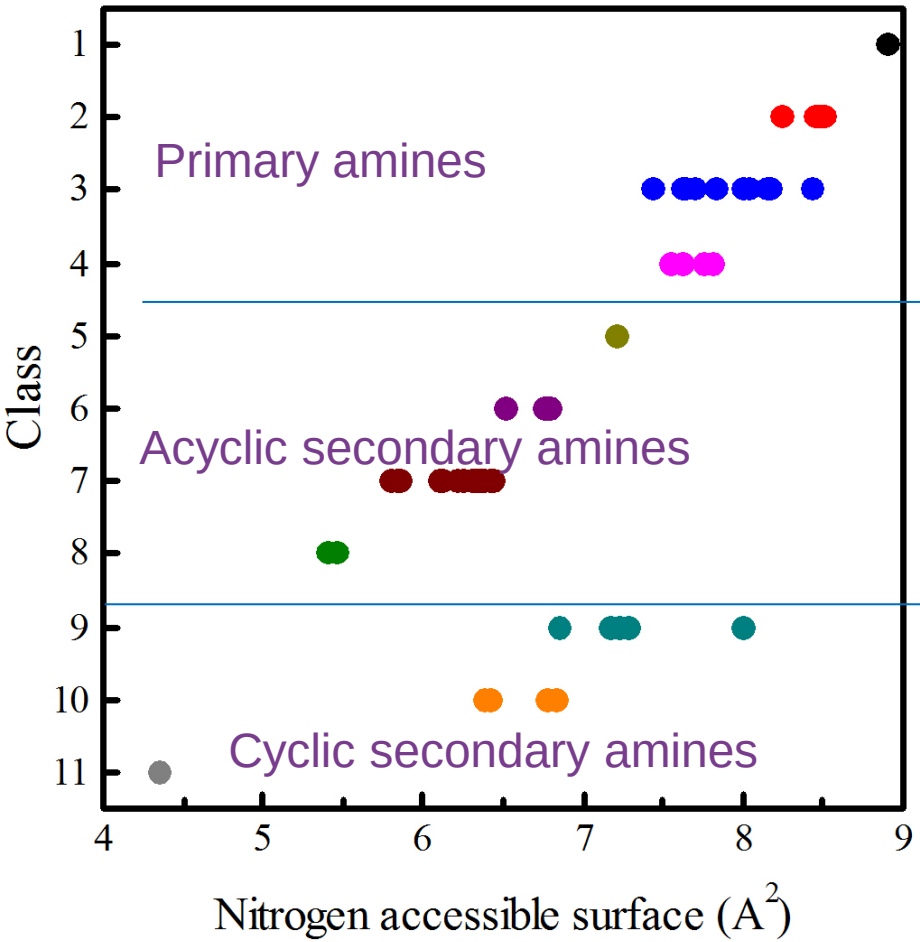
[1] Pinsent B.R.W., Pearson L. et Roughton F.J.W., The kinetics of combination of carbon dioxide with hydroxide ions, *Transactions of the Faraday Society*, 1956, **52**, pp.1512-1520.
[2] Vaidya P.D., Kenig E.Y., CO_2-alkanolamine reaction kinetics: A review of recent studies, *Chemical Engineering & Technology*, 2007, **30**, n°11, pp.1467-1474.
[3] McCann N. et al. Kinetics and Mechanism of Carbamate Formation from CO_2(aq), Carbonate Species, and Monoethanolamine, *The Journal of Physical Chemistry A*, 2009, **113**, n°17, pp.5022-5029.

