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Assessment of chlorine stability in recycled handwashing water: Role of amide-type compounds from soaps

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Introduction

Motivation and Objectives

- Stand-alone handwashing system can safely recycle and reuse handwashing water.
- To develop and implement a handwashing system (Figure 1) in healthcare facilities and schools in Mali, Nigeria, and Burkina Faso in Africa to improve hand hygiene.

Research Questions and Approaches

- In handwashing water reuse, a chemical disinfectant (e.g., chlorine) is needed.
- The stability of chlorine needs to be understood for effective dosing.
- The compounds with amide structures (from hand soaps) could control the fate of chlorine in handwashing water (Table 1).
- We selected six surrogate amides and investigated
  (i)   the reaction mechanisms,
  (ii) the temperature-dependent reaction kinetics, and
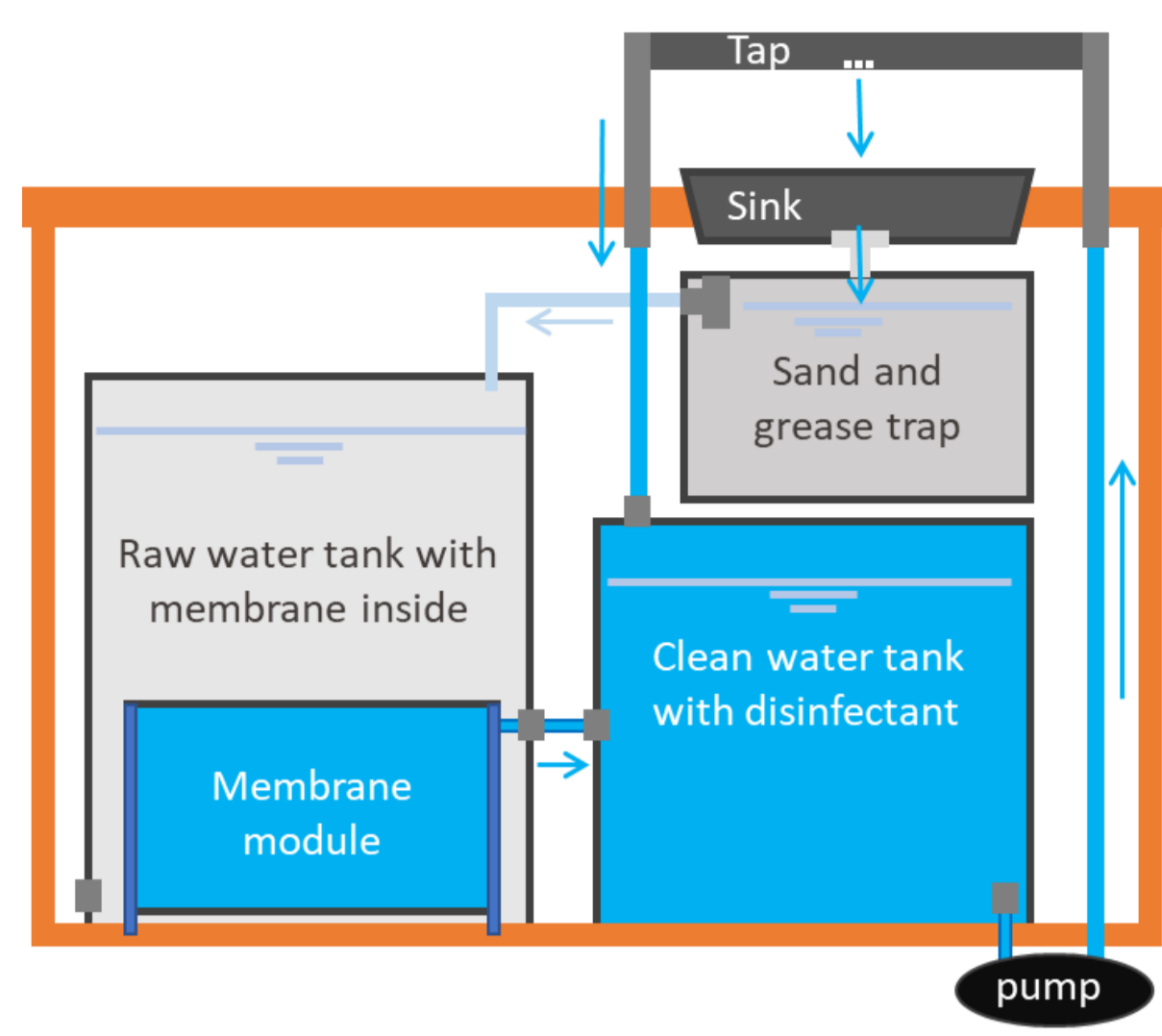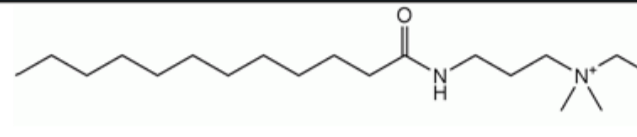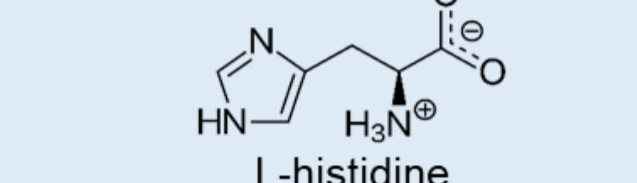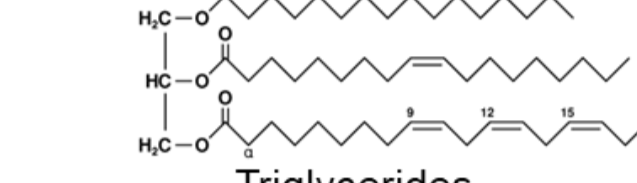 (iii) the products formation between amides and chlorine.
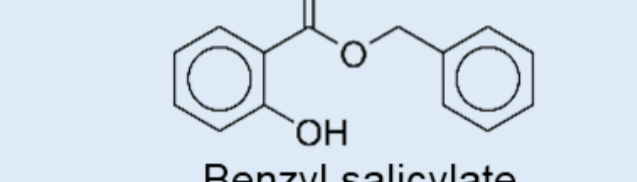

