Supporting information

Misconceptions about the Chemistry of Aqueous Chlorine Atoms and $HClOH^{\bullet}$(aq) , and a Revised Mechanism for the Photochemical Peroxydisulfate/Chloride Reaction

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Contents:

Mechanism used in the simulations of the data of Alegre et al.[1]

1	$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^\bullet$	$k = 2.7E8\ M^{-1}\ s^{-1}$
2	$Cl^\bullet + Cl \rightleftharpoons Cl_2^{\bullet-}$	$k_f = 8.5E9\ M^{-1}\ s^{-1}$, $k_r = 6E4\ s^{-1}$
3	$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Cl_2 + Cl^- + Cl^-$	$\log k = 8.8 + 1.6\mu^{1/2}/(1 + \mu^{1/2})$
4	$Cl^\bullet + H_2O \rightleftharpoons ClOH^{\bullet-} + H^+$	$k_f = 1.5E5\ s^{-1}$, $k_r = 3E10\ M^{-1}\ s^{-1}$
5	$ClOH^{\bullet-} \rightleftharpoons HO^\bullet + Cl^-$	$k_f = 6.1E9\ s^{-1}$, $k_r = 4.3E9\ M^{-1}\ s^{-1}$
6	$Cl_2 + H_2O \rightarrow ClOH + Cl^- + H^+$	$k = 11\ s^{-1}$
7	$Cl_2 + Cl^- \rightleftharpoons Cl_3^-$	$k_f = 1E10\ M^{-1}\ s^{-1}$, $k_r = 5.6E10\ s^{-1}$
8	$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-}$	$k = 1.2E5\ M^{-1}\ s^{-1}$
9	$SO_4^{2-} + HO^\bullet \rightarrow SO_4^{\bullet-} + HO^-$	$1E6\ M^{-1}\ s^{-1}$
10	$HO^\bullet + HO^\bullet \rightarrow H_2O_2$	$5.5E9\ M^{-1}\ s^{-1}$
11	$H^+ + OH^- \rightleftharpoons H_2O$	$k_f = 1E10\ M^{-1}\ s^{-1}$, $k_r = 1E{-}4\ M\ s^{-1}$

Mechanism and rate constants as in Table 1 of Alegre et al. with the following exceptions. Reaction 6 in Allegre et al. is omitted because of its insignificant contribution at the pH of the simulations (pH 3). Reaction 4 above replaces reactions 8, 9 and 10 in Alegre et al. The rate constant for forward reaction 4 is determined by the pK_a of $Cl^\bullet$ ($pK_a = 5.3$)[2] and the rate constant for the reverse of reaction 4. The reverse of reaction 4 above replaces reaction 11 in Alegre et al. Reaction 7 in Alegre et al. is omitted because it is equivalent to the reverse of reaction 2 above. Reaction 14 in Allegre et al. is omitted because it is equivalent to forward reaction 2 above. Reaction 10 above is added as mentioned at the bottom right of page 3119 in Alegre et al. with its rate constant as in Buxton et al.[3] Reaction 11 is added to maintain pH equilibrium.

The ionic strength adjustment to the rate constant for eq 3 needs to be applied. The solutions of Alegre et al. had $[K_2S_2O_8]$ = 5 mM in the conventional flash and 20 mM in the laser experiments and various amounts of NaCl; the pH was 3 - 2 due to impurities in the $K_2S_2O_8$. At $\mu = 0.1$ M, $k_3 = 1.5E9$.

Note that step 8 (reaction of $SO_4^{\bullet-}$ with $S_2O_8^{2-}$) consumes a very small fraction of the $SO_4^{\bullet-}$ at the Cl^- concentrations used. The $S_2O_8^{\bullet-}$ produced is not consumed in the mechanism of Alegre et al.

A comprehensive list of the 18 reported illegal loops involving $HClOH^{\bullet}$.

