

Supporting Information

for

Continuous formation of *N*-chloro-*N,N*-dialkylamine solutions in well-mixed meso-scale flow reactors

A. John Blacker^{*1} and Katherine E. Jolley¹

Address: ¹ Institute of Process Research and Development, School of Chemistry and School of Chemical and Process Engineering, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, Leeds, UK

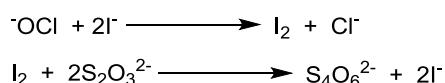
Email: A. John Blacker* - j.blacke@leeds.ac.uk

* Corresponding author

**Details of the titration method for determination of NaOCl strength,
determination of amine partition coefficients, GC analytical
conditions and calorimetry**

Titration of NaOCl (aq)

1 mL acetic acid and 0.35 g of KI was diluted to 50 mL with distilled water. To the solution was added 1 mL of the NaOCl solution obtained from Sigma-Aldrich. 0.1 M Na₂S₂O₃ (aq) was then titrated into the aqueous solution of KI, acetic acid and NaOCl until the orange solution becomes colourless. The concentration of the initial NaOCl solution can thus be determined using the equations below.



Determination of fraction of amine partitioning in the organic phase of a biphasic organic/aqueous solution

100 µL of amine (when liquid at room temperature) or 100 mg of amine (when solid at room temperature) was added to a biphasic solution comprising of 1 mL of the organic solvent (toluene or EtOAc) and 1 mL water. The resulting solution was mixed thoroughly and then allowed to stand and the phases separate. 100 µL of the organic and aqueous phases of each solution were in turn added to 1 mL of MeOH and analysed by GC. The concentration of amine in each phase was determined and used to calculate K_D using the equation below:

$$K_D = \frac{[\text{amine}] \text{ in organic}}{[\text{amine}] \text{ in aqueous}}$$

GC Analysis of amines

GC Method: HP-5 column 30 m × 0.32 mm × 0.25 µm, H₂ 10 psi, split ratio 5:1, $T = 35^\circ\text{C}$ 3 min, 10 °C/min to 200 °C, 200 °C 3 min, 280 °C 3 min.

Morpholine: 2.2 min

Piperidine: 1.8 min

N-Benzylmethylamine: 7.1 min

N-Methyl-*p*-toluenesulfonamide: 6.1 min

Dibutylamine: 3.4 min

Dibenzylamine: 16.2 min

Toluene: 1.5 min

Calorimetry

1. To a 50 mL vessel was added 20 mL of 1 M solution of morpholine in water. 1.1 M NaOCl (aq) was then fed into the morpholine solution according to the required plan as detailed below.

To determine the enthalpy of the reaction, power compensation calorimetry was used with the reaction plan as detailed below.

Steady State 1:

Stir 300 rpm

Reactor temperature: 5 °C

Circulator temperature: -15 °C

Time: 60 min

Feed Step:

Stir 300 rpm

Reactor temperature: 5 °C

Circulator temperature: -15 °C

Feed 1.1 M NaOCl (aq) at 1 mL/min for 20 min (20 mL, 22 mmol NaOCl)

Time: 20 min

Steady State 2:

As for Steady State 1

The enthalpy (kJ mol^{-1}) of the reaction was determined using IQ analytical software.

2. To a 50 mL vessel was added 20 mL of 1 M solution of morpholine in toluene.

To determine the enthalpy of the reaction, power compensation calorimetry was used with the reaction plan as detailed below:

Steady State 1:

Stir 300 rpm

Reactor temperature: 5 °C

Circulator temperature: -15 °C

Time: 60 min

Feed Step:

Stir 300 rpm

Reactor temperature: 5 °C

Circulator temperature: -15 °C

Feed 1.1 M NaOCl (aq) at 1 mL/min for 20 min (20 mL, 22 mmol NaOCl)

Time: 20 min

Steady State 2:

As for Steady State 1

The enthalpy (kJ mol^{-1}) of the reaction was determined using IQ analytical software.

