The effects of iodide on diethylenetriamine (DETA) oxidation

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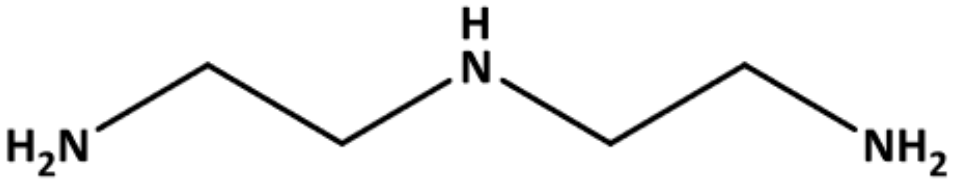
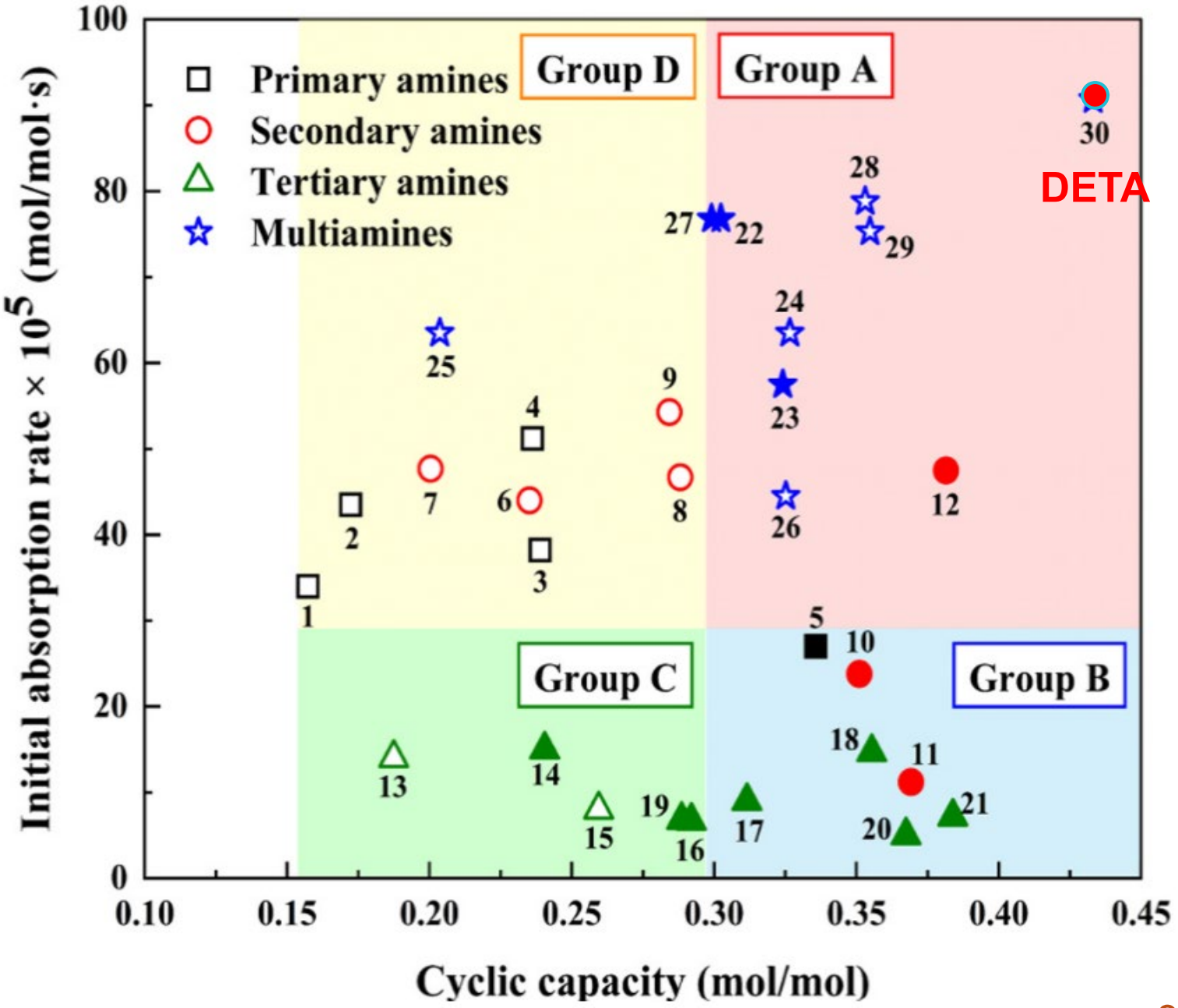
Outline

- Introduction: inhibition by iodide
- Apparatus
  - High Oxygen Pressure Reactor (HOPR)
  - High Gas Flow reactor (HGF)
- Analytical methods: GC, Peroxide Determination
- Results with DETA
  - HOPR and HGF
  - Peroxide
- Conclusions: iodide decomposes peroxide

DETA has great CO_2 capture performance



Diethylenetriamine (DETA)



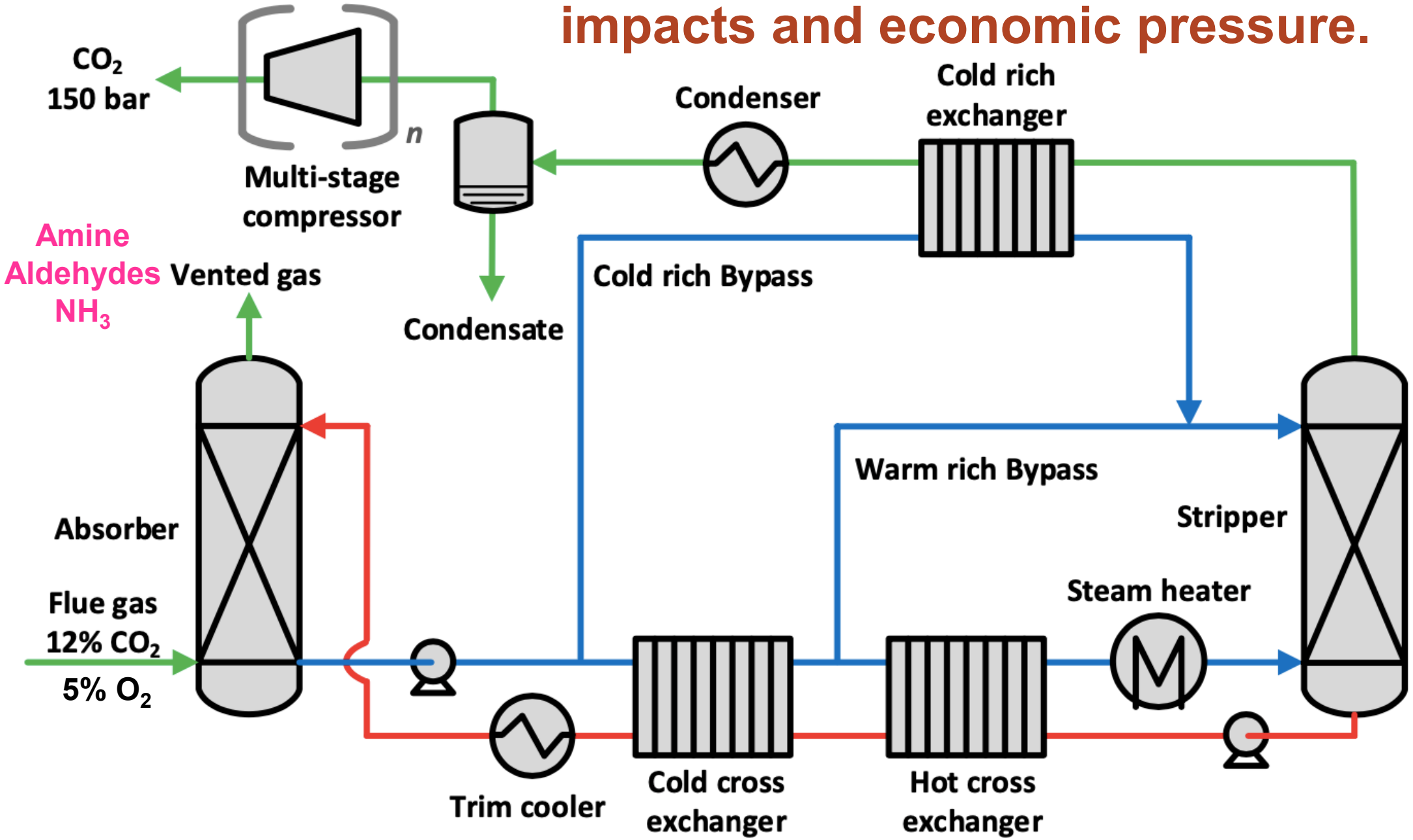
(Kim, 2024)