Subsequent reports with illegal loops. In addition to the publications having reversible loops involving reactions 1, 2, or 3 that violate closure (meaning that the rate constants do not agree with the requirements imposed by the loop composition), there are many publications that use reactions 1, 2, or 3 in illegal loops, which violate the principle of detailed balancing. As has been explained elsewhere, illegal loops are sets of reactions like reversible loops except where one or more of the steps are irreversible and unopposed by other irreversible steps.[4] Although it is often possible to rectify illegal loops by making the irreversible steps reversible with rate constants defined by the other steps, this is unlikely to be satisfactory in the present system because of the unreliability of those other rate constants.

One of the illegal loops was reported previously as illegal Loop D:[5]

Illegal Loop 1 (D)

$HClOH^{\bullet} \rightarrow Cl^{\bullet} + H_2O$

$Cl_2^{\bullet-} + H_2O \rightleftharpoons HClOH^{\bullet} + Cl^-$

$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^{\bullet-}$

This loop is the same as the first reversible loop (eqs 1, 3, and 4 in the main text) except that its first step is irreversible. Eighteen publications were previously identified as having mechanisms that included Loop D.[5] Here we report an additional 38 publications that have mechanisms including Loop D.[6–43] In our previous report we showed that correcting Loop D by supplying the requisite value for the reverse rate constant in the first step had no effect on the simulations of the overall mechanism in one of the publications. This outcome was traced to the fact that the first step could be eliminated entirely without affecting the results of the simulation. The rate constants in Matthew and Anastasio for the steps in illegal Loop 1 require a value of 1.5 s^{-1} for the reverse rate constant of the first step.[44] Simulations of the loop with initial concentrations of 0.01 M Cl^- and 1 μM $Cl^{\bullet}$ yield a steady-state $HClOH^{\bullet}$ concentration of 2.6×10^{-11} M irrespective of whether the reverse of the first step is included or not. This result arises because the second and third steps are much faster and establish the equilibrium concentration of $HClOH^{\bullet}$, and it explains why the first step can be omitted entirely. Loop 7 below is an example of the opposite behavior, where supplying the required rate constant in an illegal loop leads to major changes in the concentrations.

Another illegal loop:

Illegal Loop 2

$HClOH^{\bullet} \rightarrow Cl^{\bullet} + H_2O$

$Cl_2^{\bullet-} + H_2O \rightleftharpoons HClOH^{\bullet} + Cl^-$

$Cl^{\bullet} + OH^- \rightarrow ClOH^{\bullet-}$

$ClOH^{\bullet-} + Cl^- \rightleftharpoons Cl_2^{\bullet-} + OH^-$

This illegal loop appears in at least 19 publications.[13, 19, 24, 25, 29, 34, 38, 41, 45–55]

Illegal Loop 3 differs from Loop 2 by having only the first step irreversible:

Illegal Loop 3

$HClOH^{\bullet} \rightarrow Cl^{\bullet} + H_2O$

$Cl_2^{\bullet-} + H_2O \rightleftharpoons HClOH^{\bullet} + Cl^-$

$Cl^{\bullet} + OH^- \rightleftharpoons ClOH^{\bullet-}$

$ClOH^{\bullet-} + Cl^- \rightleftharpoons Cl_2^{\bullet-} + OH^-$

This illegal loop appears in Zhao et al. 2019,[56] and Zhou et al. 2019.[57]

Illegal loop 4 differs from Loop 2 by having only the third step irreversible:

Illegal Loop 4

$HClOH^{\bullet} \rightleftharpoons Cl^{\bullet} + H_2O$

$Cl_2^{\bullet-} + H_2O \rightleftharpoons HClOH^{\bullet} + Cl^-$

$Cl^{\bullet} + OH^- \rightarrow ClOH^{\bullet-}$

$ClOH^{\bullet-} + Cl^- \rightleftharpoons Cl_2^{\bullet-} + OH^-$

This illegal loop appears in at least 5 publications.[58–62]

Another illegal loop involving reactions 1, 3 and 4 has the first step in Loop 1 irreversible in the opposite direction:

