



HAL
open science

Deracemization of sodium chlorate in the presence of sodium dithionate

Manon Schindler, Clément Brandel, Woo-Sik Kim, Gerard Coquerel

► **To cite this version:**

Manon Schindler, Clément Brandel, Woo-Sik Kim, Gerard Coquerel. Deracemization of sodium chlorate in the presence of sodium dithionate. Biwic 25th, Sep 2018, Rouen, France. hal-01953035

HAL Id: hal-01953035

<https://hal.science/hal-01953035>

Submitted on 12 Dec 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Schindler Manon^{a*}, Brandel Clément^a, Kim Woo-Sik^b, Coquerel Gérard^a

^a Normandie Univ, UNIROUEN, Laboratoire SMS EA 3233, F-76130 Mont-Saint-Aignan, France

^b Kyung Hee University (경희대학교), Functional Crystallization Center, Seoul, South Korea

*E-mail: manon.schindler@etu.univ-rouen.fr



INTRODUCTION

- **Deracemization** via crystallization has the advantage to give access to 100% yield of pure enantiomers in the solid state.¹
- Achiral inorganic salt sodium chlorate (NaClO_3) crystallizes in a chiral space group $P2_13$ giving rise to two enantiomorphous crystals (Figures 1 and 2).^{3,4}
- While deracemization of NaClO_3 by **attrition** (i.e. Viedma ripening) has been widely described,⁵ **temperature cycles induced deracemization (TCID)** has been specifically used for organic compounds.^{6,7}
- **Sodium dithionate** ($\text{Na}_2\text{S}_2\text{O}_6$), as impurity, generates morphological and growth kinetics changes of NaClO_3 crystals.⁸ Via the similar geometry of the ClO_3^- ions and the SO_3^- moiety of the dithionate ions, $\text{Na}_2\text{S}_2\text{O}_6$ docks onto $\{111\}$ faces of NaClO_3 (Figure 3) and triggers the secondary nucleation of the counter NaClO_3 enantiomorph giving a phenomenon of epitaxy (Figure 4).⁹

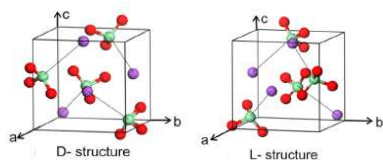


Figure 1 Enantiomorphous structures of NaClO_3

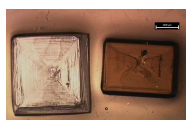


Figure 2 Crystals of NaClO_3 from aqueous solution observed under polarized light.

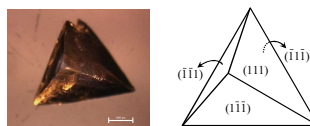


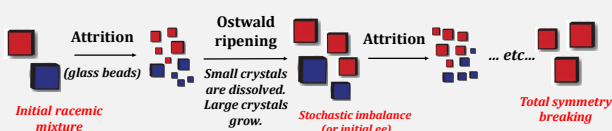
Figure 3 Crystal of NaClO_3 showing the tetrahedral morphology, obtained by evaporation of solvent at room temperature in presence of $\text{Na}_2\text{S}_2\text{O}_6$.



Figure 4 Epitaxy of NaClO_3 showing two opposite handedness obtained by evaporation of solvent at room temperature in presence of $\text{Na}_2\text{S}_2\text{O}_6$.

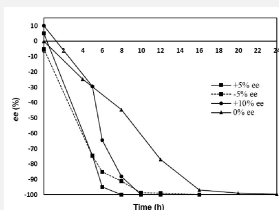
ATTRITION ENHANCED DERACEMIZATION

I. Theory: Viedma ripening



III. Results

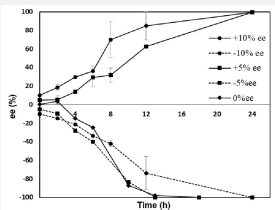
Preliminary tests using Alfa Aesar commercial NaClO_3



! \ Systematic final ee at -100% ! \

Impurities in Alfa Aesar commercial product?

Deracemization tests using recrystallized NaClO_3



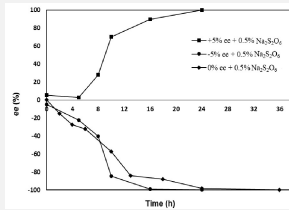
Total deracemization of NaClO_3 toward expected final ee.

II. Experimental conditions



- 20 mL of saturated solution at 20 °C + 5 g of NaClO_3 crystals + 15 g of glass beads (1.5 mm).
- Thermostated round bottom flasks at 20 °C.
- Magnetic stirring (1000 rpm).
- Samplings are submitted to growth step to count crystals.

With impurity: $\text{Na}_2\text{S}_2\text{O}_6$, 0,5% mol



No specific effect of $\text{Na}_2\text{S}_2\text{O}_6$ on NaClO_3 deracemization.