Appendices





Appendices



Methylamine

Linear primary amines

Moderately hindered primary amines

Severally hindered primary amines

Dimethylamine

Linear acyclic secondary amines

Moderately hindered acyclic secondary amines

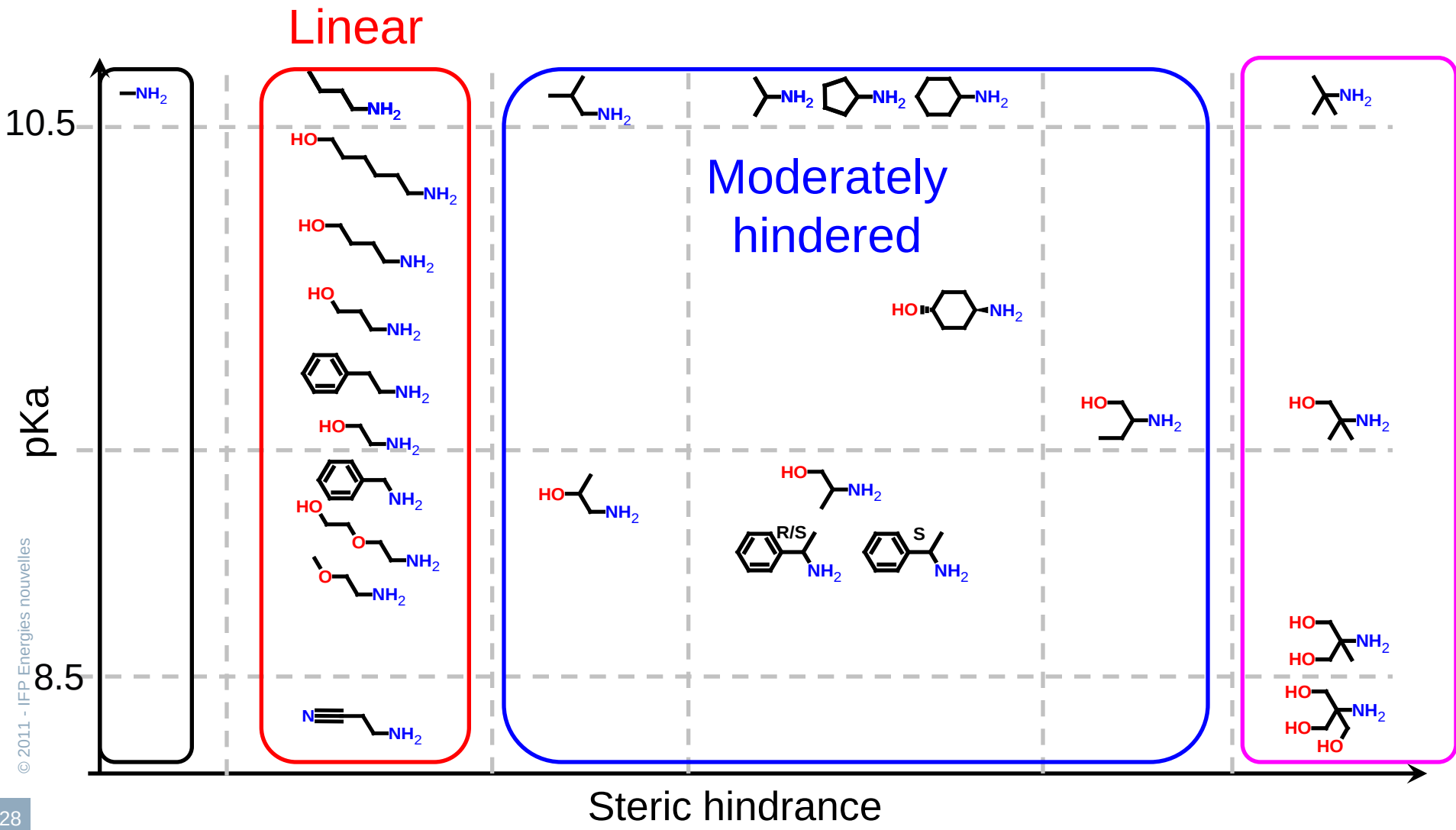
Severally hindered acyclic secondary amines

