Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for: Exploring the Mechanism of Hypochlorous Acid Decomposition in Aqueous Solutions

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pH Dependence of Rates and Speciation

The calculation of the speciation is restricted to only include HOCl, OCl^-, Cl_2O_2 and $Cl_3O_2{}^-$. The HOCl−−−OCl^- complex was excluded as it essentially corresponds to weakly bound HOCl and OCl^-. The following set of reactions was used for the thermodynamic modelling:

Rxn 1:

$HOCl \rightleftharpoons OCl^- + H^+$

Rxn 2:

$2HOCl \rightleftharpoons Cl_2O + H_2O$

Rxn 3:

$2HOCl + OCl^- \rightleftharpoons Cl_3O_2{}^- + H_2O$

Based on these chemical equations the respective equilibrium constants can be defined as

$$K_{Rxn1} = \frac{[OCl^-][H^+]}{[HOCl]} \tag{1}$$

$$K_{Rxn2} = \frac{[Cl_2O][H_2O]}{[HOCl]^2} \tag{2}$$

$$K_{Rxn3} = \frac{[Cl_3O_2^-][H_2O]}{[HOCl]^2[OCl^-]} \tag{3}$$

where K is the respective equilibrium constant and [X] the concentration os species X. The concentration of water in water, $[H_2O]$ was calculated to be 55.56 M. Considering the problems associated with calculating acid-base equilibrium constants accurately, we decided to use the literature value of

$$pK_{Rxn1} = 7.40$$

for Rxn 1. This value is taken from reference[S1] and has been obtained under standard conditions at low ionic strength. The equilibrium constants for Rxn2 and Rxn3 on the other hand are calculated from Gibbs free energies obtained from density functional theory (DFT) modelling through equation 4.

$$K = e^{-\frac{\Delta G}{RT}} \tag{4}$$

ΔG corresponds to the Gibbs free energy, R to the gas constant and T to the temperature. Inserting the ΔG values from DFT obtained at a temperature of 353 K of

$$\Delta G_{Rxn2} = -0.082eV \tag{5}$$

$$\Delta G_{Rxn3} = -0.357eV \tag{6}$$

the equilibria constants can be calcualted. In order to solve the equation system, the total mass balance needs to be added as a 4th equation.

$$[HOCl]_0 = [HOCl] + [OCl^-] + 2[Cl_2O] + 3[Cl_3O_2^-] \tag{7}$$

$[HOCl]_0$ corresponds to the initial HOCl concentration. Inserting equations 1 to 3 into equation 7 results into

$$\frac{3K_{Rxn3}K_{Rxn1}}{[H^+][H_2O]}[HOCl]^3 + \frac{2K_{Rxn2}}{[H_2O]}[HOCl]^2 + (1 + \frac{K_{Rxn1}}{[H^+]})[HOCl] - [HOCl]_0 = 0 \tag{8}$$

Through finding the roots of the equation and extracting the solution in the intervall

$$0 \leq [HOCl] \leq [HOCl]_0$$

the concentration of HOCl is obtained. Inserting this result into equations 1 to 3 the concentrations of all other relevant species are obtained.

Based on the speciation the reaction rates for the two obtained reaction mechanisms can be calculated. In the mechanism proceeding through $Cl_3O_2{}^-$, the rate detrmining step is

$Cl_3O_2{}^- \longrightarrow Cl_2O_2 + Cl^-$

Accordingly, the rate law is given by

$$\frac{d[ClO_3^-]}{dt} = k_{Cl_3O_2^-}[Cl_3O_2^-] \tag{9}$$

where $k_{Cl_3O_2^-}$=0.44 s^{-1} is the rate constant, taken from DFT calcualtions assuming a temperature of 353 K. Correspondingly, the rate law for the second order decomposition under alkaline conditions

$2OCl^- \longrightarrow ClO_2{}^- + Cl^-$

is given by

$$\frac{d[ClO_3^-]}{dt} = k_{ClO_2^-}[OCl^-]^2 \quad (10)$$

$k_{ClO_2^-} = 0.00016$ s^{-1} has been obtained from DFT calculations assuming a temperature of 353 K.