Figure 1. Scheme of the handwashing station. (figure credit: Domini Jaggi at FHNW)

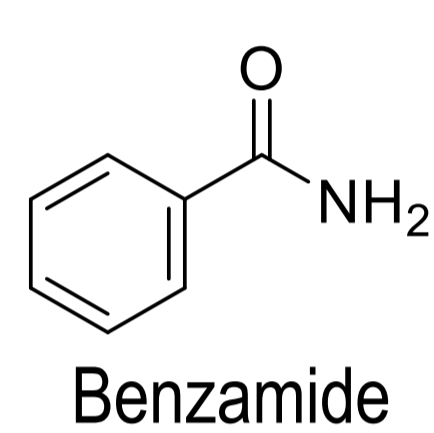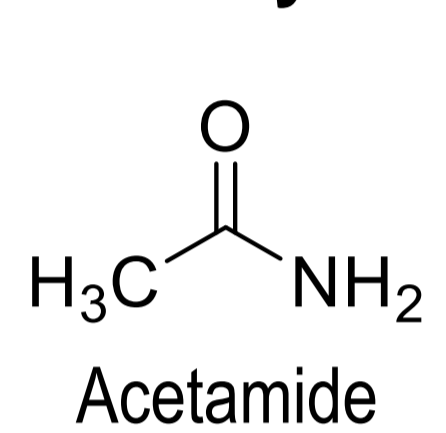**Table 1.** Chemicals and their properties in handwashing water

Groups	Representative Chemicals	Source (function)	Concentration level	Apparent rate constants with chlorine ($M^{-1}s^{-1}$)	Half-life times ($t_{1/2}$)
Amide	Cocamidopropyl betaine	Hand soap (surfactant)	mg/L	< 0.25 [1]	Hours to days
Amino acid	L-histidine	Human sweat	µg/L	10^2-10^4 [2]	Seconds
Olefin	Triglycerides	Human skin	µg/L	0.1-10 [3]	Minutes to hours
Phenolic compound	Benzyl salicylate	Hand soap (preservative)	µg/L	10^4 [2]	Seconds