DETA has great performance in biphasic solvents

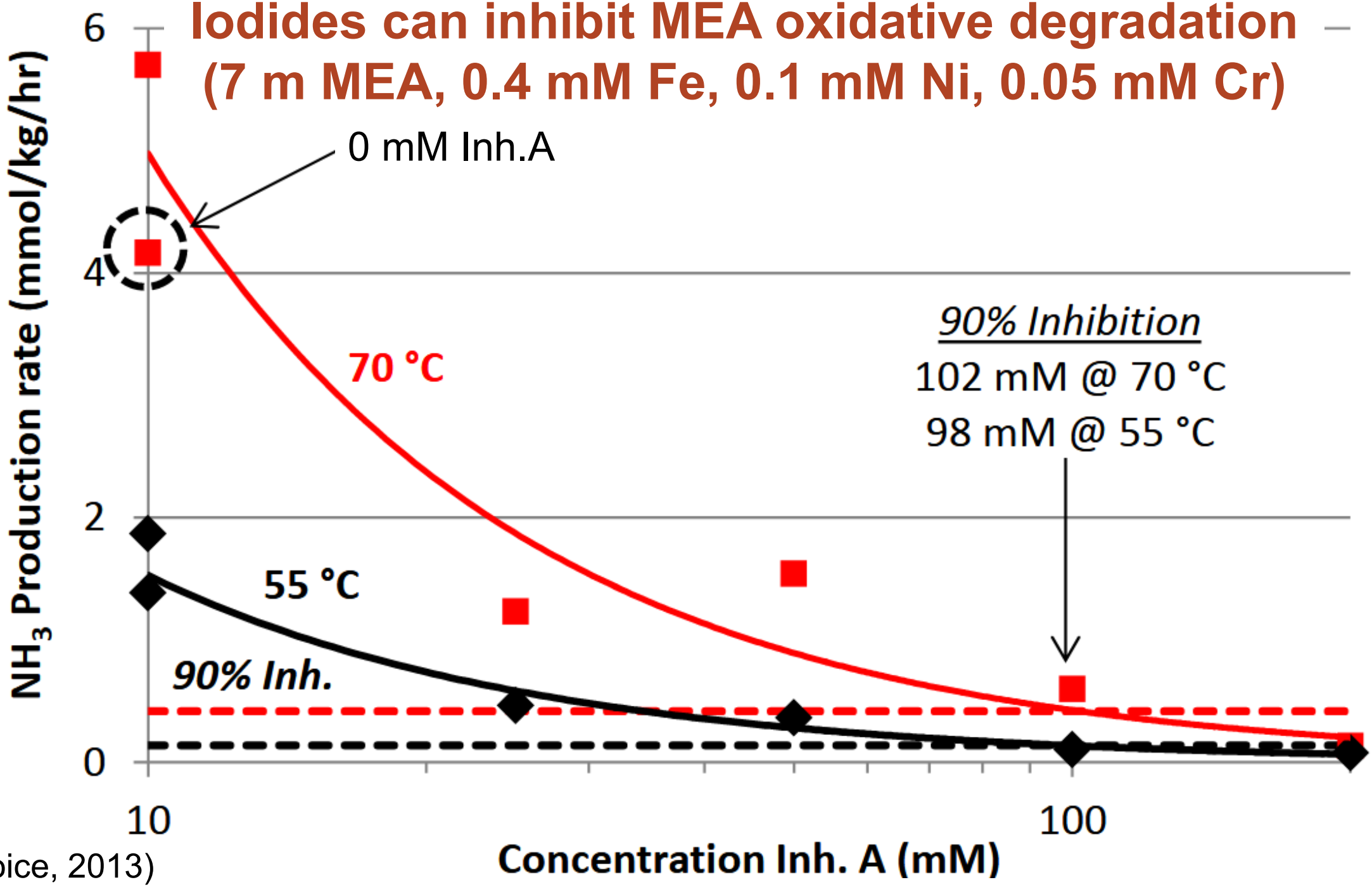
Solvent	Cyclic capacity (mol/L)
2.5DETA-4TMS	4.5
2DETA-3DGM	3.6
2.6DETA-4.8DMSO	3.4
5MEA	1.6

(Xu, 2019)

Amine oxidation leads to environmental impacts and economic pressure.