Summary of Experimental Rate Constants

Table S1: Summary of experimentally obtained rate constants for HOCl decomposition.

h

T [K]	Electrolyte	Rate constant [$M^{-2}s^{-1}$]	Source
323	1M $NaClO_4$	0.09	Adam 1992[S2]
353	6M $NaClO_3$	9.4	Kalmar 2018[S1]
343	526 g/l $NaClO_3$ + 113 g/l NaCl	7.19	Wanngård 2017[S3]
353	15-80 mM HOCl	2.39	Sandin 2015[S4]
353	80 mM HOCl	0.38	Endrödi 2018[S5]
353	80 mM HOCl + 1.9 M NaCl	0.53	Endrödi 2018[S5]
353	80 mM HOCl 1.9 M $NaClO_3$	0.52	Endrödi 2018[S5]
353	80 mM HOCl + 5.2 M $NaClO_3$	1.2	Endrödi 2018[S5]
353	80 mM HOCl + 5.2 M $NaClO_3$ + 1.9 M NaCl	1.9	Endrödi 2018[S5]
343	540 g/l $NaClO_3$ + 110 g/l NaCl	7.1	Spasojevic 2018[S6]

References

(S1) Kalmar, J.; Szabo, M.; Simic, N.; Fabian, I. *Dalton Trans.* **2018**, *47*, 3831–3840.

(S2) Adam, L.; Fabian, I.; Suzuki, K.; Gordon, G. *Inorg. Chem.* **1992**, *31*, 3534–3541.

(S3) Wanngård, j.; Wildlock, M. *Chem. Eng. Res. Des.* **2017**, *121*, 438 – 447.

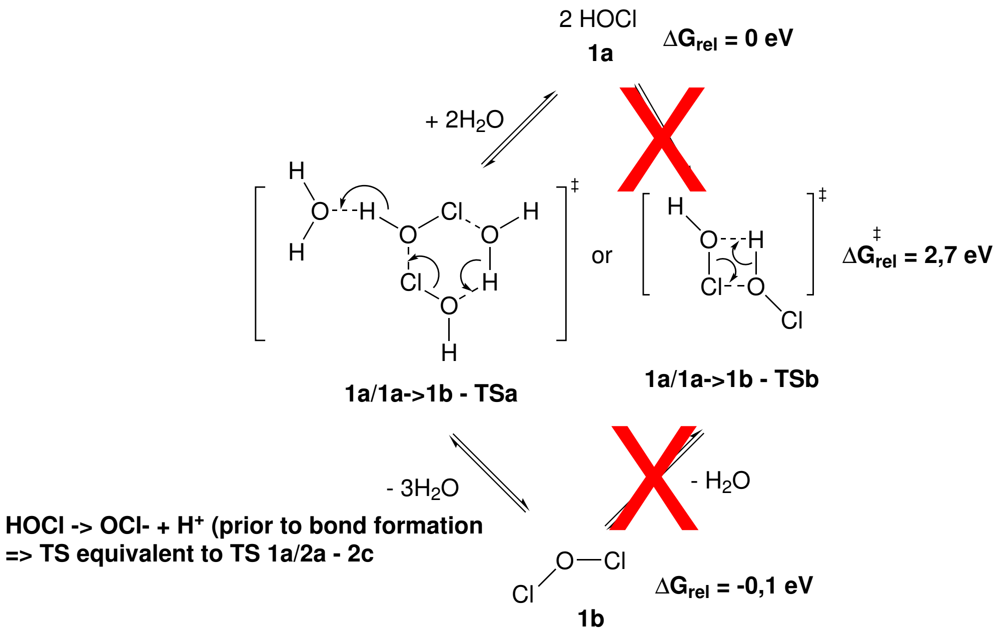
(S4) Sandin, S.; Karlsson, R.; Cornell, A. *Ind. Eng. Chem. Res.* **2015**, *54*, 3767–3774.

(S5) Endrödi, B.; Sandin, S.; Wildlock, M.; Simic, N.; Cornell, A. *J. Chem. Technol. Biotechnol.* **2019**, *94*, 1520–1527.

(S6) Spasojevic, M.; Markovic, D.; Trisovic, T.; Spasojevic, M. *J. Electrochem. Soc.* **2018**, *165*, E8–E19.