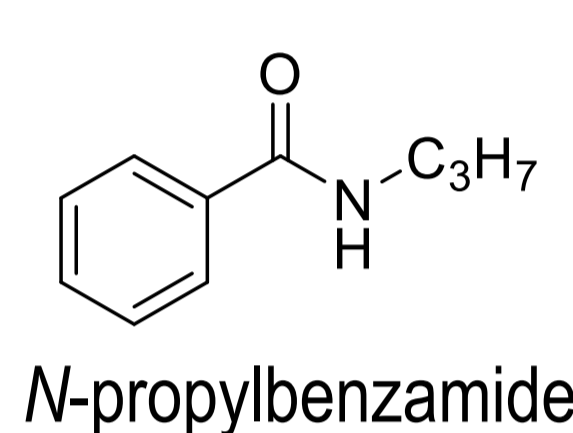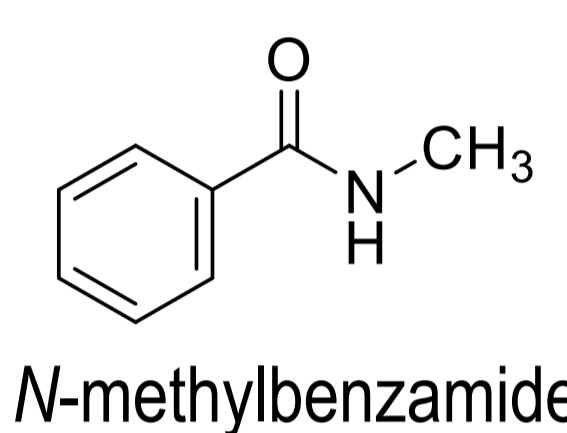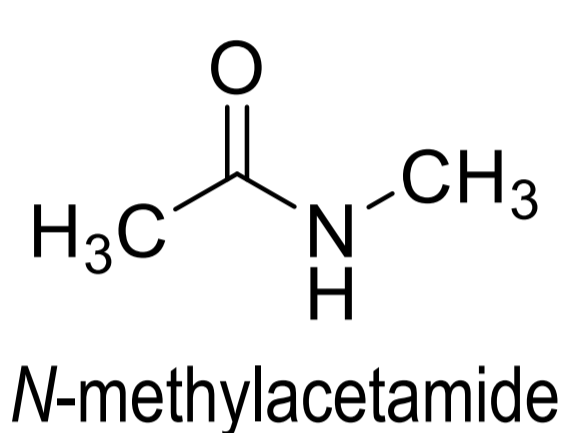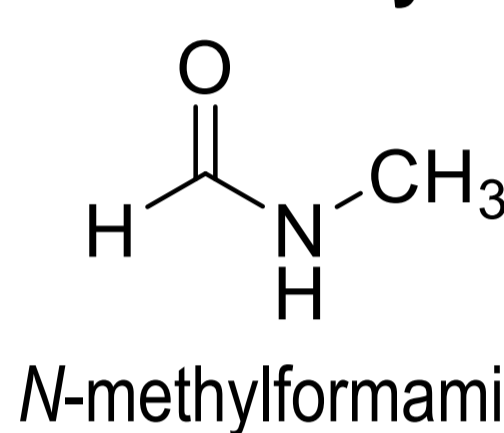[1]This study; [2]Deborde and von Gunten, Water Research 42 (2008) 13-51; [3]Li et al., Water Research 187 (2020) 116424.

Materials and Methods

Primary amides

Acetamide   Benzamide

Secondary amides

N-methylformamide   N-methylacetamide   N-methylbenzamide   N-propylbenzamide

- Chlorine was measured using a spectrophotometer directly and/or using the DPD method.
- Benzamide, N-methylbenzamide, N-propylbenzamide, and phenolic compounds were measured using HPLC-DAD.
- Chlorinated amides were measured using DPD + iodide.

