Supporting Information

Continuous Flow Oxidation of Benzylic and Aliphatic Alcohols Using Bleach: Process Improvement by Precise pH Adjustment in Flow with CO_2

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Content

Aqueous chlorine speciation

The equilibrium composition of aqueous solution of NaOCl is pH-dependent and theoretical chlorine speciation as the function of pH is shown in Figure S 1 and in Figure S 2 and was calculated according to equilibrium constants listed in Table S 1.

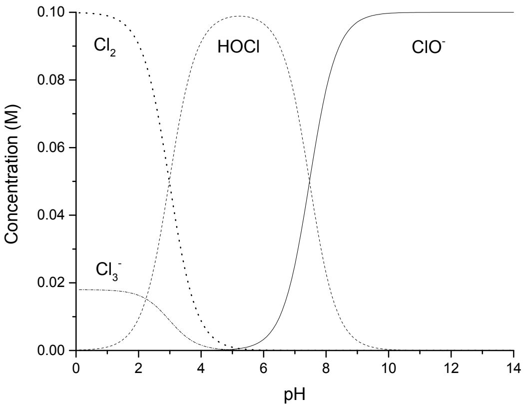

Figure S 1 Theoretical chlorine speciation in 0.1 M total chlorine and 1 M chloride as the function of pH. . Equilibrium constant listed in Table S 1

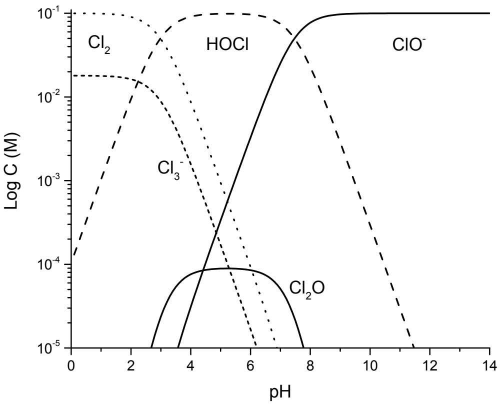

Figure S 2 Theoretical chlorine speciation in 0.1 M total chlorine and 1 M chloride as the function of pH. . Equilibrium constant listed in Table S 1

Table S 1 Equilibrium constants for chlorine species formation reactions. Values taken from ref. [1]

Reaction	Equilibrium constant
$HOCl \rightleftharpoons H^{+} + OCl^{-}$	$pKa = 7.47$
$Cl_2 + H_2O \rightleftharpoons HOCl + H^{+} + Cl^{-}$	$\log K = -2.98$
$Cl_2 + Cl^{-} \rightleftharpoons Cl_3^{-}$	$\log K = -0.74$
$ClO^{-} + \left[Cl^{-}\right]^2 + \left[H^{+}\right]^2 \rightleftharpoons Cl_3^{-} + H_2O$	$\log K = 9.7$
$ClO^{-} + \left[Cl^{-}\right]^2 + \left[H^{+}\right]^2 \rightleftharpoons Cl_3^{-} + H_2O$	$\log K = 12.9$

The acid dissociation constant (pKa) of hypochlorous acid (HOCl) is 7.5.[1] For pH higher than 9.5, the hypochlorite ion (ClO^-) is the predominant form of active chlorine. For pH between 7 and 9, the amount of HOCl becomes significant (Fig. S2 and S3). For pH below 7, molecular chlorine (Cl_2) becomes a significant component of the aqueous bleach solution, and the oxidative property could be attributed, to some extent, to Cl_2. Hypochlorous acid (HOCl) is a more active oxidizer than hypochlorite (ClO^-), *i.e.* the half-cell oxidation-reduction potential, E_0, at 25°C is 1.48V and 0.81 V respectively.[2] The redox reaction of other chloride oxyanions are complex, but under aqueous conditions, the oxidative property of ClO_2^- and ClO_3^- are much lower than HOCl and ClO^-.[1]

Stabilities of chlorine species

Frost diagram (Figure S 3) may be used to gauge the inherent stabilities of different oxidation states of chlorine. In acidic solution, we see that the reaction Gibbs energy of HOCl with an oxidation number of 1 lies above the average value for the two species on either side, *i.e.* Cl_2 and $HClO_2$. As a result, there is a tendency for HOCl to disproportionate into the two other species. This is not the case for basic solution, *i.e.* ClO^-.