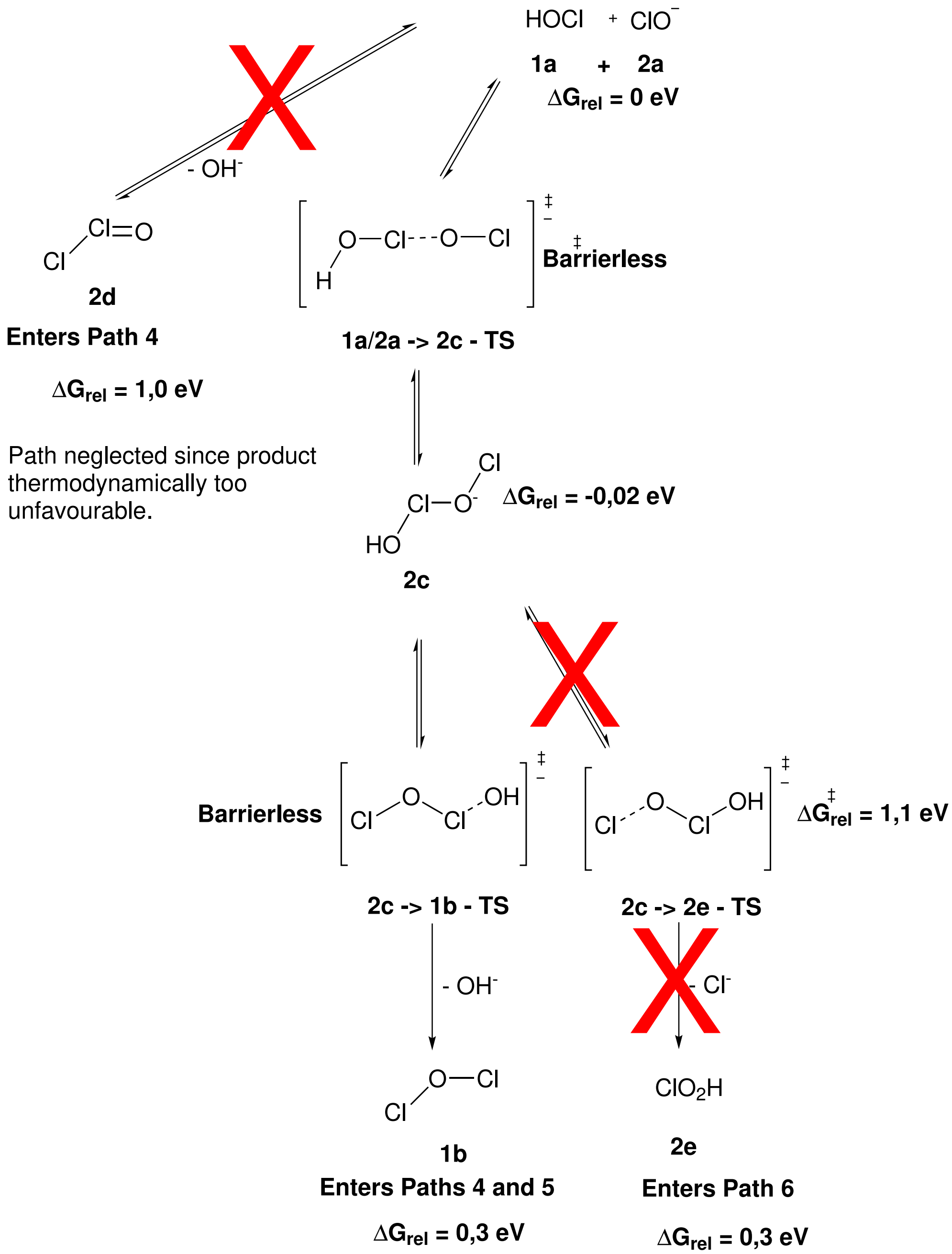
Summary of Considered Reaction Mechanisms