Results and Discussion

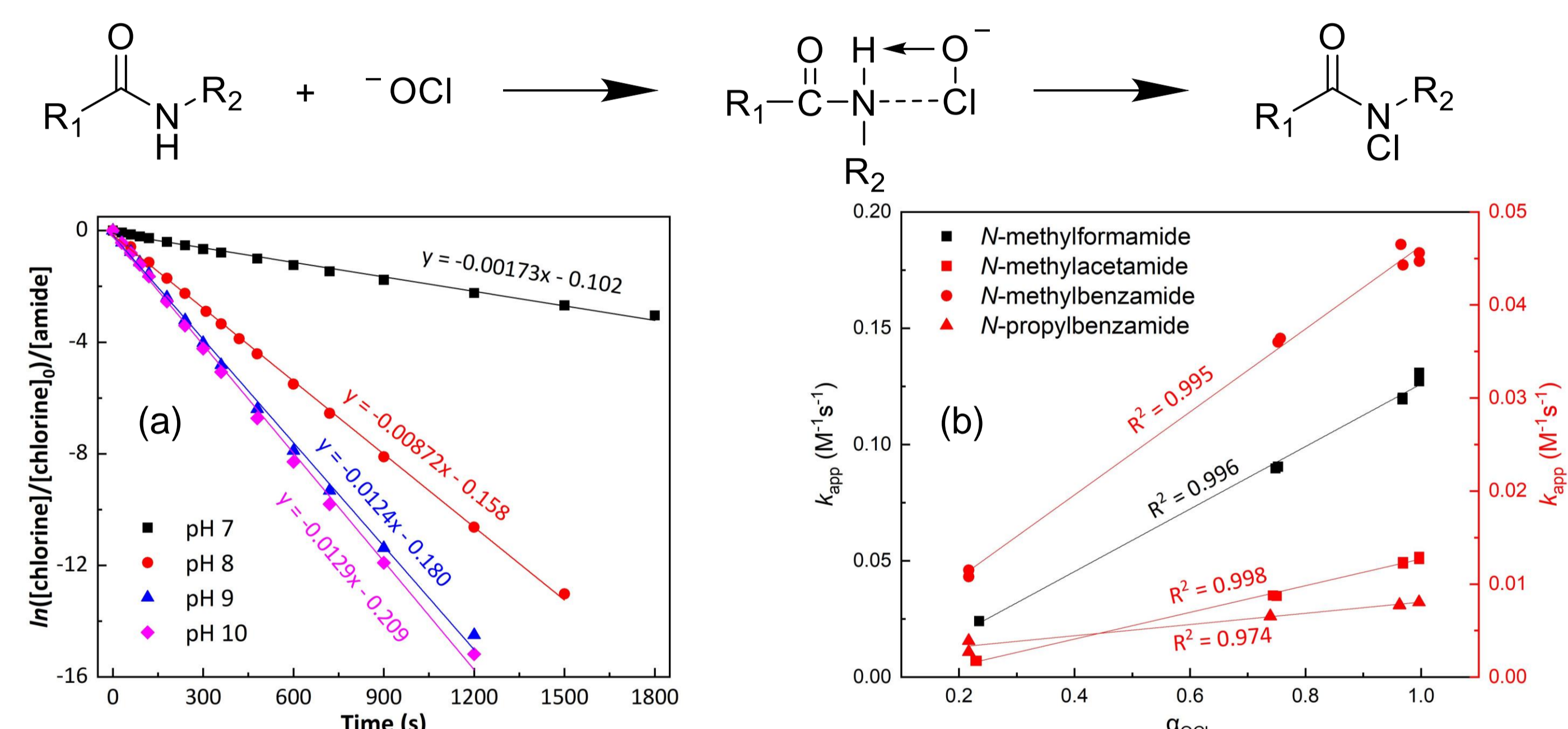### Chlorine reaction with secondary amides

Figure 2. (a) Chlorine decrease in the presence of excess N-methylacetamide as a function of time at different pHs. (b) Apparent second-order rate constants for reactions of secondary amides with chlorine as a function of α_{OCl^-}. N-methylformamide/N-methylacetamide : $[Chlorine]_0$ = 0.4-1.5 mM, $[Amide]_0$ = 10-200 mM; N-methylbenzamide: $[Chlorine]_0$ = 60 µM, $[Amide]_0$ = 8 mM; N-propylbenzamide: $[Chlorine]_0$ = 12-40 mM, $[Amide]_0$ = 40 µM.