Non sterically hindered cyclic secondary amines

Moderately hindered cyclic secondary amines

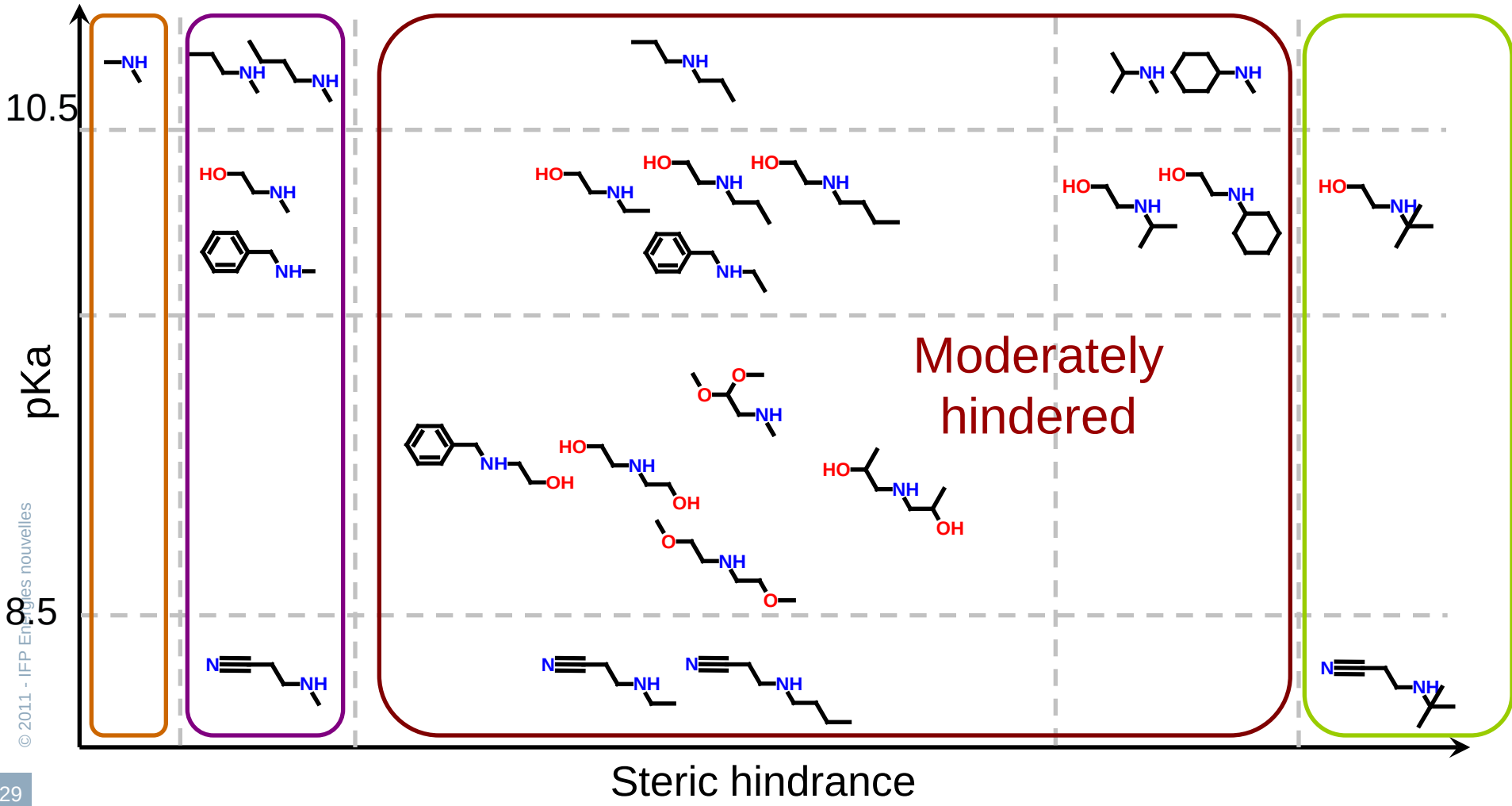
Severally hindered cyclic secondary amines

Appendices



Appendices

Linear methylamines



Appendices