Path 1 - Low pH

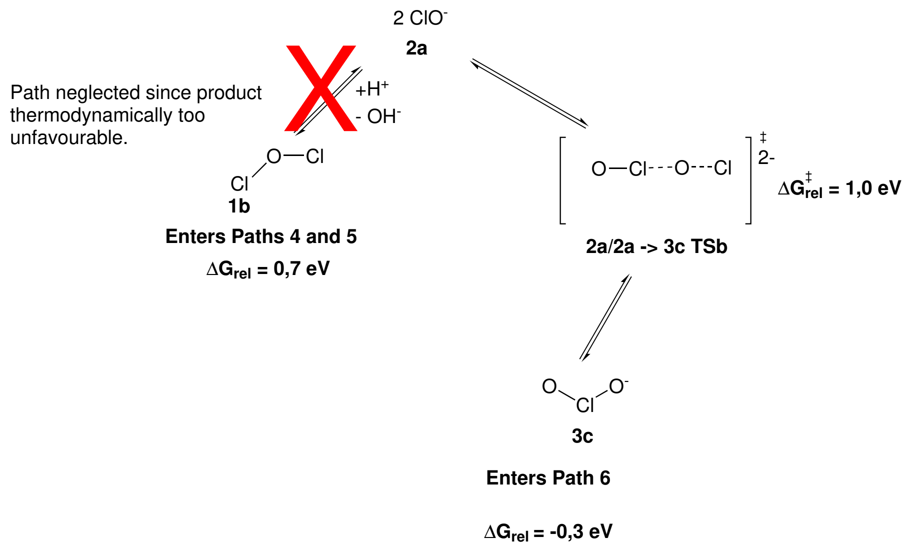


Enters Paths 4 and 5

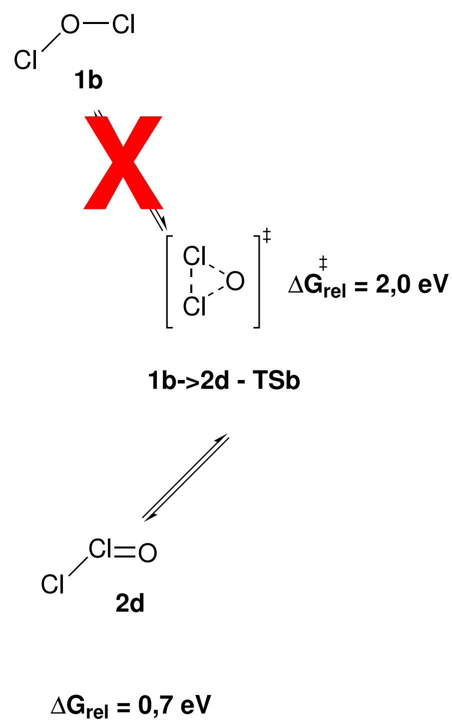
Path 2 - Intermediate pH



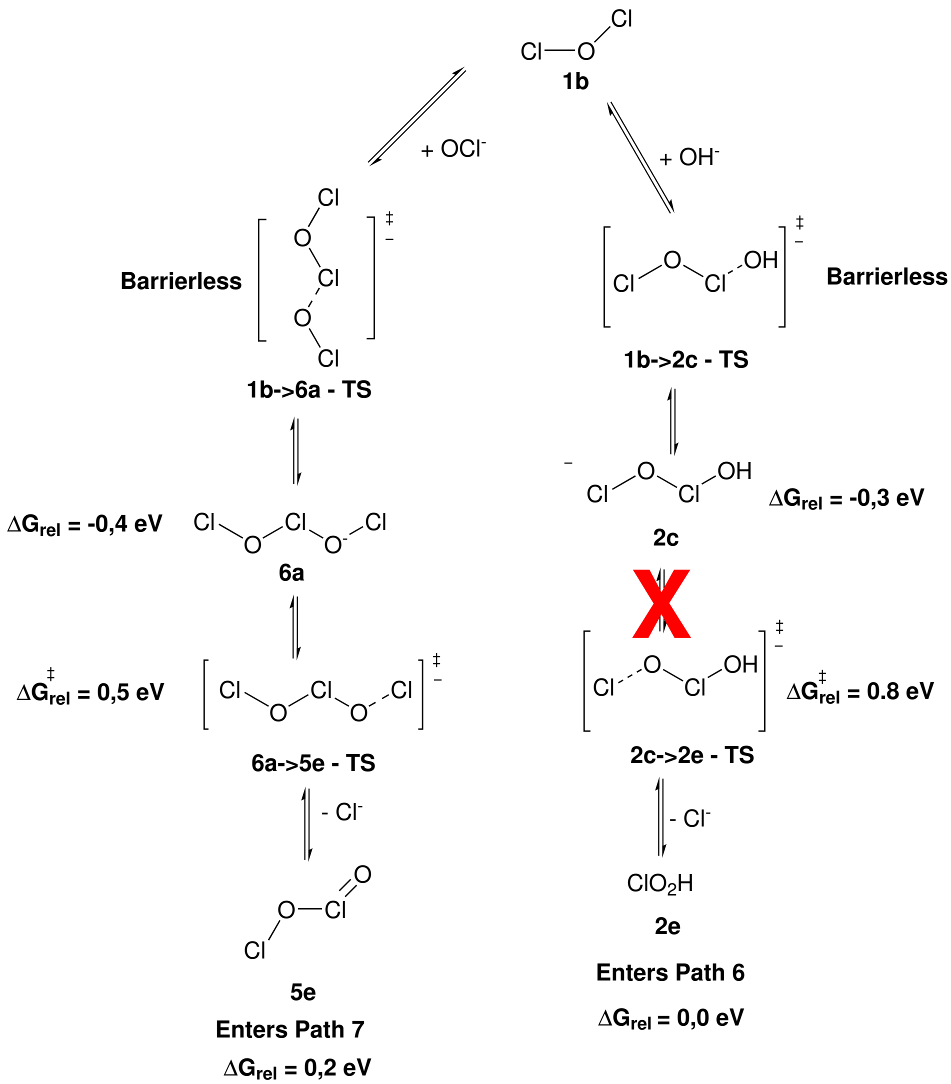
Path3 - High pH (potentially direct formation of chlorite!)



