Bimolecular versus trimolecular reaction pathways of H_2O_2 with the hypochlorous species and implications for wastewater reclamation

Supporting Information

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Text S1: Wastewater pretreatment

The wastewater samples were subjected to successive pre-filtration using qualitative filter papers (Grade 102, Whatman, UK) after collection. The filtered wastewater was then acidified and kept in dark storage at 4°C before use. Prior to conducting kinetic measurements, each sample underwent an additional filtration through 0.22 μm filters to further remove any particles that could potentially clog the stopped-flow spectroscopy.

Text S2: Wastewater characterization

Inorganic metal cations including Ca^{2+}, Na^+, Mg^{2+}, K^+, Mn^{2+}, Fe_{total} were quantified by an inductively coupled plasma optical emission spectrometer (7700, Agilent, U.S.). Inorganic ions including NO_2^-, Br^-, SO_4^{2-}, and Cl^- were quantified by an ion chromatography instrument (ICS−1100, Thermo, USA). Conductivity was detected by a conductivity meter (DDSJ−318, Leici, China). Total organic carbon (TOC) of the wastewater was measured by a TOC analyzer (TOC−L CPH CN200, Shimadzu, Japan). The alkalinity was determined using an automatic potentiometric titrator (Titrando 905, Metrohm, Switzerland) through the standard hydrochloric acid method. According to the standard methods of the American Public Health Association,[1] ammonium nitrogen (NH3-N) was measured by colorimetry on an ultraviolet spectrophotometer (UV1780, Shimadzu, Japan). The biochemical oxygen demand after 5 days (BOD5) and chemical oxygen demand (COD) were measured according to the national standard methods of water quality testing.[2, 3]

Text S3: Operational procedure for the stopped-flow spectroscopy

Before the kinetic experiments, a gas supply at 8 bar was used to power the operation of the pneumatic rams and stop valves of the sample handling unit. The standard operating mode of the SX20 was single-mixing. Both hypochlorous species and H_2O_2 were loaded into syringe drivers with the same inject speed, and they were forced through the mixer and optical cell by a pneumatically controlled ram. In this process, the mixed reactants from the optical cell enter a stop syringe, and the flow ceases when the stop syringe plunger contacts a trigger switch. The switch stops the flow and starts the data acquisition. It should be noted that the two syringe drivers were of the same size to achieve a mixing ratio of 1:1. In the liquid channel, a 150W xenon lamp was used as a light source, and a- photomultiplier was used to record the signals.

Text S4: Detailed information for trimolecular reaction dynamics simulation

In our experiment, H_2O_2 was present at a significantly higher concentration than ClO^-, making it possible for the participation of multiple H_2O_2 molecules in the reaction. To explore the reactions involving two H_2O_2 molecules and one ClO^-, another batch of trajectories were calculated for the collisions of H−bonded $[H_2O_2 \cdot ClO]^-$ with a second H_2O_2 at 300 K, with the collision impact parameter b randomly chosen in the range of $0 - 3.0$ Å and E_{CM} at 0.5 and 1.0 eV, respectively. One hundred trajectories were calculated at each E_{CM}.

It turned out that the majority of the $[H_2O_2 \cdot ClO]^- + H_2O_2$ trajectories led to the formation of a $[HOOH \cdot ClO \cdot HOOH]^-$ intermediate complex. To explore the subsequent reaction and products of the resulting intermediate, thermal decomposition of the $[HOOH \cdot ClO \cdot HOOH]^-$ complex was simulated in a third batch of trajectories. To enhance the reaction probability within the practical trajectory integration time (of ~3 ps), we adopted a conventional approach and increased temperature in the simulations to 1500 K. Note that this temperature was higher than the decomposition temperature under experimental condition. As a result, some trajectories may find reaction pathways with activation barriers ($\Delta^{\ddagger}G^o$) too high to be of relevance. The point is that with enough trajectories, all of probable reaction pathways can be identified. Once these pathways are located, their reaction PES would be mapped out and only those of actual relevance would be taken into account in the subsequent kinetics modeling.