Illegal Loop 5

$Cl^{\bullet} + H_2O \rightarrow HClOH^{\bullet}$

$HClOH^{\bullet} + Cl^- \rightleftharpoons Cl_2^{\bullet-} + H_2O$

$Cl_2^{\bullet-} \rightleftharpoons Cl^{\bullet} + Cl^-$

This illegal loop appears in at least three publications.[63–65] Martire et al. include this loop with the first step shown as reversible but with no reverse rate constant provided.[66]

A 6th illegal loop treats the second step as being irreversible:

Illegal Loop 6

$Cl^{\bullet} + H_2O \rightleftharpoons HClOH^{\bullet}$

$HClOH^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet-} + H_2O$

$Cl_2^{\bullet-} \rightleftharpoons Cl^{\bullet} + Cl^{-}$

This illegal loop appears in a 2020 publication.[67]

There are several illegal loops in which the acid dissociation of $HClOH^{\bullet}$ (eq 2, main text) is irreversible. One of these was identified in our earlier publication as Loop E:[5]

Illegal Loop 7 (E)

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^{+}$

$Cl_2^{\bullet-} + H_2O \rightleftharpoons HClOH^{\bullet} + Cl^{-}$

$HOCl^{\bullet-} + Cl^{-} \rightleftharpoons Cl_2^{\bullet-} + OH^{-}$

$H^{+} + OH^{-} \rightleftharpoons H_2O$

In addition to the 24 publications previously identified as having illegal Loop E, it also appears in 26 newly identified publications.[7, 12, 14, 15, 17, 20–22, 27–32, 35–40, 42, 61, 62, 68–72] The rate constants in Xiang et al. 2022 require a value of 5.7×10^{11} M^{-1} s^{-1} for the reverse of the first step.[72] Simulations of Loop 7 at pH 3 with 1 mM Cl^{-} and 1 μM $Cl_2^{\bullet-}$ show that the steady-state concentration of $HClOH^{\bullet}$ changes from 9.8×10^{-14} M to 2.6×10^{-10} M when the reverse rate constant of the first step is increased from zero to its required value. This example thus shows that correcting an illegal loop can have large consequences.

Illegal loop 8 differs from Loop 7 by having two irreversible steps:

Illegal Loop 8

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^{+}$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^{-}$

$HOCl^{\bullet-} + Cl^{-} \rightleftharpoons Cl_2^{\bullet-} + OH^{-}$

$H^{+} + OH^{-} \rightleftharpoons H_2O$

This illegal loop appears in Li et al. 2017,[73] Guan et al. 2018,[74] and Zhang et al. 2019.[75]

Illegal loop 9 differs from Loop 7 by having the first three steps irreversible:

Illegal Loop 9

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^{+}$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$

$HOCl^{\bullet-} + Cl^- \rightarrow Cl_2^{\bullet-} + OH^-$

$H^+ + OH^- \rightleftharpoons H_2O$

This loop appears in Wu et al. 2019,[76] Chow et al. 2021,[77] and Wu et al. 2021.[78]

Illegal loop 10 also differs from Loop 7 by having three irreversible steps, but in this case one of the irreversible steps is the reaction of H^+ with OH^-. Mechanisms with this irreversible step are unable to simulate the pH properly.

Illegal Loop 10

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^+$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$

$HOCl^{\bullet-} + Cl^- \rightleftharpoons Cl_2^{\bullet-} + OH^-$

$H^+ + OH^- \rightarrow H_2O$

This illegal loop appears in Li et al. 2022.[79]

Another group of illegal loops involving the irreversible acid dissociation of $HClOH^{\bullet}$ also includes the conversion of $HOCl^{\bullet-}$ to $Cl^{\bullet}$. One of these is Loop 11:

Illegal Loop 11

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^+$

$HOCl^{\bullet-} + H^+ \rightleftharpoons Cl^{\bullet} + H_2O$

$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^{\bullet-}$

$Cl_2^{\bullet-} + H_2O \rightleftharpoons HClOH^{\bullet} + Cl^-$

This loop appears in at least 16 publications.[7, 9, 12, 13, 15, 20, 21, 24, 25, 34, 38, 41, 43, 45, 80–82]