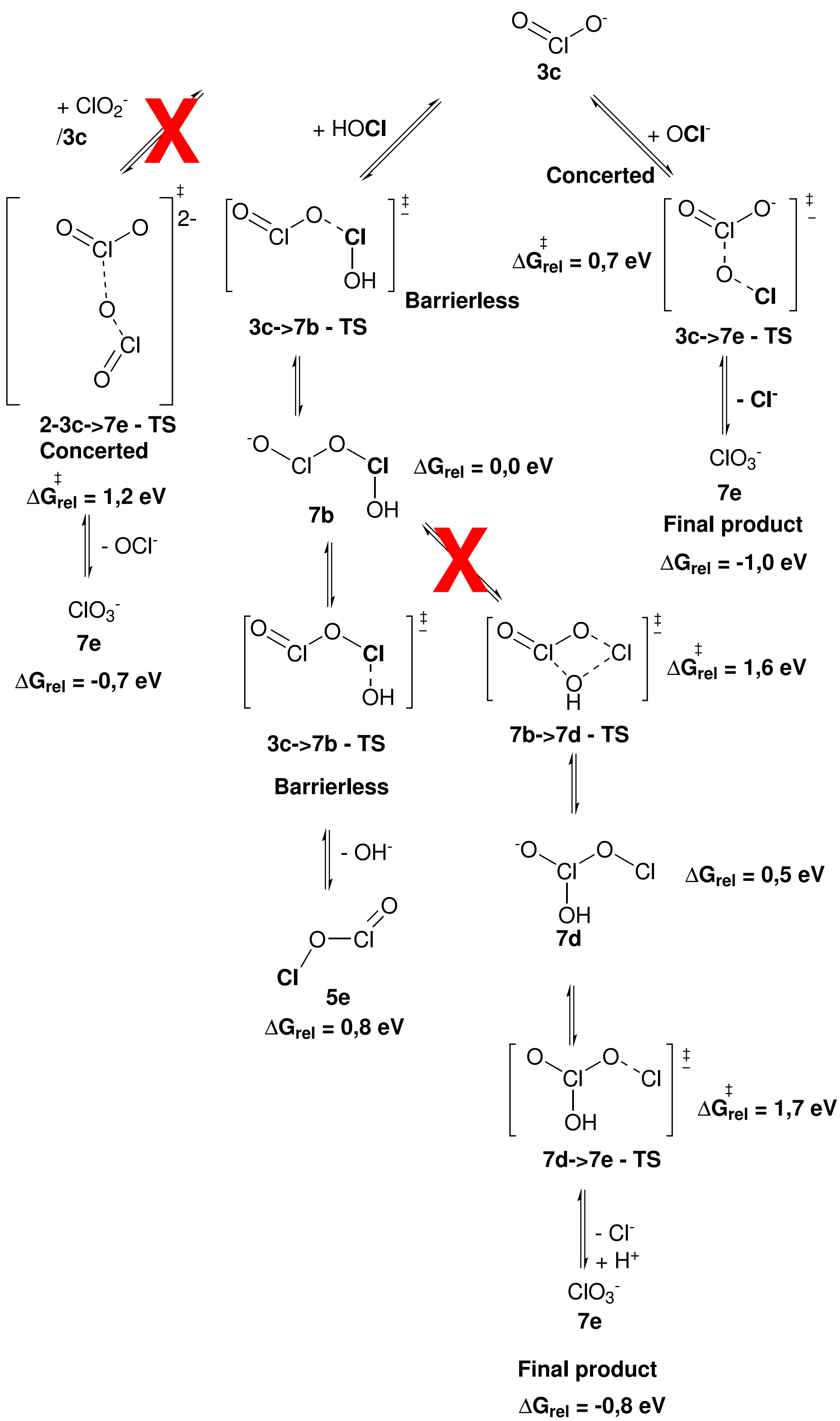
Path4 - ClClO/ClOCl equilibrium



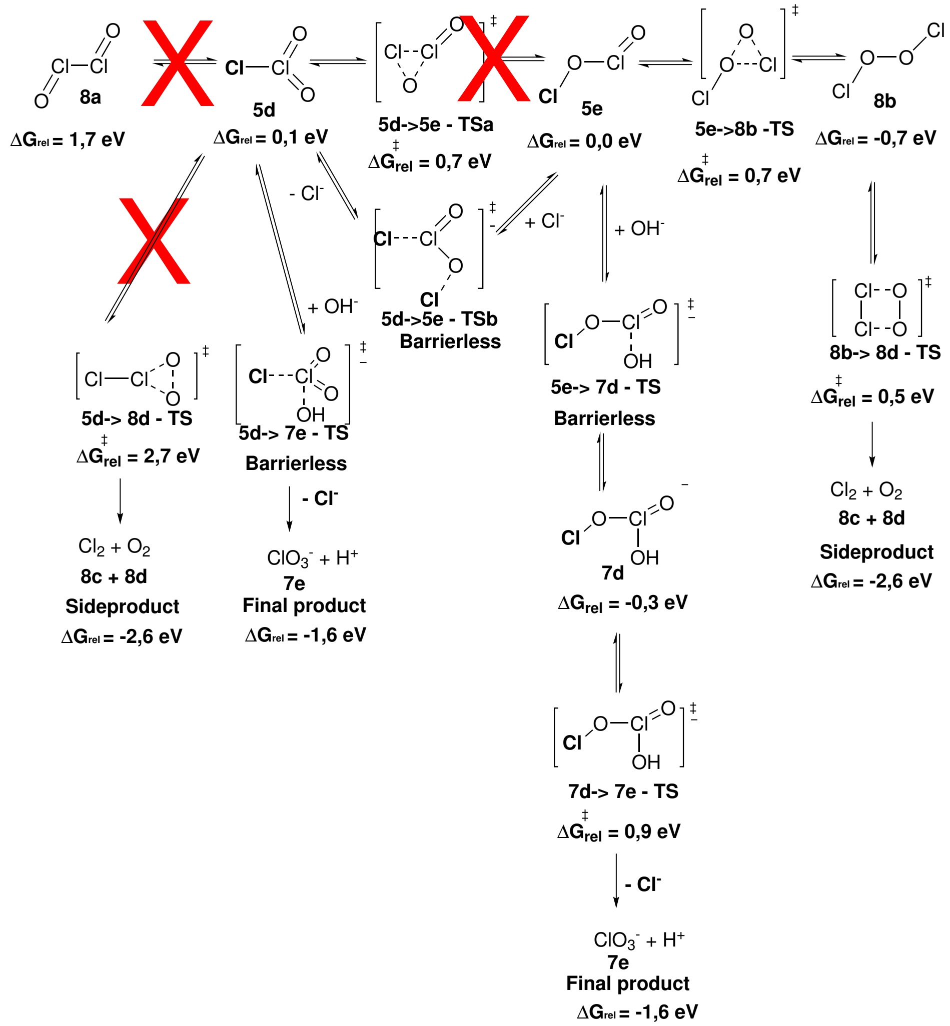
Path5 - ClOCl decomposition (intermediate 1b)



Path6 - ClO_2^- decomposition (intermediate 1b)



Path7 - Cl_2O_2 chemistry/ O_2 evolution



Summary of Gibbs Free Energies

Table S2: Summary of Gibbs free energies obtained at the M06/6-311$**$++/pbf solvation level of theory.

Structure	G_{tot} (incl solvation; 298.15K) [Ha]
Cl^- (no ΔG corrections)	-460.384366
H_2	-1.1723
Cl_2	-920.358703
H_2O	-76.43078
OH^-	-75.965813
O_2 (triplet)	-150.308046
HOCl	-535.949129
ClOCl/1b	-995.470253
OCl^-/2a	-535.497816
HOCl−−−Ocl^-/2c	-1071.447806
ClClO/2d	-995.444714
ClO_2H/2e	-611.046372