Text S5: Calculation of theoretical rate constant

The Arrhenius equation was used to describe the empirical relationship between the k values and $\Delta^{\ddagger}G°$:

$$k = A \times \exp\left(-\frac{\Delta^{\ddagger}G°}{RT}\right)$$

where A is the preexponential factor and R is the ideal gas constant. The preexponential factor A was set to be 8×10^{11} M^{-1} min^{-1}.[4]

Table S1: The characteristics of municipal and ammonium-rich wastewaters using modified sequencing batch reactor (MSBR) and anammox sequencing batch reactor (SBR).

Parameter	Municipal wastewater	Ammonium-rich wastewater
pH	7.55	8.50
alkalinity (mg L^{-1} as CaCO$_3$)	117	733
Conductivity (μS cm^{-1})	542	3.55
TOC (mM$_C$ L^{-1})	4.32	5.67
BOD$_5$ (mg L^{-1})	1.20	18.5
COD (mg L^{-1})	7.00	57.0
ammonium nitrogen (mg L^{-1})	4.52	50.6
Cl$^-$ (mM)	57.8	31.9
SO$_4^{2-}$ (mM)	42.2	772
NO$_2^-$ (mM)	0.37	71.5
Ca^{2+} (mM)	59.0	33.6
Na$^+$ (mM)	34.7	253
Mg^{2+} (mM)	6.53	41.8
K$^+$ (mM)	13.8	630
Mn^{2+} (mM)	0.09	0.01
Fe$_{total}$ (mM)	0.01	0.11

Note: every parameter was measured in triplicate after samples being collected.

Table S2: Reactions and equilibrium constants (25 °C) for HClO and H_2O_2 in aqueous solution.

Reaction	Equilibrium constant	pK_a	References
$Cl_2 + H_2O \rightleftharpoons HClO + Cl^- + H^+$	$K_1 = 4.0 \times 10^{-4}$ M^2	3.4	Cotton *et al.* (1972)[5]
$HClO \rightleftharpoons H^+ + ClO^-$	$K_2 = 3.0 \times 10^{-8}$ M	7.5	Harris (2012)[6]
$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	$K_3 = 2.5 \times 10^{-12}$ M	11.6	Holleman and Wiberg (1985)[7]

Table S3: The derivation of k_1 (M^{-1} s^{-1}) with the known $k_{2,overall}$ (M^{-1} s^{-1}), $k'_{2,overall}$ (s^{-1}), and fitted k'_1 (s^{-1}) on the basis of HClO/ClO$^-$ speciation.

$k_{2,overall}$	[H$_2$O$_2$] (mM)	$k'_{2,overall}$	k'_1	k_1
	0.015	41.2 ± 4.88	0.726 ± 0.002	
	0.018	49.4 ± 5.86	1.12 ± 0.001	
2746 ± 325.3	0.021	57.7 ± 6.83	1.19 ± 0.010	42.3 ± 13.5
	0.024	65.9 ± 7.81	1.19 ± 0.004	
	0.027	74.2 ± 8.78	1.33 ± 0.003	