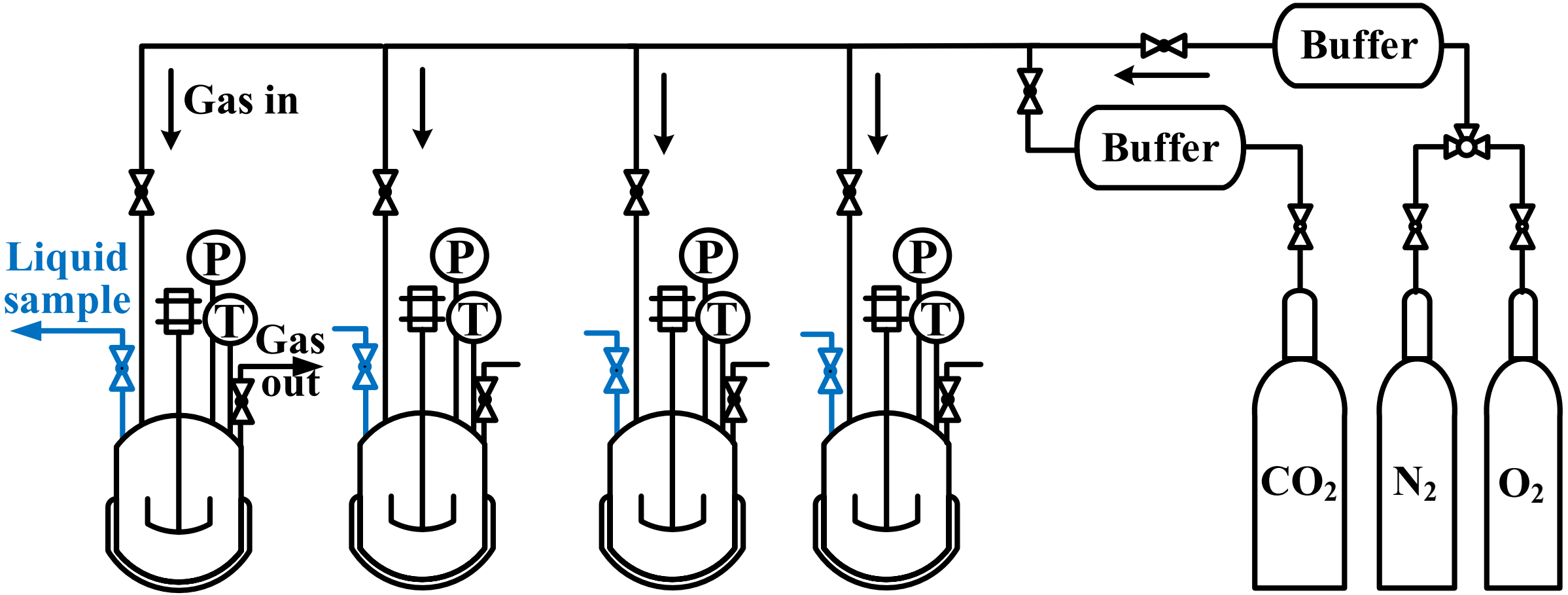


Iodides can inhibit MEA oxidative degradation (7 m MEA, 0.4 mM Fe, 0.1 mM Ni, 0.05 mM Cr)



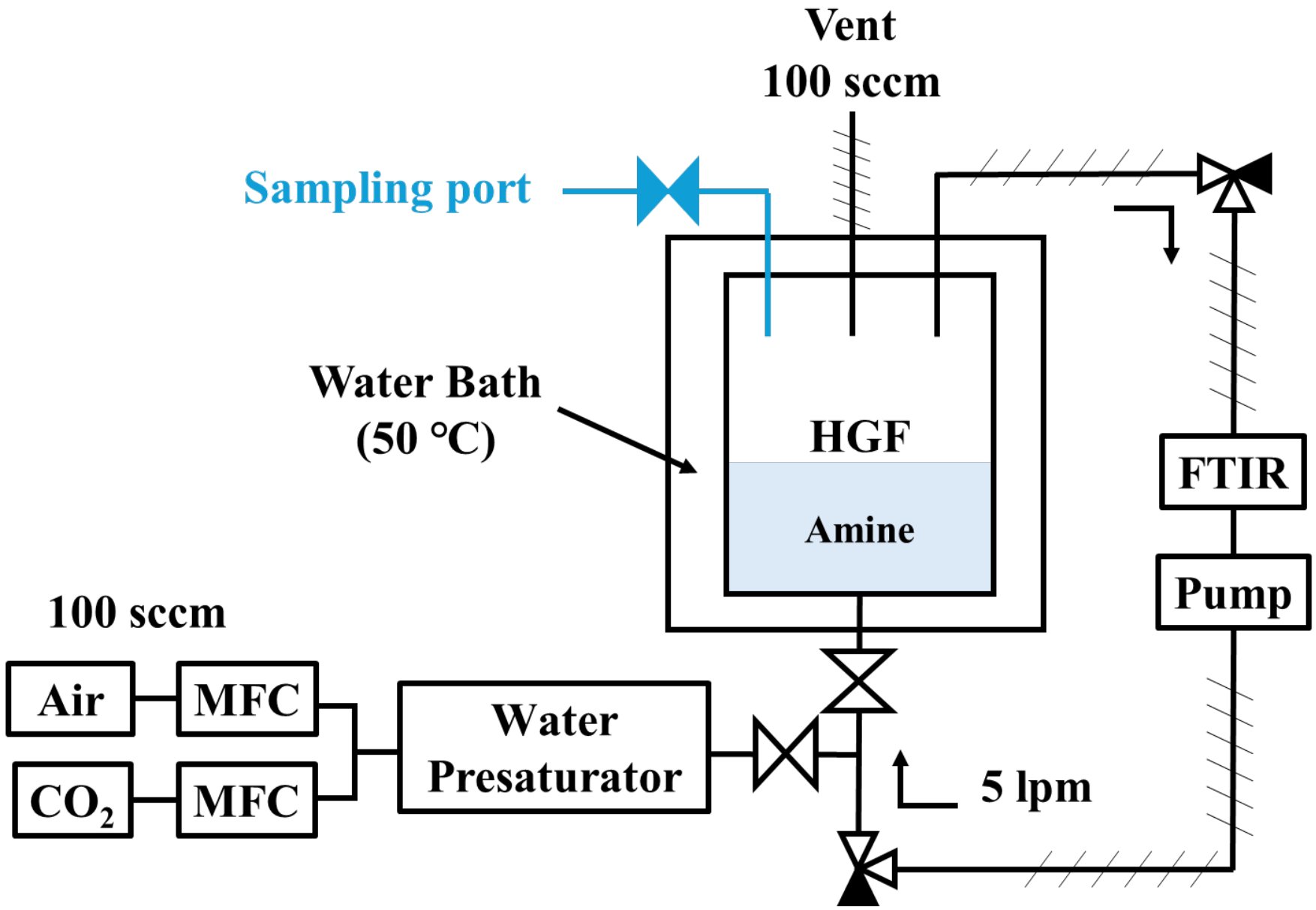
(Voice, 2013)

High Oxygen Pressure Reactor (HOPR)



- 300 kPa pure oxygen
- Temperature: 60℃

High Gas Flow reactor (HGF)