ClO_2-/3c	-610.614838
$ClCl(O)_2$/5d	-1070.564401
ClOClO/5e	-1070.569626
$ClOClOCl^-$/6a	-1530.981096
$OClOClOH^-$/7b	-1146.563165
$ClOCl(O)(OH)^-$/7d	-1146.546294
$ClO_3{}^-$/7e	-685.757866
OClClO/8a	-1070.506765
ClOOCl/8b	-1070.596666
TS 1a/1a $\rightarrow$ 1b - TSb	-1071.796889

TS 1a2a → 2c	barrierless
TS 2c → 2e	-1071.407181
TS 2c TS 2c → 2e	barrierless
TS 2a2a → 3c	-1070.960108
TS 1b → 2d - TSb	-995.398312
TS 1b → 6a	barrierless
TS 6a → 5e	-1530.947068
TS 7b → 7d	-1146.506491
TS 5e → 5d	-1070.539017
TS 5e → 5d (Cl- catalysed)	barrierless
TS 5e → 8b	-1070.543646
TS 8b → O2	-1070.54965
TS 7d → 7e	-1146.503311
TS 5d → O2	-1070.471924
TS 3c+2a → 7e	-1146.086955
TS 5d → 7e	barrierless
TS 3c+3c → 7e	-1221.184328