Figure S1: Picture of the pilot-scale sequencing batch reactor (hydraulic retention time = 24 hr, T = 37 °C, volume = 8 L, volumetric exchange rate = 25%, $pH_{influent}$ = 6.8–7.0, and $pH_{effluent}$ = 8.5).
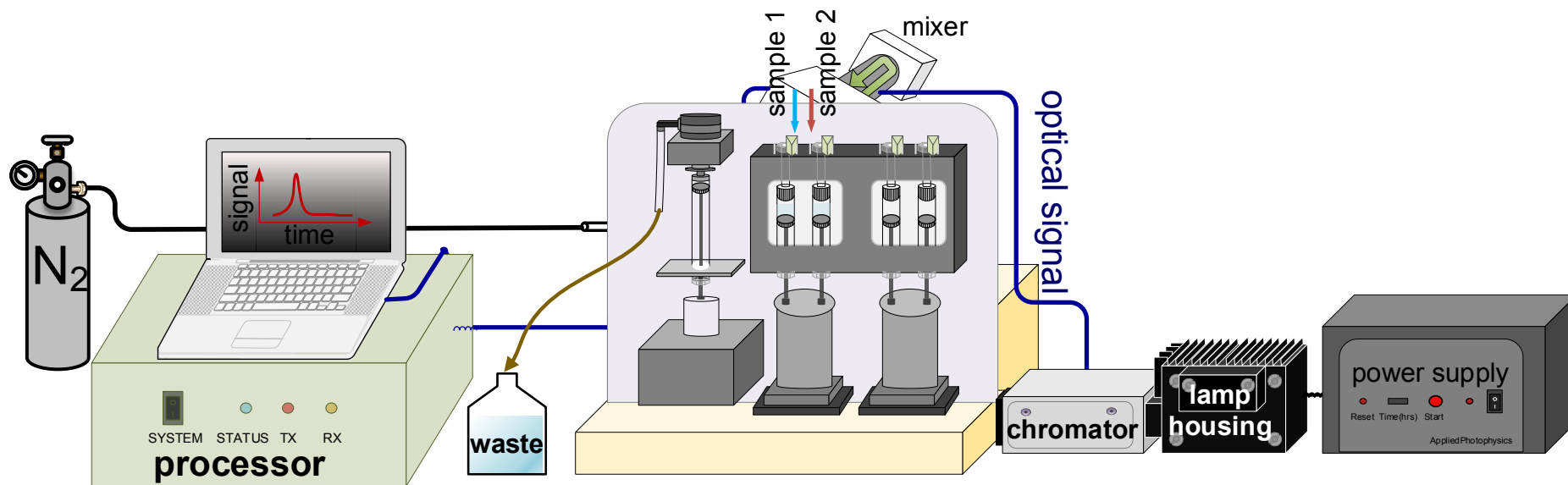
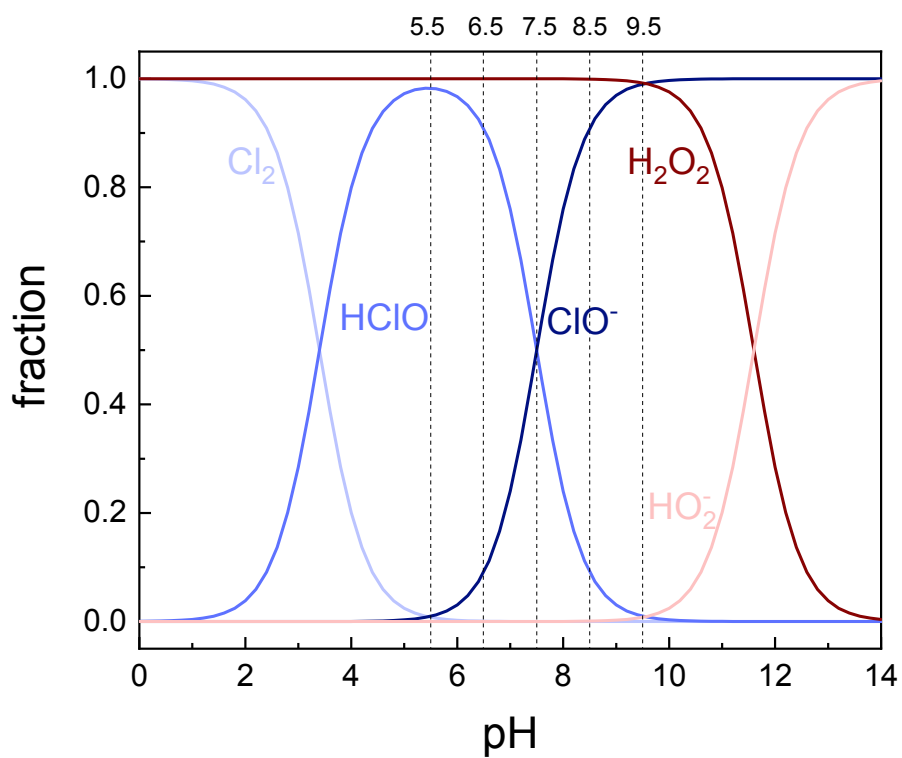Figure S2: The schematic diagram for the modified stopped flow spectroscopy in this study.