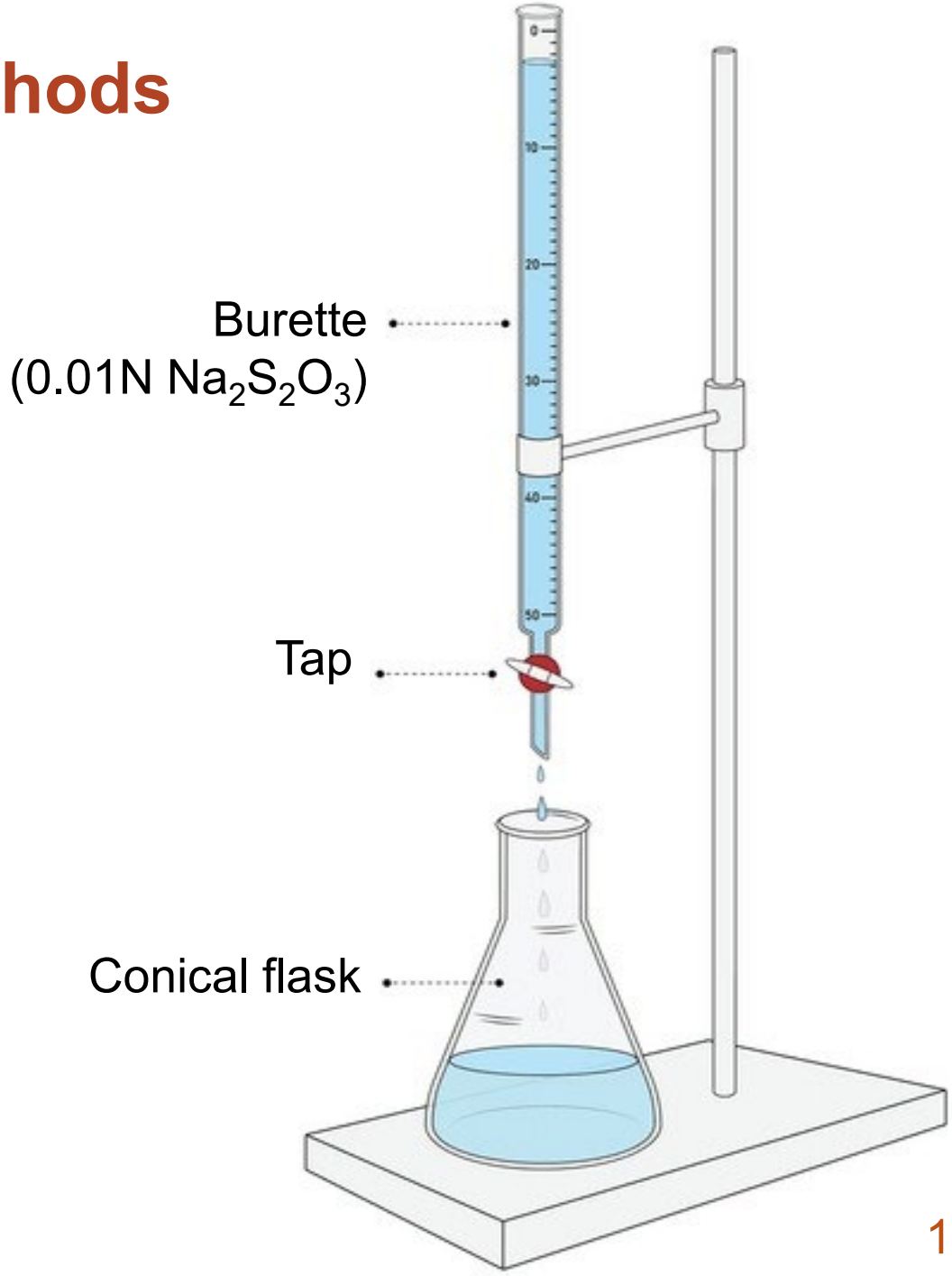


Analytical methods

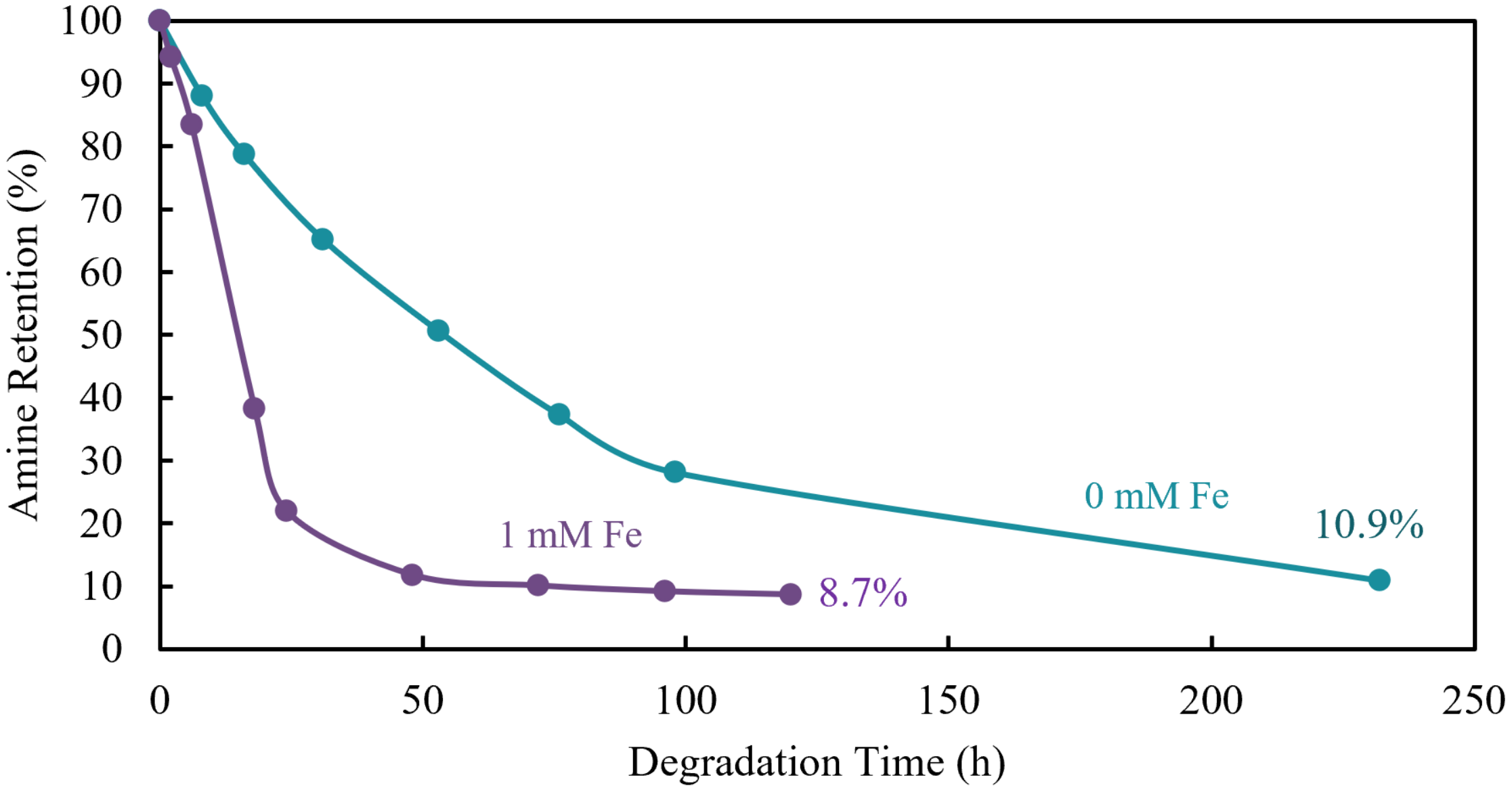
- GC: Amine Retention analysis
- Peroxide Determination: Iodometric titration
  - 2g sample + 20mL 1N H_3PO_4 + 1mL saturated KI + 1mL 1%starch solution
  - Quickly titrate with $Na_2S_2O_3$
  - Detection limit: 0.5 mmol/kg

$$R\text{-}OOH + 2I^- \rightarrow R\text{-}OH + I_2$$

$$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$$



DETA Retention in HOPR
(30 wt% DETA, α=0.4, 300 kPa O_2, 60℃)