Chlorine reaction with primary amides

Figure 3. Observed and calculated chlorine decay (a) and chloro-benzamide formation (b) in the reaction of chlorine with benzamide at different pHs. $[chlorine]_0$ = 0.1 mM, $[Benzamide]_0$ = 8 mM. In the calculation: k_1 = 0.3 $M^{-1}s^{-1}$, k_2 = 5 $M^{-1}s^{-1}$, k_3 = 12 $M^{-1}s^{-1}$, and k_4 = (2.5-4.6)×10^{-4} s^{-1}.

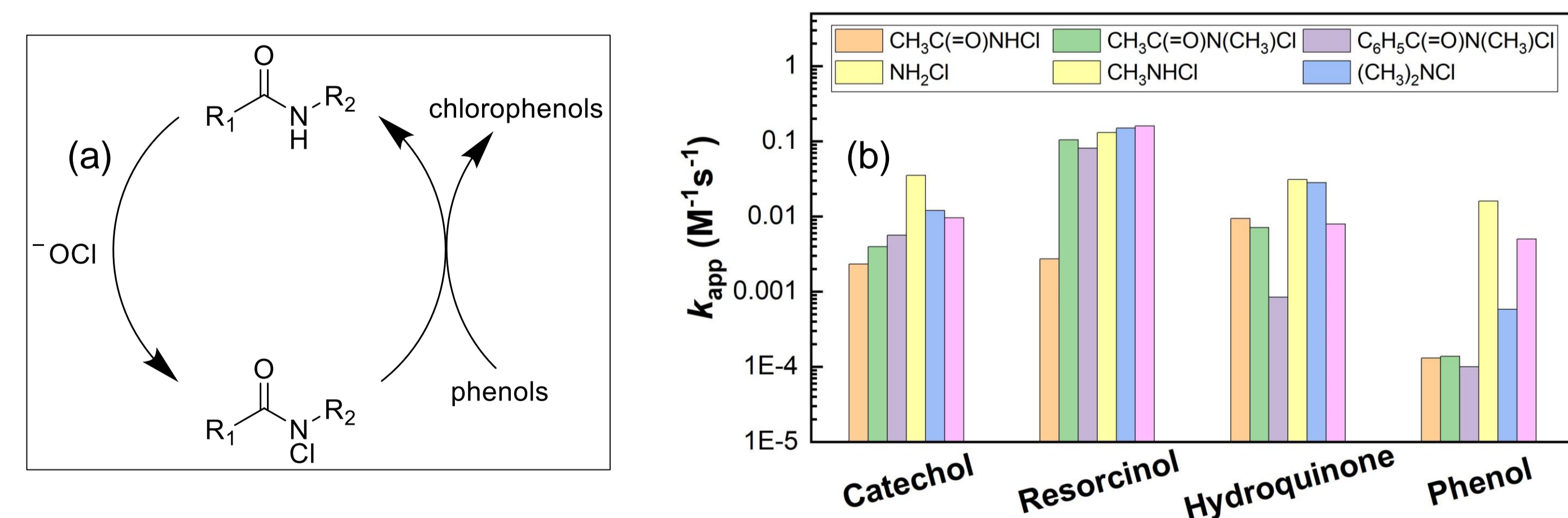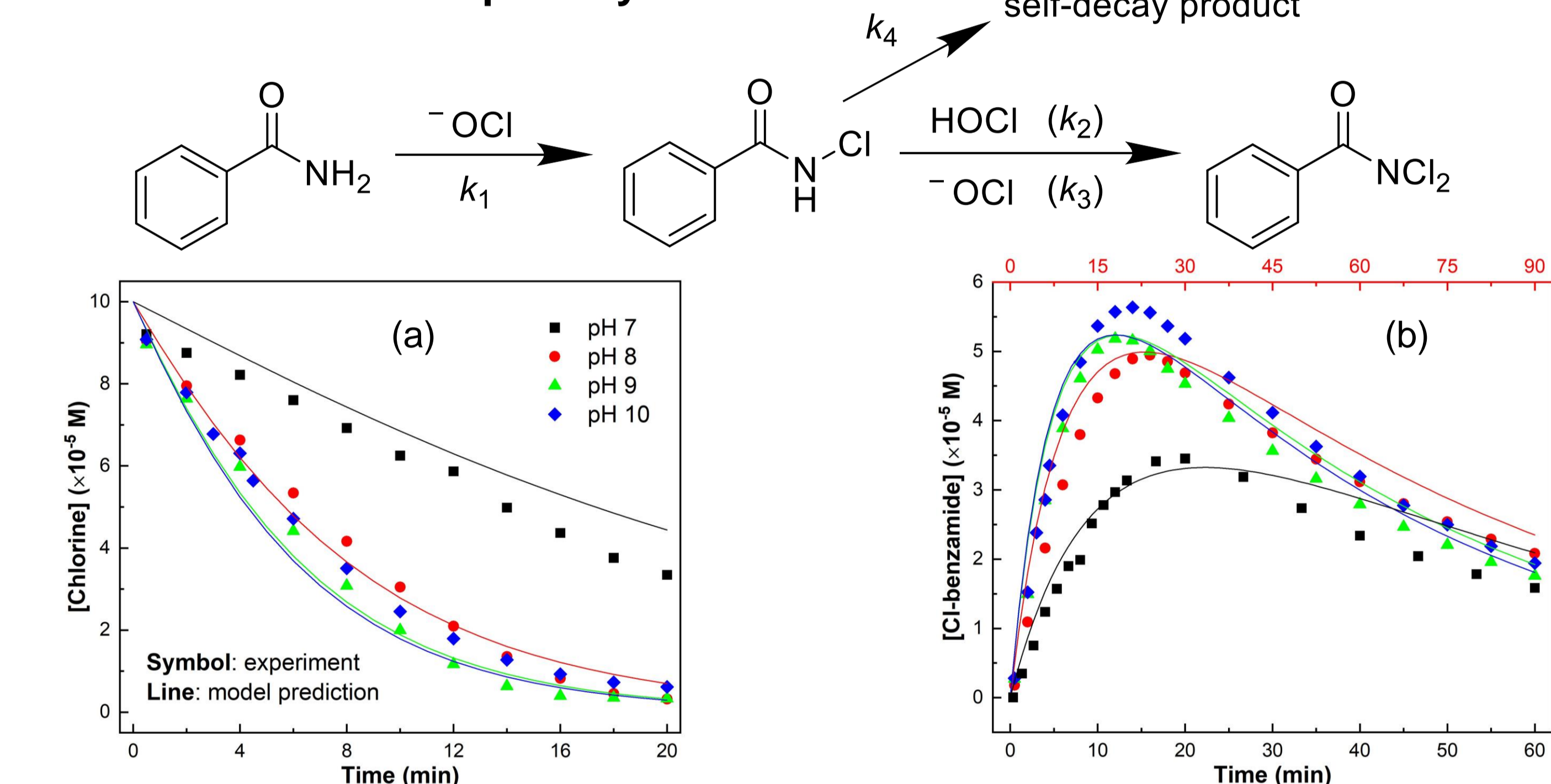### Reactivity of chlorinated amides with phenolic compounds

Figure 4. (a) Reaction pathways of chlorinated amides. (b) Apparent second-order rate constants for reactions of different phenolic compounds with chlorinated amides in comparison with chloramines (Heeb et al., Water Research 110 (2017) 91-101). Cl-acetamide/Cl-methylacetamide: phenols in excess; Cl-methylbenzamide: chlorinated amide in excess; pH 7.