Figure S3: The fraction of different species (Cl_2, $HClO$, ClO^-, H_2O_2, and HO_2^-) as a function of pH. The vertical dotted lines represent the tested pH conditions.
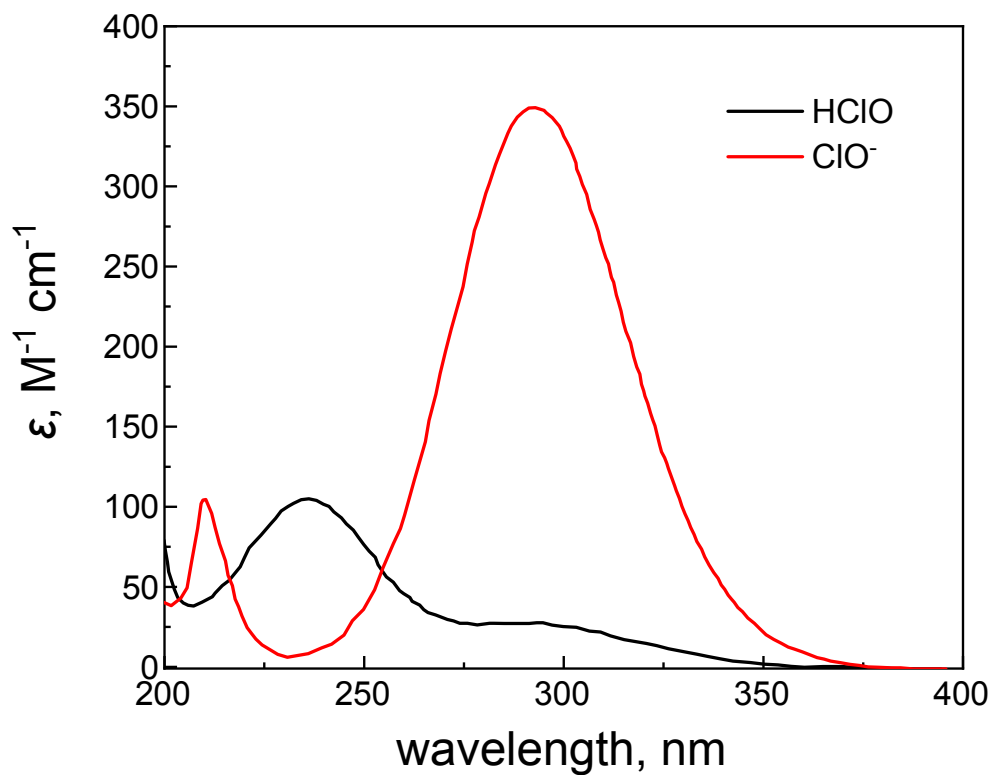
Figure S4: UV spectra of HClO and ClO⁻ (This figure is reproduced from Figure S2 in Lee *et al*, Copyright 2020 American Chemical Society).[8]
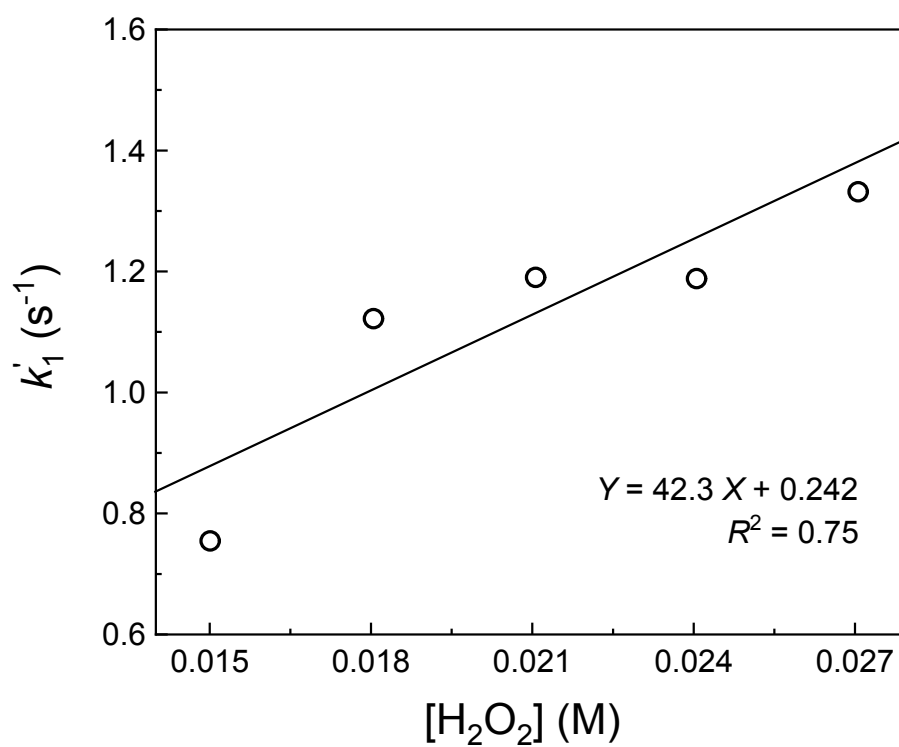
Figure S5: The k_1' values of the reaction of HClO and H_2O_2 as function