DETA Retention in HOPR
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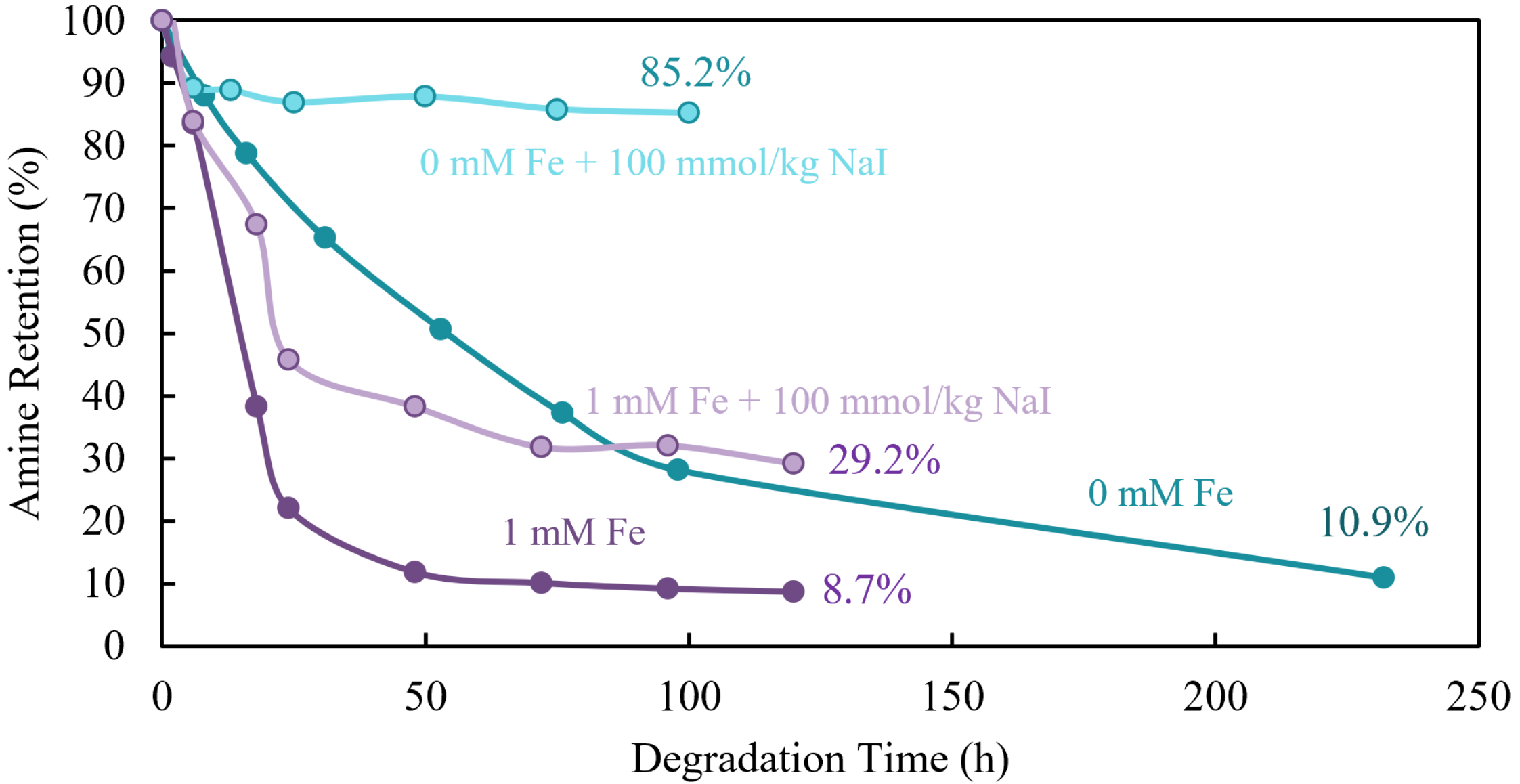
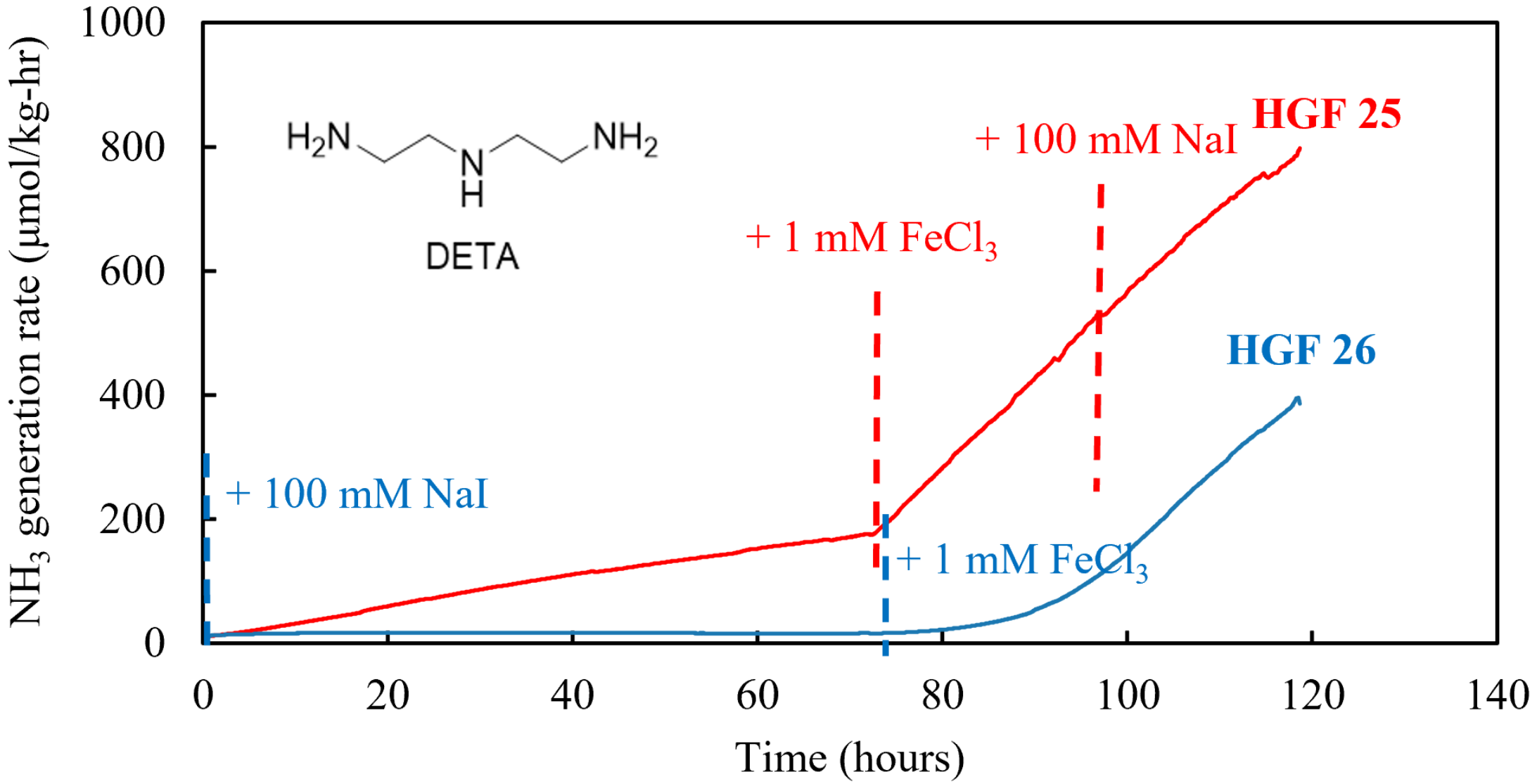
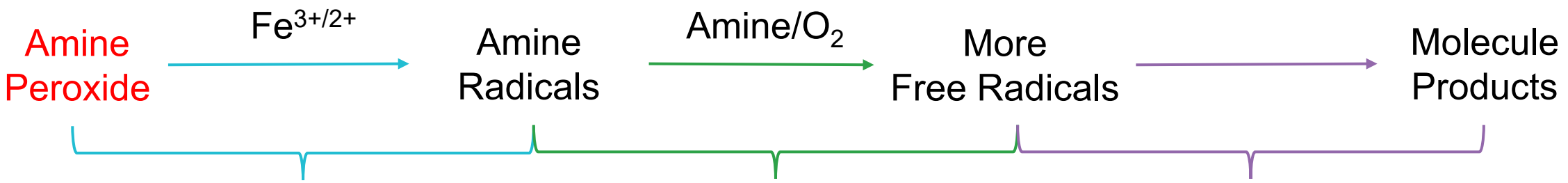