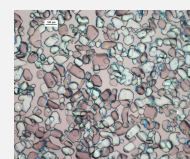
→ Could higher amount of $\text{Na}_2\text{S}_2\text{O}_6$ influence NaClO_3 deracemization?

! \ Higher amount of $\text{Na}_2\text{S}_2\text{O}_6$ could hamper growth step of crystals ! \

Determination of ee

Enantiomeric excess is determined according to the equation [1] by manual counting NaClO_3 crystals of each chirality under polarized light microscopy.

$$ee\% = \frac{m_d - m_l}{m_d + m_l} \times 100 \quad \text{Eq. [1]}$$



ee = 0%



ee = 100%

CONCLUSION & PERSPECTIVES

ATTRITION

TCID

Deracemization

- ❖ Total deracemization of NaClO_3 toward expected final ee via attrition.
- ❖ First deracemization of NaClO_3 via temperature cycles.

Deracemization in presence of $\text{Na}_2\text{S}_2\text{O}_6$ (0,5% mol)

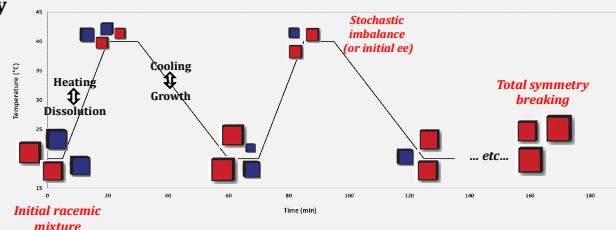
- ❖ No specific effect on attrition enhanced deracemization.
- ❖ No epitaxy observed in samplings
- ❖ Significant delay of NaClO_3 deracemization via TCID in the presence of $\text{Na}_2\text{S}_2\text{O}_6$.

Perspectives

- ❖ Influence of higher amount of $\text{Na}_2\text{S}_2\text{O}_6$ on deracemization.
- ❖ Investigation of the $\text{Na}_2\text{S}_2\text{O}_6$ impact during the delayed period in TCID experiments.

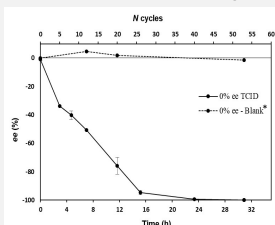
TEMPERATURE CYCLES INDUCED DERACEMIZATION (TCID)⁴

I. Theory



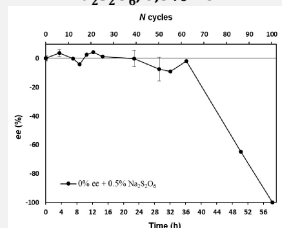
III. Results

Deracemization tests using recrystallized NaClO_3



First NaClO_3 deracemization by TCID

With impurity: $\text{Na}_2\text{S}_2\text{O}_6$, 0,5% mol



Starting of deracemization is significantly delayed by the presence of $\text{Na}_2\text{S}_2\text{O}_6$

II. Experimental conditions

- 10 mL of saturated solution + 5 g of NaClO_3 crystals.
- Thermostated round bottom flasks
- Magnetic stirring (500 rpm).
- Temperature cycles between 26 and 40 °C. (12% more of solid dissolved at 40 °C)
- Heating rate: 1.2 °C/min
- Cooling rate: 0.8 °C/min

→ No epitaxy observed in samplings.

→ What is the effect of $\text{Na}_2\text{S}_2\text{O}_6$ on the system during the delayed period?

→ Could higher amount of $\text{Na}_2\text{S}_2\text{O}_6$ totally block deracemization?

*Blank: reactor subjected to a constant temperature of 20 °C

References

- [1] W. L. Noorduin *et al.*, *Angew. Chem. Int. Ed.* **2009**, *48* (51), 9600–9606.
- [2] F. S. Kipping; W. J. Pope, *J. Chem. Soc. Trans.*, **1898**, *73*, 606–617.
- [3] D. K. Kondepudi *et al.*, *Sciences*, **1990**, *250*, 975–976.
- [4] J. Ahn *et al.*, *Cryst. Growth Des.* **2018**, *18* (1), 297–306.
- [5] C. Viedma, *Phys. Rev. Lett.*, **2005**, *94* (6).
- [6] K. Suwannasang *et al.*, *Cryst. Growth Des.* **2016**, *16*, 6461–6467.
- [7] F. Cameli *et al.*, *CrystEngComm* **2018**, *20* (21), 2897–2901.
- [8] R. Ristic *et al.*, *J. Phys. Chem.*, **1993**, *97* (41), 10774–10782.
- [9] Z.-P. Lan, *et al.*, *Growth & Design*, **2014**, *14* (11), 6084–6092.1

Acknowledgments

This work was funded by the Normandy region and European regional development fund (FEDER).