of $[H_2O_2]$. The slope of line is k_1 (42.3 ± 13.5 $M^{-1}\,s^{-1}$). The error bars are smaller than the symbol size and   thus   invisible.
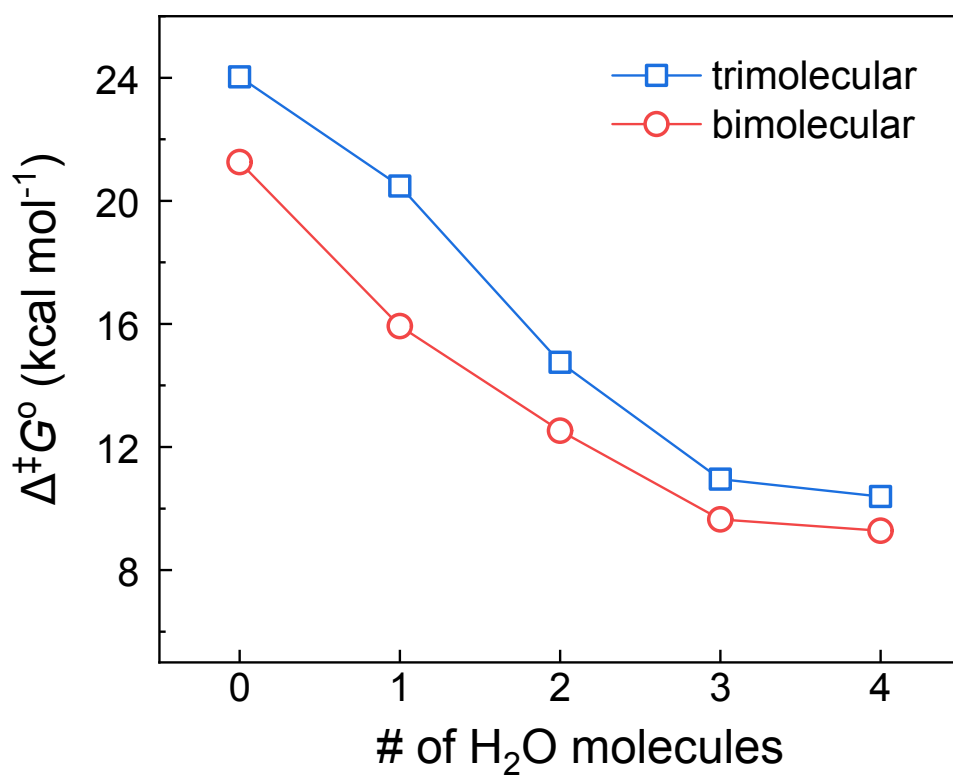
Figure S6: The reaction $\Delta^{\ddagger}G^{\circ}$ of bimolecular and trimolecular pathways between ClO^{-} and H_2O_2 with different numbers of explicit H_2O molecules at ωB97XD/aug−cc−pVQZ//ωB97XD/6−31+G(d,p) level of theory.

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