NH_3 generation rate of HGF 25 and HGF 26 (30 wt% DETA, α = 0.4, 50℃)



Amine oxidation mechanism



$$ROOH \xrightarrow{Fe^{3+}} RO\cdot + \cdot OH$$

$$RO\cdot + DETA \rightarrow DETA\cdot + ROH$$
$$DETA\cdot + O_2 \rightarrow DETAOO\cdot$$
$$ROO\cdot + DETA \rightarrow DETA\cdot + ROOH$$

$$ROOH + DETA \rightarrow DETAO$$
$$ROOH \rightarrow DETA + O_2$$
$$R\cdot + R\cdot \rightarrow R - R$$

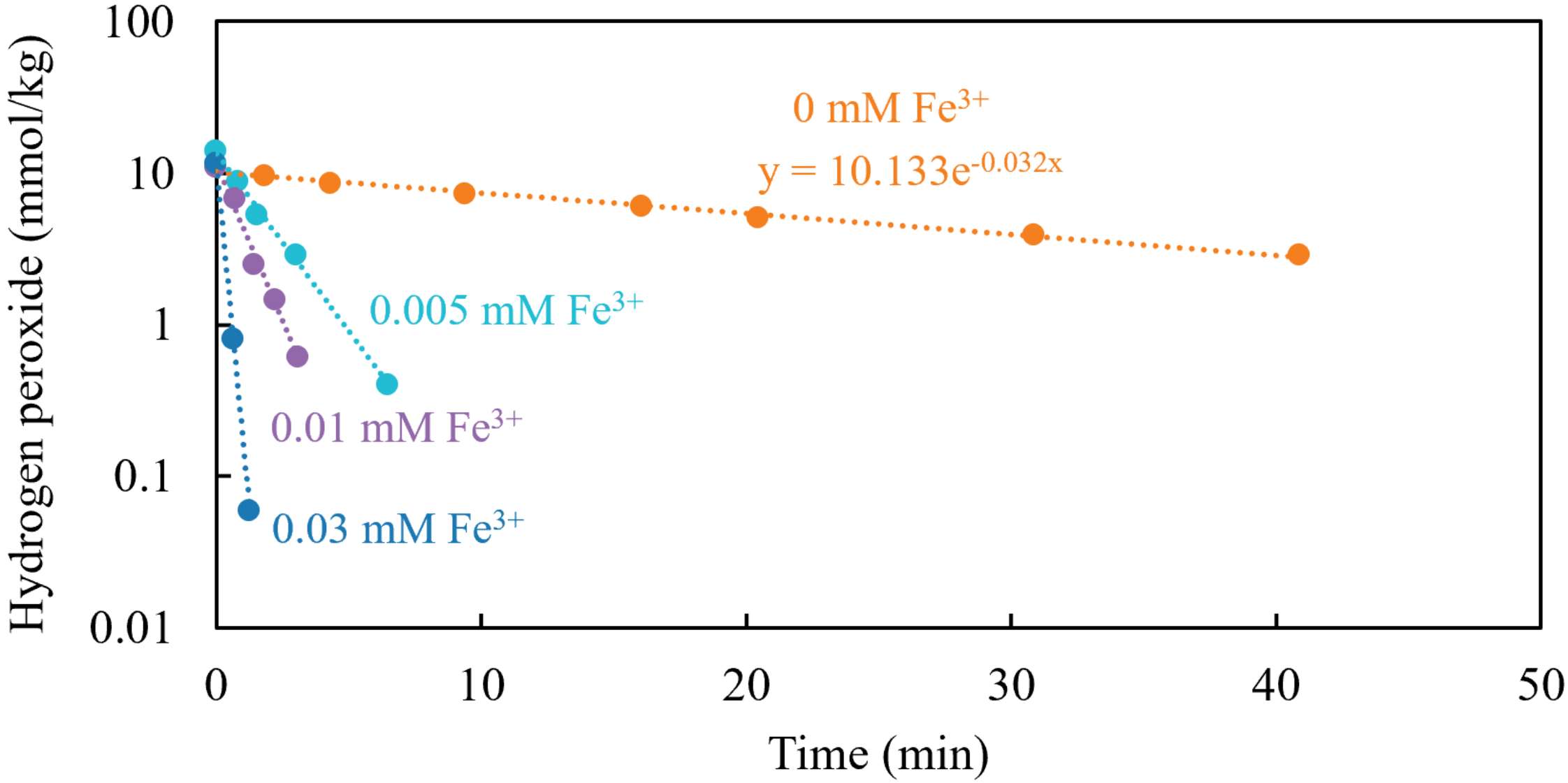
$$I^- + ROOH \rightarrow ROH + IO^-$$

$$IO^- + ROOH \rightarrow ROH + I^- + O_2$$ Iodide can work in cycles.

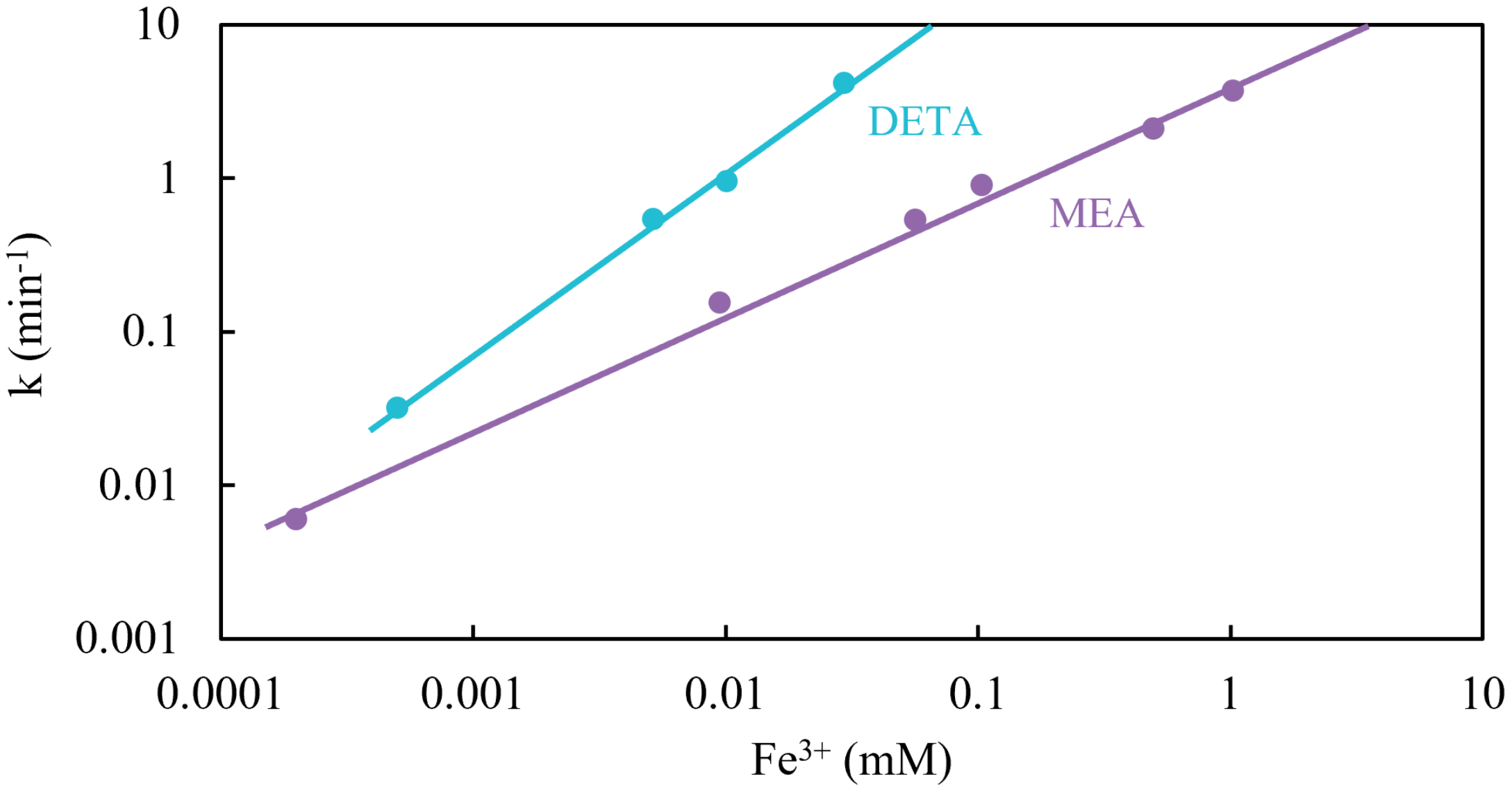
- Fenton reaction: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$
- Peroxide also appears in amine without iron.