Chlorine reaction with amides at different temperatures
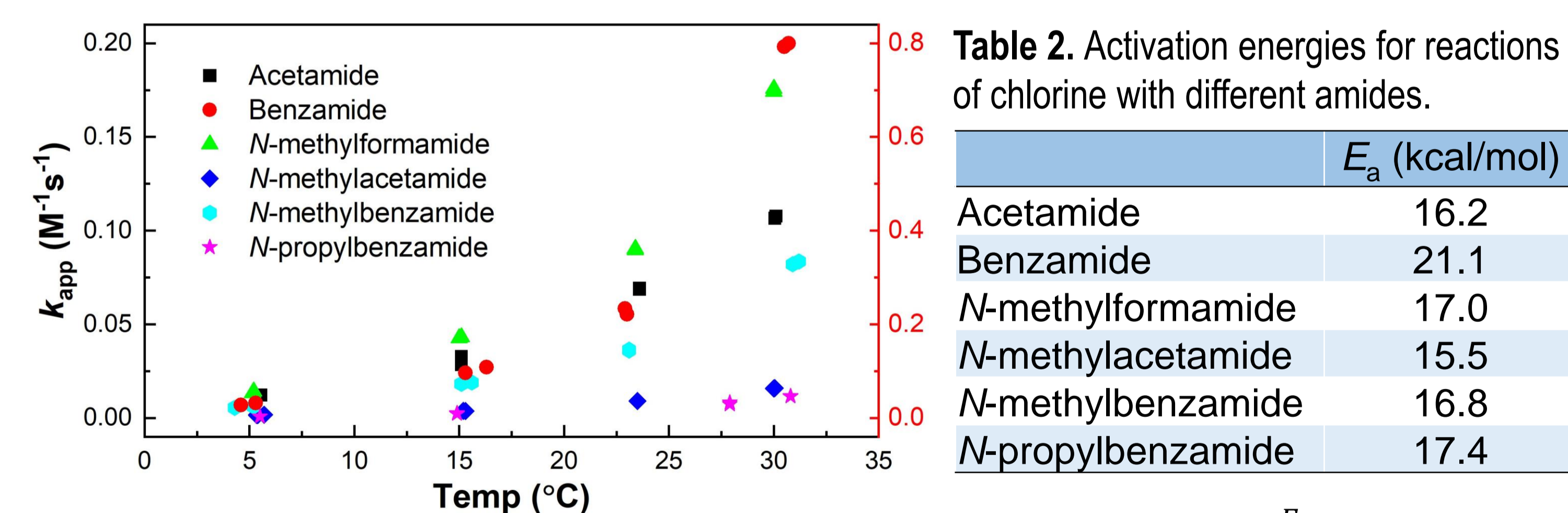

Figure 5. Apparent second-order rate constants for reactions of chlorine with amides at different temperatures at pH 8. Amides were in excess, chlorine was measured photometrically (for aliphatic amides) or using DPD method (for aromatic amides).

Table 2. Activation energies for reactions of chlorine with different amides.

	E_a (kcal/mol)
Acetamide	16.2
Benzamide	21.1
N-methylformamide	17.0
N-methylacetamide	15.5
N-methylbenzamide	16.8
N-propylbenzamide	17.4

$$k = Ae^{\frac{-E_a}{RT}}$$

Arrhenius equation

Conclusions

➢ In handwashing water, chlorine stability on a long-term scale is controlled by amides that are introduced into the water from soaps.

➢ Apparent second-order rate constants for the reactions of chlorine with the selected amides at pH 8 were in the range of 6.6×10^{-3}-0.23 $M^{-1}s^{-1}$. Based on this, chlorine has a half-life time ($t_{1/2}$) of 8.4 hours to 12.2 days in the presence of 0.1 mM amide.

➢ Hypochlorite ($^-$OCl) dominates the reactions of amides with chlorine.

➢ Chlorine stability in the presence of amides can be predicted as a function of pH and temperature.

➢ Chlorinated amides react with electron-rich moieties (e.g., phenols) with apparent second-order rate constants in the order of 10^{-4}-0.1 $M^{-1}s^{-1}$ at pH 7.

Acknowledgements

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