Summary of Structures

2

O2 triplet

O1 0.0000000000 0.0000000000 0.5979550000

O4 0.0000000000 0.0000000000 -0.5979550000

2

H2

H1 0.0000000000 0.0000000000 0.3734886640

H2 0.0000000000 0.0000000000 -0.3734886640

2

Cl2

Cl1 0.0000000000 0.0000000000 1.0120640000

Cl2 0.0000000000 0.0000000000 -1.0120640000

3

H2O

O1 -0.0626836954 -0.0214337522 0.0000000000

H2 0.2501216355 0.8933007512 0.0000000000

H3 0.7447140985 -0.5531315502 0.0000

2

OH-

O1 0.0000000000 0.0000000000 -0.0570156268

H2 0.0000000000 0.0000000000 0.9048793732

3

HOCl/1a

Cl1 -0.0522090000 -0.5599460000 0.0000000000

O3 0.0508360000 1.1393600000 0.0000000000

H3 1.0047170000 1.3461610000 0.000000000

3

ClOCl/1b

Cl1 0.0936980000 1.4393150000 0.0000000000

O2 0.7474470000 -0.1405570000 0.0000000000

Cl3 -0.4355840000 -1.3750230000 0.0000000000

2

OCl-/2a

O1 0.0000000000 0.0000000000 1.1814420000

Cl2 0.0000000000 0.0000000000 -0.5403970000

5

HOCl—OCl-/2c

Cl3 -0.0492360000 -0.3710610000 0.1333920000

O4 1.1604420000 0.6324890000 0.7829140000

Cl5 3.1815600000 -0.0781750000 -0.1763630000

O5 4.7407240000 -0.5483360000 -0.8837140000

H5 4.6221670000 -1.4648700000 -1.1839550000

3

ClClO/2d

Cl1 -0.3853910000 1.3309780000 0.0000000000

Cl2 -0.2022010000 -0.7902270000 0.0000000000

O3 1.2846220000 -1.1822160000 0.00000000

4

ClO2H/2e

Cl1 4.2851180000 2.5390930000 1.0769960000

O2 3.0949790000 2.5675140000 2.2782530000

H3 3.3582070000 3.2526510000 2.9272820000

O4 5.4069270000 1.5578450000 1.4895040000

3

ClO2-/3c

Cl1 -0.4171540000 -0.1417530000 0.0000000000

O2 0.8793100000 -1.0909680000 0.0000000000

O3 0.0326920000 1.4008750000 0.000000000

4

ClClOO/5d

Cl1 -0.1427150000 -0.0249410000 0.0367570000

Cl2 2.1584820000 0.0775980000 -0.1048310000

O3 2.4133880000 1.5079280000 0.0333520000

O4 2.4068930000 -0.4288860000 -1.4511960000

4

ClOClO/5e

Cl1 0.0190510000 0.0114170000 -0.0420000000

O2 1.7163200000 0.0265140000 0.1513920000

Cl3 2.4668070000 1.5838200000 -0.0998530000

O4 2.5121070000 1.8875810000 -1.5961390000

5

ClOClOCl-/6a

Cl1 -2.9056230000 0.5529080000 -0.3806690000

O2 -1.9061560000 -0.5503720000 0.4211430000

Cl3 0.0000000000 0.0000000000 0.3760730000

O4 1.9061560000 0.5503720000 0.4211430000

Cl5 2.9056230000 -0.5529080000 -0.3806690000

6

OClOClOH-/7b

O2 -0.7043390000 -1.2411160000 0.4892120000

Cl3 -0.2893350000 0.2401880000 0.0617070000

O4 1.0011570000 0.6737530000 0.9067870000

Cl5 3.0432650000 -0.2666200000 -0.1785780000

O5 4.4583360000 -0.8509300000 -1.0088130000

H6 4.8880670000 -1.4750010000 -0.3982560000

6

ClOClOOH-/7d

O2 -1.6121260000 -1.5380280000 0.3573560000

Cl3 -0.5198730000 -0.1896620000 0.1760020000

O4 1.2359650000 1.3622400000 0.0212610000

Cl5 2.6659030000 0.4433010000 0.0219290000

O5 -1.4603940000 1.0387870000 0.4157910000

H6 -2.0656000000 -1.6524900000 -0.4999850000

4

ClO3-/7e

Cl1 0.0386100000 0.0417930000 0.0624690000

O2 1.5526470000 0.0048730000 0.0026450000

O3 -0.3463320000 1.5162290000 0.0061070000

O4 -0.3570420000 -0.4398240000 1.4442270000

4

OClClO/8a

O1 1.7812940991 6.5379826547 0.6990103692

Cl2 2.4039564489 8.1691746562 0.9653685356

Cl3 -0.3075778610 6.4743959786 2.1976128512