(Dalmázio, 2008)
(Tachiev, 2000)

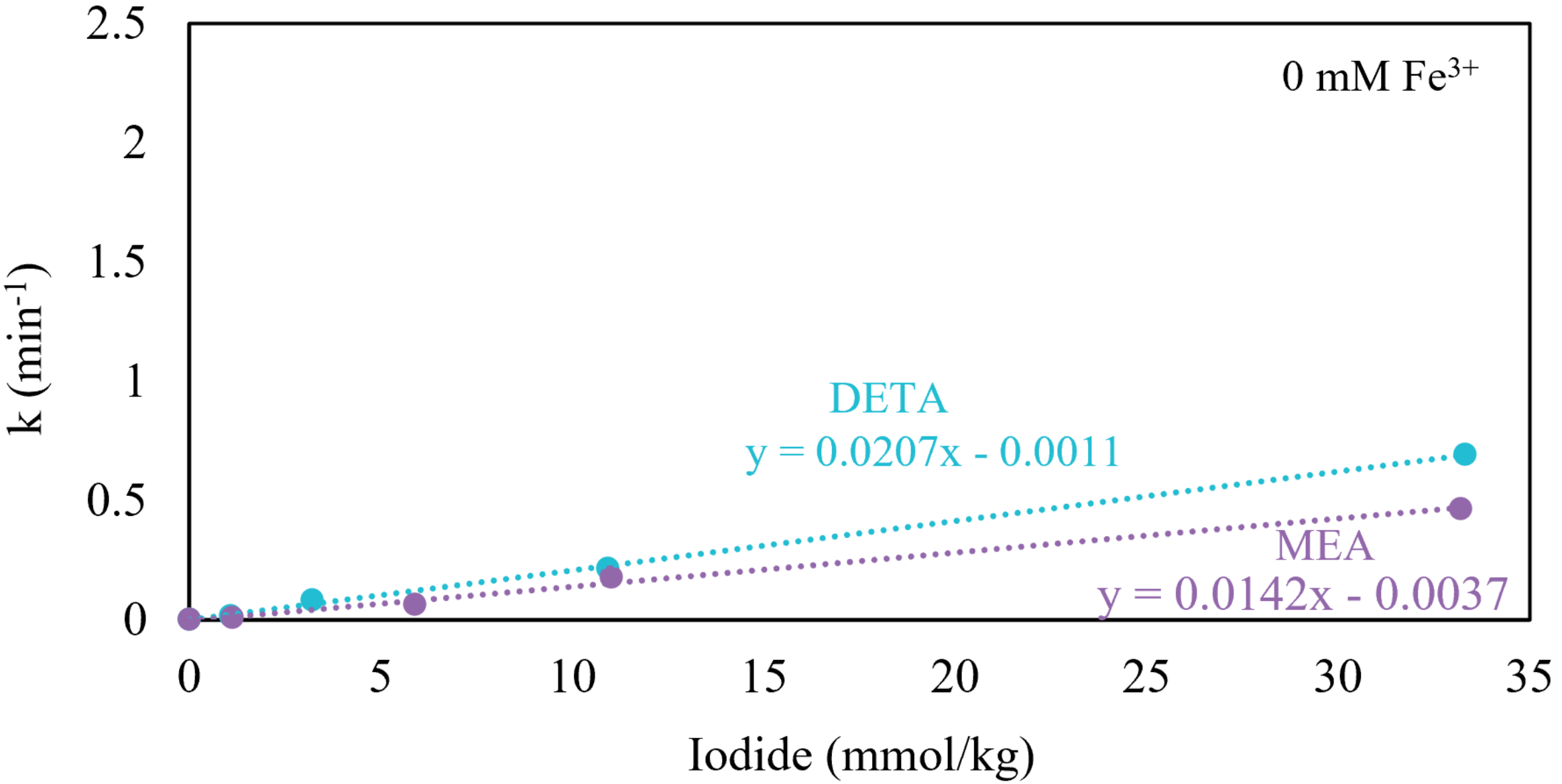
Hydrogen peroxide consumption in DETA (30 wt% DETA, α = 0.4, 22℃)



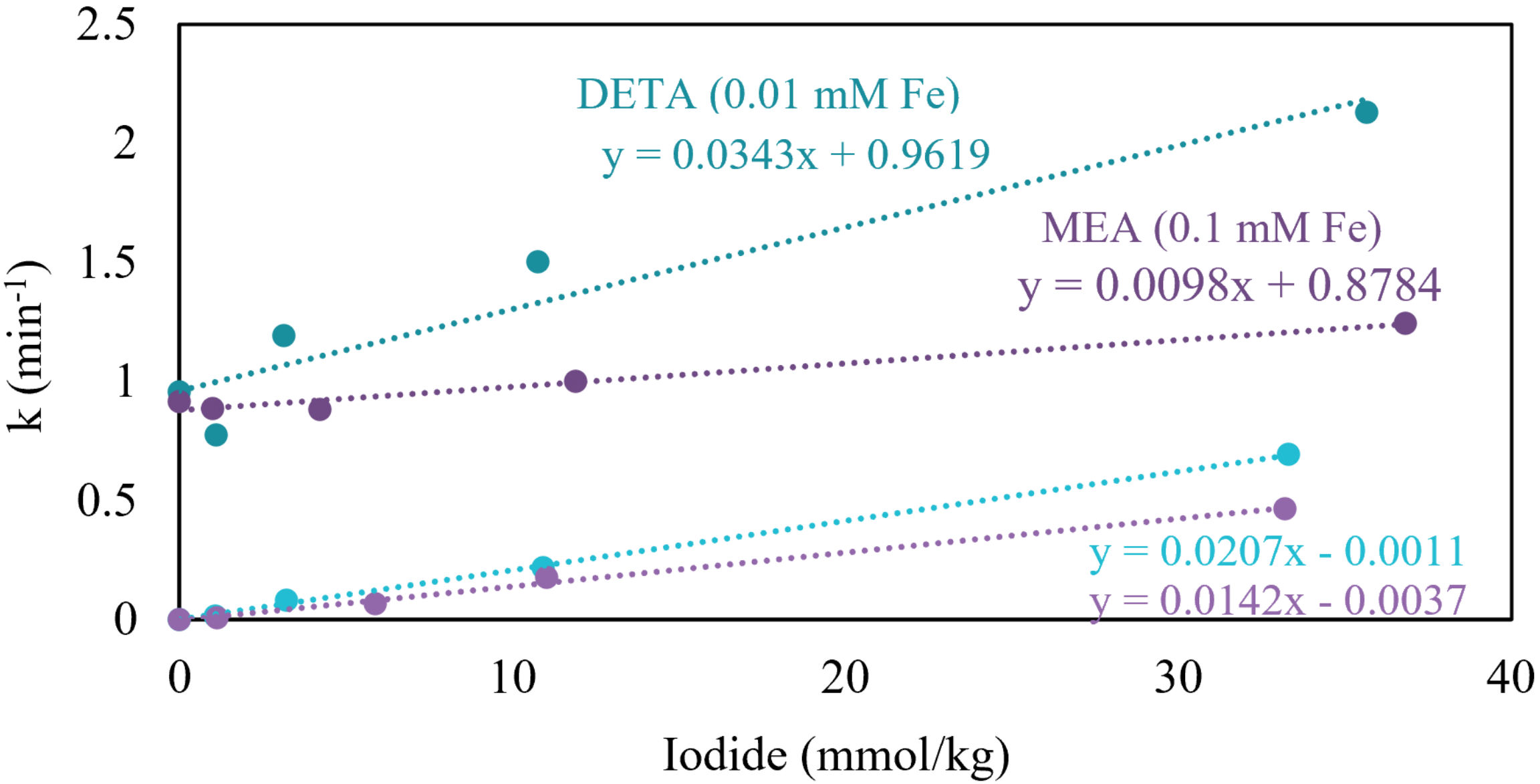
Peroxide consumption rate with Ferric in DETA and MEA (30 wt% DETA, 30 wt% MEA, α = 0.4, 22℃)