An illegal loop that differs from Loop 11 by having two irreversible steps is as follows:

Illegal Loop 12

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^+$

$HOCl^{\bullet-} + H^+ \rightleftharpoons Cl^{\bullet} + H_2O$

$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^{\bullet-}$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$

This illegal loop appears in at least 9 publications.[19, 74, 75, 79, 83–87]

An illegal loop that differs from Loop 11 by having three irreversible steps is as follows:

Illegal Loop 13

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^+$

$HOCl^{\bullet-} + H^+ \rightleftharpoons Cl^{\bullet} + H_2O$

$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-}$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$

This illegal loop appears in Li et al. 2017,[73] and Li et al. 2020.[88]

An illegal loop that differs from Loop 11 in having all steps irreversible is as follows:

Illegal Loop 14

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^+$

$HOCl^{\bullet-} + H^+ \rightarrow Cl^{\bullet} + H_2O$

$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-}$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$

This illegal loop appears in Wu et al. 2019,[76] Chow et al. 2021,[77] and Wu et al. 2021.[78]

An illegal loop involving the irreversible acid dissociation of $HClOH^{\bullet}$ and the reversible hydration of $Cl^{\bullet}$ is as follows:

Illegal Loop 15

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^+$

$Cl^{\bullet} + H_2O \rightleftharpoons HClOH^{\bullet}$

$HOCl^{\bullet-} + H^+ \rightarrow Cl^{\bullet} + H_2O$

This illegal loop appears in at least 8 publications.[44, 58, 61, 62, 68, 69, 89, 90]

Loop 16 is the same as Loop 15 except that the last step is reversible:

Illegal Loop 16

$HClOH^{\bullet} \rightarrow HOCl^{\bullet-} + H^+$

$Cl^{\bullet} + H_2O \rightleftharpoons HClOH^{\bullet}$

$HOCl^{\bullet-} + H^+ \rightleftharpoons Cl^{\bullet} + H_2O$

This illegal loop appears in Fu et al. 2019,[59] Yang et al. 2019,[60] Jirasek and Lukes 2020,[67] and Asghar et al. 2022.[82]

Another category of illegal loops treats the $HClOH^{\bullet}$ acid dissociation as reversible where some other reaction is irreversible. Two of these are as follows:

Illegal Loop 17

$H^+ + HOCl^{\bullet-} \rightleftharpoons HClOH^{\bullet}$

$HClOH^{\bullet} + Cl^- \rightleftharpoons Cl_2^{\bullet-} + H_2O$

$Cl_2^{\bullet-} + OH^- \rightarrow HOCl^{\bullet-} + Cl^-$

$H_2O \rightleftharpoons H^+ + OH^-$

This illegal loop appears in Alegre et al. 2000,[1] and Szabo et al. 2016.[91]

Illegal Loop 18

$HClOH^{\bullet} \rightleftharpoons H^+ + HOCl^{\bullet-}$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$

$HOCl^{\bullet-} + Cl^- \rightleftharpoons Cl_2^{\bullet-} + OH^-$

$H^+ + OH^- \rightleftharpoons H_2O$

Illegal loop 18 appears in Sun et al. 2022.[92]

It is possible to make Loops 1, 3 – 7, 11, 16, 17 and 18 legal by supplying the requisite reverse rate constants, which can be calculated easily from the other rate constants in the loops. The results, however, are unlikely to be satisfactory given the dubious support for some of the other rate constants in the loops. Similarly, Loops 2 and 15 can be made legal by supplying the well-established rate constant for the reverse of the third step,[93] which would then define the reverse rate constant for the first step; the result, again, is unlikely to be satisfactory. To make Loops 8 – 10 and 12 – 14 legal would require supplying rate constants for two reactions involving $HClOH^{\bullet}$, which cannot be done reliably at this time.

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