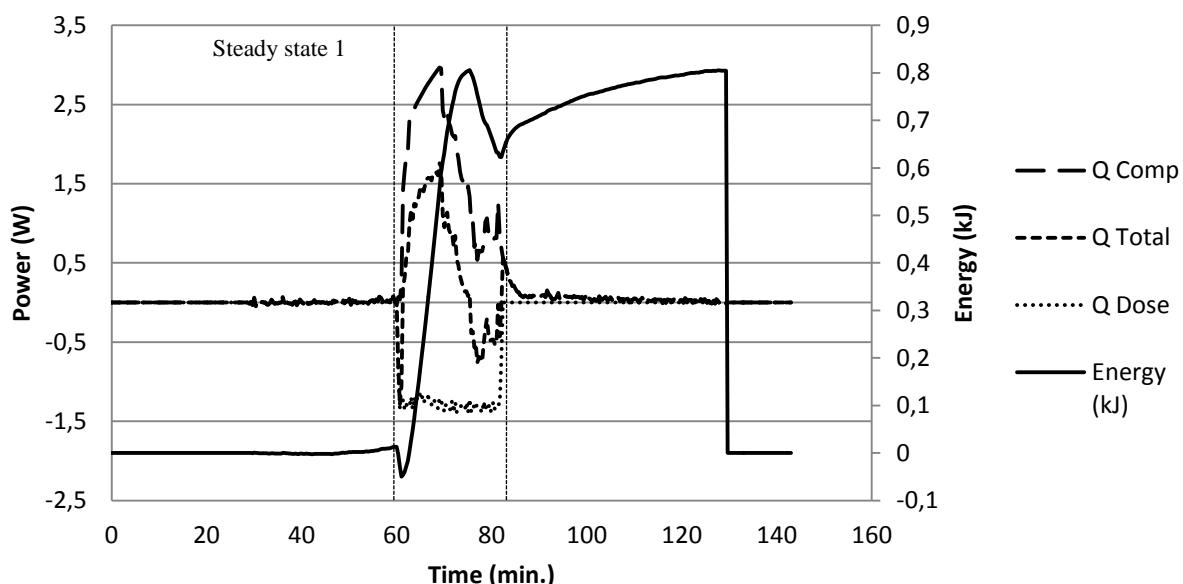


Figure 1: Calorimeter trace for biphasic reaction of morpholine (toluene) and NaOCl (aq). Q Comp: compensatory power, Q Total: total power, Q Dose: power delivered

by dosing of room temperature NaOCl (aq) to cooled reaction solution, Energy: heat energy.

3. To determine the adiabatic temperature rise, 1.1 M NaOCl (aq) was fed into 1 M morpholine in toluene. The following reaction plan was used.

Steady State 1:

Stir 300 rpm

Reactor temperature: room temperature, no temperature control used

Time: 60 min

Feed Step:

Stir 300 rpm

Reactor temperature: room temperature, no temperature control used

Feed 1.1 M NaOCl (aq) at 1 mL/min for 20 min (20 mL, 22 mmol NaOCl)

Time: 20 min

Steady State 2:

As for Steady State 1

The temperature rise due to the reaction was determined (Figure 2) by comparison of the initial temperature at the start of the feed step and the maximum temperatures reached during the feed (Experiment 1). The control reactions for the equivalent additions of water to toluene; water to morpholine/toluene and NaOCl aq. to toluene, the ΔH was found to be negligible in all cases by calorimetry (eg. Experiment 2).

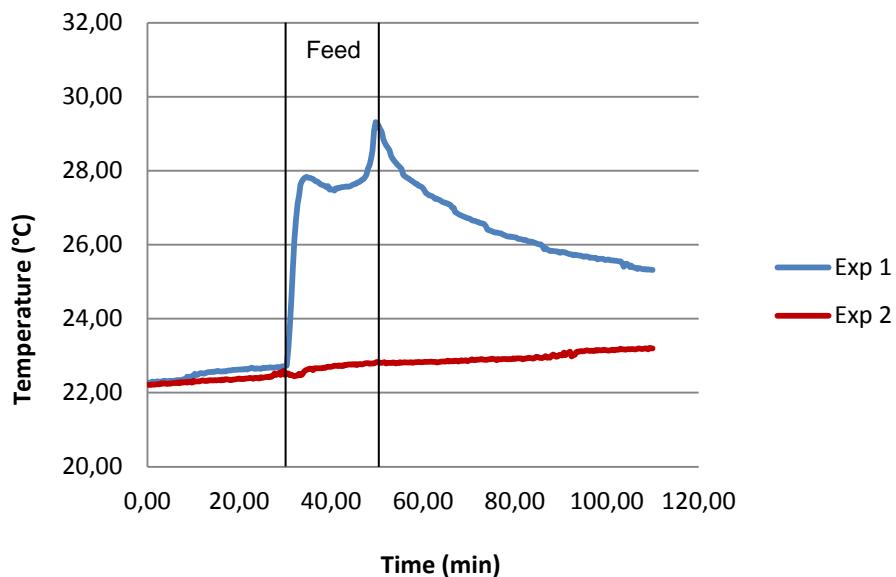
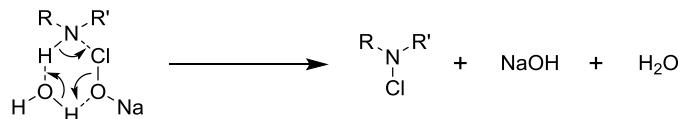


Figure 2: Temperature rise for addition of room temperature NaOCl (aq) to room temperature morpholine (toluene) (Exp 1) and addition of room temperature water to room temperature toluene (Exp 2).

Calculation of enthalpy change of reaction

Proposed mechanism for chloroamine formation [1].



Average bond enthalpies [2]:

| Bond formation | Bond breakage |
|------------------------------|------------------------------|
| N–Cl 200 kJmol ⁻¹ | N–H 388 kJmol ⁻¹ |
| O–H 463 kJmol ⁻¹ | O–H 463 kJmol ⁻¹ |
| O–H 463 kJmol ⁻¹ | O–Cl 203 kJmol ⁻¹ |

$$\Delta H_{rxn} = (388 + 463 + 203) - (200 + 463 + 463) \text{ kJ mol}^{-1} \\ = -72 \text{ kJ mol}^{-1}$$

References

1. Weil, I.; Morris, J. C. *Journal of the American Chemical Society* **1949**, *71*, 1664-1671.
2. Atkins, P.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F. *Inorganic Chemistry*, Eds 4; Vol. Oxford University Press: Oxford, UK, 2006.