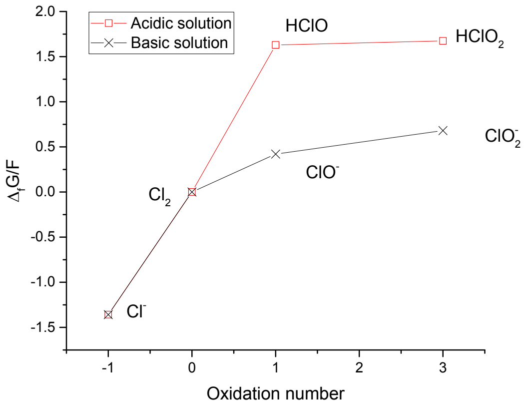

Figure S 3 Frost diagram for chlorine. The red line refers to acid conditions, pH = 0 and the black line to pH = 14. Values taken from ref. [3]

Decomposition of bleach solution

The kinetics and mechanism of decomposition of bleach solution is complex.[4] The formation of oxygen (Eqn. 1) and chlorate (ClO_3^-) (Eqn. 2) from aqueous ClO^- solution is very slow and are minor decomposition pathways.

$$2\ {}^{-}OCl \longrightarrow O_2 + 2\ Cl^- \qquad (1)$$

$$3\ {}^{-}OCl \longrightarrow ClO_3^- + 2\ Cl^- \qquad (2)$$

The main pathway of ClO^- decomposition is pH dependent (eqn. 3) and involves chlorite ion (ClO_2^-) as an intermediate that is rapidly transformed into ClO_3^-.[4] As implied by the stoichiometry of the reaction and demonstrated experimentally, the rate of the decomposition reaches a maximum at pH close to 7.3.[4]

$$2HOCl + {}^{-}OCl \longrightarrow ClO_3^- + 2\ H^+ + 2\ Cl^- \qquad (3)$$

GC-FID chromatogram of the reaction mixture

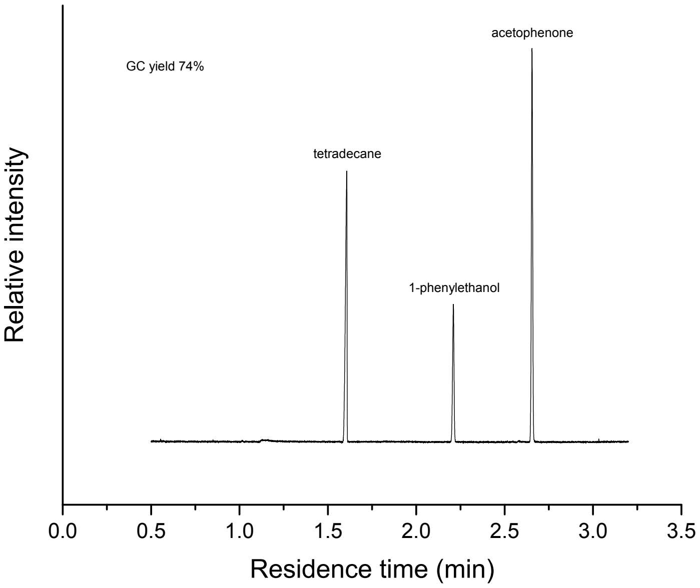

Figure S 4 GC chromatogram (Agilent 6890 GC equipped with FID detector and Red dot FFAP column (5 m x 0.05 mm x 0.05 µm) of the crude after quenched on-line with aqueous $NaHSO_3$ *flowed by dilution (Figure 5, residence time 0.75 min, 1.3 eq of NaOCl, GC yield 74%).*

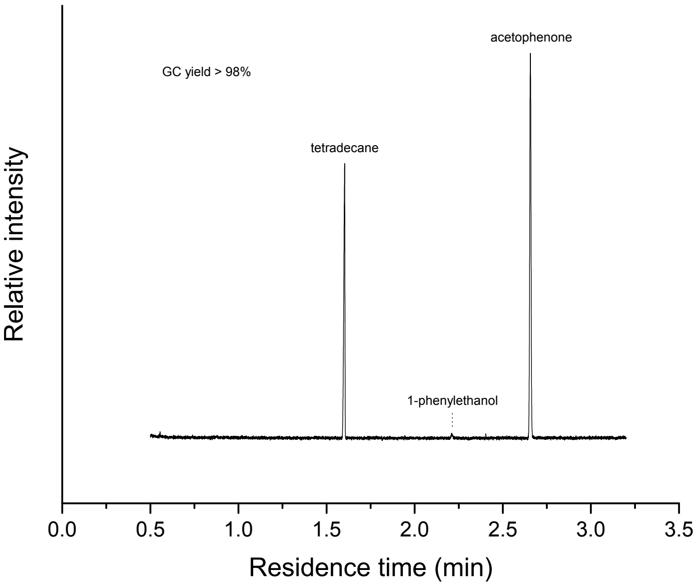

Figure S 5 GC chromatogram (Agilent 6890 GC equipped with FID detector and Red dot FFAP column (5 m x 0.05 mm x 0.05 µm) of the crude after quenched on-line with aqueous $NaHSO_3$ *flowed by dilution (Figure 5, residence time 1.5 min, 2 eq of NaOCl, GC yield > 98%).*

References

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