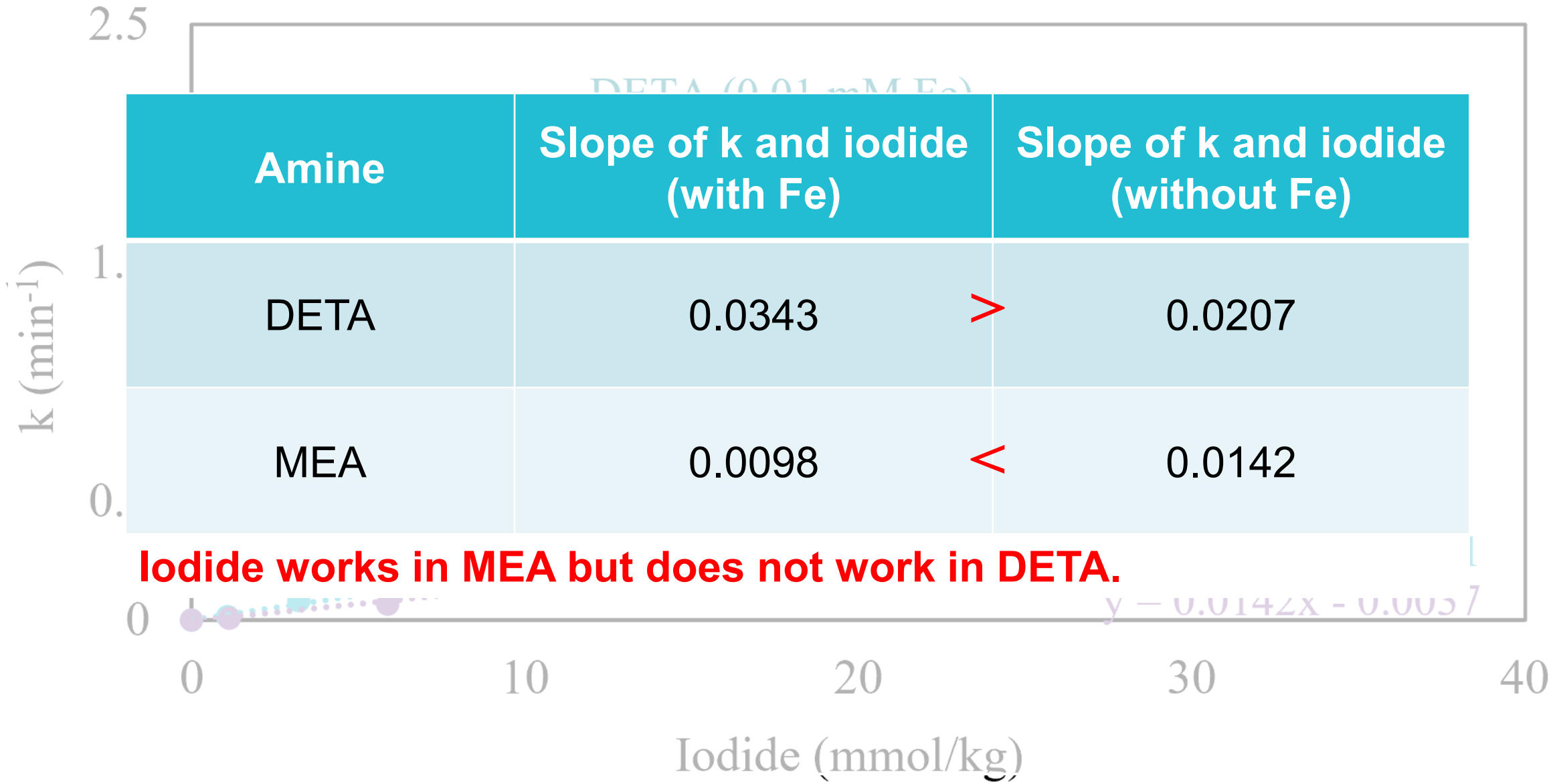
Peroxide consumption rate with iodide in DETA and MEA (30 wt% DETA, 30 wt% MEA, α = 0.4, 22℃)



Peroxide consumption with iodide in DETA and MEA (30 wt% DETA, 30 wt% MEA, α = 0.4, 25℃)



Peroxide consumption with iodide in DETA and MEA (30 wt% DETA, 30 wt% MEA, α = 0.4, 25℃)



Amine	Slope of k and iodide (with Fe)		Slope of k and iodide (without Fe)
DETA	0.0343	>	0.0207
MEA	0.0098	<	0.0142

Iodide works in MEA but does not work in DETA.

Conclusions

- 100 mM Iodide inhibits DETA oxidation in the absence of Fe^{3+}.
  - Iodide reacts with peroxide
    - Probably forming non-radical products
    - Terminating radical propagation

- With Fe^{3+}, iodide is not effective in DETA but works in MEA.
  - Fe^{3+} in DETA reacts with peroxide faster.
  - But iodide in MEA compete with Fe^{3+} to react with peroxide.

- The effects of iodide depend on the peroxide reaction with iron in amine oxidation.

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Thank You

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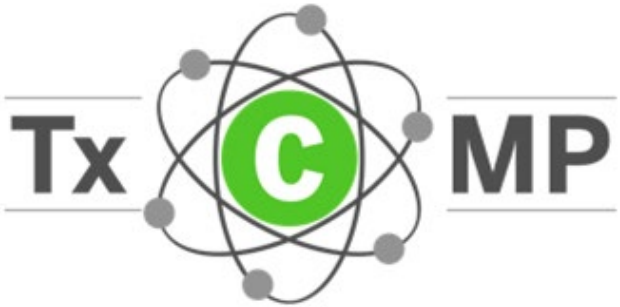

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