O4 1.3488526040 5.9852019687 1.8236644750

4

ClOOCl/8b

Cl1 0.3214070000 0.0402030000 0.4009870000

O2 1.5977170000 0.0447050000 -0.8166610000

O3 2.2760700000 1.1865820000 -0.8165080000

Cl4 3.5511990000 1.1915020000 0.402183000

6

TS 1a1a-1b TSb

Cl1 -3.3392260000 -0.7417090000 1.4533200000

O2 -3.9373730000 0.9760720000 1.3604520000

O4 -2.6549840000 -2.7064410000 1.5462620000

Cl5 -1.5248030000 -2.7474480000 2.8012040000

H6 -4.4151670000 1.0859620000 0.5203490000

H7 -3.8513460000 -1.1231210000 0.301609000

5

TS 2c-2e

Cl3 -0.4861240000 -0.1878340000 0.4836950000

O4 1.7648340000 -0.1998250000 0.4903350000

Cl5 2.9229730000 -0.4300320000 -0.6557090000

O5 4.8218340000 -0.4478740000 -0.7942850000

H5 5.0743100000 -1.3384550000 -0.4968420000

4

TS 2a2a-3c

O1 3.9441140000 1.8384080000 6.4232490000

Cl2 4.6634660000 0.3457350000 6.1847010000

O4 3.9875960000 -0.7631890000 4.4850500000

Cl5 3.4352250000 -2.0146990000 2.8186320000

3

TS 1b-2d - TSb

Cl1 -0.1180160000 1.5551580000 0.0000000000

Cl2 -0.3809960000 -1.1980640000 0.0000000000

O3 1.0932100000 -0.7794170000 0.0000000000

5

TS 6a-5e

Cl1 -2.8041260000 0.6893250000 -0.4271060000

O2 -1.9920720000 -0.1532580000 0.7589880000

Cl3 -0.0315790000 -0.6179920000 0.2249490000

O4 1.2617780000 0.2765890000 0.2163620000

Cl5 3.4500570000 -0.4305670000 -0.4766160000

6

TS 7b-7d

O1 -0.5177670000 -0.7870910000 -0.9799480000

Cl2 0.9467000000 -0.2989170000 -0.7271790000

O3 0.9197680000 0.1700020000 1.3644820000

Cl4 2.3688800000 0.6890530000 1.9503510000

O5 3.0950800000 0.2179130000 -1.1760220000

H6 3.4885960000 -0.6307470000 -0.9374460000

4

TS 5e-5d - TSa

Cl1 -0.3540722084 0.2321588694 0.2337032750

Cl2 2.3212197843 0.6481076103 -0.9751968109

O3 2.2636679330 1.0395187702 0.4243343852

O4 2.6244551854 -0.7533791293 -1.2214841603

4

TS 5e-8b

Cl1 -0.0967093435 -0.4213188709 0.0170839898

O2 1.1750508294 0.5249029053 -0.2657683983

Cl3 2.6225204212 2.3141612443 -0.1741175743

O4 3.0740649570 1.1652801530 -1.1317929027

4

TS 8b-O2

Cl1 0.5829447309 0.2040754224 1.2212779409

O2 1.8045244025 0.1056076597 -1.4464985260

O3 2.4049289585 1.0840019415 -1.1767410840

Cl4 3.1103797728 1.0805009311 0.5955463180

6

TS 7d-7e

Cl1 -1.1600680000 4.2707460000 -1.2968610000

O2 -2.7806480000 3.2677620000 -0.9539560000

O3 -1.2342520000 4.0331870000 -2.9698250000

O4 -1.3162420000 5.7516580000 -1.0381410000

H5 -2.1688740000 3.7873580000 -3.1557590000

Cl6 -4.5777860000 2.0771680000 -0.82580400

4

TS 5d-O2

Cl1 0.3615983575 -0.4797715185 -0.4925411641

Cl2 2.2691128652 1.0259883130 -0.0943081543

O3 3.4652248669 1.7043439488 -1.0667167816

O4 2.1521217854 0.6030869764 -1.6358155926

5

TS 3c2a-7e

Cl1 0.0815429964 -0.0451163876 0.0899850908

O2 1.6134569670 -0.3194905196 -0.1215484056

O3 -0.0554379059 2.0489064846 0.5193352557

O4 -0.3997000372 -0.7662817616 1.3998073486

Cl5 -0.1843955069 4.0876238579 0.9383301058

6

TS 3c3c-7e

Cl1 3.0468120000 1.0221370000 -16.2690000000

O2 2.2354650000 -0.1724340000 -16.8760990000

O3 3.2125470000 0.8193820000 -14.7252030000

O4 1.7781220000 2.7386390000 -16.4709460000

Cl5 0.6054080000 4.4113950000 -16.7115240000

O6 -0.6160070000 4.4459470000 -15.6026780000