

Supplementary Material for "On the Complexity of Kinetics and Mechanism of the Thiosulfate–Periodate Reaction"

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Table S1: All the conceivable reactions between the species postulated in the thiosulfate–periodate reaction that were taken into consideration in the beginning of the fitting procedure.

No.	Step	Rate equation
(1)	$I_2 + H_2O \xrightarrow{k_1} HOI + H^+ + I^-$	$r_1 = k_1[I_2]$
(2)	$I_3^- \xrightarrow{k_2} I_2 + H_2O$	$r_2 = k_2[I_3^-]$
(3)	$I_2O_2 \xrightarrow{k_3} HOI + HIO_2$	$r_3 = k_3[I_2O_2]$
(4)	$I_2O_2 \xrightarrow{k_4} IO_3^- + I^- + 2H^+$	$r_4 = k_4[I_2O_2]$
(5)	$S_2O_3I^- \xrightarrow{k_5} S_2O_3OH^- + H^+ + I^-$	$r_5 = k_5[S_2O_3I^-]$
(6)	$S_2O_3I^- \xrightarrow{k_6} S_2O_3^{2-} + HOI + H^+$	$r_6 = k_6[S_2O_3I^-]$
(7)	$S_2O_3^{2-} + IO_4^- + H_2O \xrightarrow{k_7} I^- + 2SO_4^{2-} + 2H^+$	$r_7 = k_7[S_2O_3^{2-}][IO_4^-]$
(8)	$S_2O_3^{2-} + IO_4^- + H^+ + H_2O \xrightarrow{k_8} 2HSO_3^- + HIO_2$	$r_8 = k_8[S_2O_3^{2-}][IO_4^-]$
(9)	$S_2O_3^{2-} + IO_4^- + H^+ \xrightarrow{k_9} S_2O_3OH^- + IO_3^-$	$r_9 = k_9[S_2O_3^{2-}][IO_4^-]$
(10)	$S_2O_3^{2-} + S_2O_3OH^- \xrightarrow{k_{10}} S_4O_6^{2-} + H_2O$	$r_{10} = k_{10}[S_2O_3^{2-}][S_2O_3OH^-]$
(11)	$S_2O_3^{2-} + IO_3^- + H^+ + H_2O \xrightarrow{k_{11}} 2HSO_3^- + HOI$	$r_{11} = k_{11}[S_2O_3^{2-}][IO_3^-]$
(12)	$S_2O_3^{2-} + IO_3^- + 2H^+ \xrightarrow{k_{12}} S_2O_3OH^- + HIO_2$	$r_{12} = k_{12}[S_2O_3^{2-}][IO_3^-]$
(13)	$S_2O_3^{2-} + HIO_2 + H^+ \xrightarrow{k_{13}} S_2O_3OH^- + HOI$	$r_{13} = k_{13}[S_2O_3^{2-}][HIO_2]$
(14)	$S_2O_3^{2-} + HIO_2 + H_2O \xrightarrow{k_{14}} 2HSO_3^- + I^- + H^+$	$r_{14} = k_{14}[S_2O_3^{2-}][HIO_2]$
(15)	$S_2O_3^{2-} + HOI + H_2O \xrightarrow{k_{15}} S_2O_3I^- + H_2O$	$r_{15} = k_{15}[S_2O_3^{2-}][HOI]$
(16)	$S_2O_3^{2-} + HOI \xrightarrow{k_{16}} S_2O_3OH^- + I^-$	$r_{16} = k_{16}[S_2O_3^{2-}][HOI]$
(17)	$S_2O_3^{2-} + I_2 \xrightarrow{k_{17}} S_2O_3I^- + I^-$	$r_{17} = k_{17}[S_2O_3^{2-}][I_2]$
(18)	$S_2O_3^{2-} + I_3^- \xrightarrow{k_{18}} S_2O_3I^- + 2I^-$	$r_{18} = k_{18}[S_2O_3^{2-}][I_3^-]$
(19)	$S_2O_3^{2-} + I_2O_2 + H^+ \xrightarrow{k_{19}} S_2O_3I^- + HIO_2$	$r_{19} = k_{19}[S_2O_3^{2-}][I_2O_2]$
(20)	$S_2O_3^{2-} + I_2O_2 + H_2O \xrightarrow{k_{20}} 2HSO_3^- + I_2$	$r_{20} = k_{20}[S_2O_3^{2-}][I_2O_2]$
(21)	$S_2O_3^{2-} + I_2O_2 + H^+ + H_2O \xrightarrow{k_{21}} S_2O_3OH^- + HOI$	$r_{21} = k_{21}[S_2O_3^{2-}][I_2O_2]$
(22)	$S_2O_3^{2-} + I_2O_2 + H_2O \xrightarrow{k_{22}} S_2O_3OH^- + HIO_2 + I^-$	$r_{22} = k_{22}[S_2O_3^{2-}][I_2O_2]$
(23)	$S_2O_3^{2-} + S_2O_3I^- \xrightarrow{k_{23}} S_4O_6^{2-} + I^-$	$r_{23} = k_{23}[S_2O_3^{2-}][S_2O_3I^-]$
(24)	$IO_4^- + S_2O_3OH^- + H_2O \xrightarrow{k_{24}} HOI + 2SO_4^{2-} + 2H^+$	$r_{24} = k_{24}[IO_4^-][S_2O_3OH^-]$
(25)	$IO_4^- + S_2O_3OH^- + H_2O \xrightarrow{k_{25}} 2HSO_3^- + IO_3^- + H^+$	$r_{25} = k_{25}[IO_4^-][S_2O_3OH^-]$
(26)	$IO_4^- + HSO_3^- \xrightarrow{k_{26}} SO_4^{2-} + IO_3^- + H^+$	$r_{26} = k_{26}[IO_4^-][HSO_3^-]$
(27)	$IO_4^- + HIO_2 \xrightarrow{k_{27}} 2HSO_3^- + H^+$	$r_{27} = k_{27}[IO_4^-][HIO_2]$
(28)	$IO_4^- + HOI \xrightarrow{k_{28}} IO_3^- + HIO_2$	$r_{28} = k_{28}[IO_4^-][HOI]$
(29)	$IO_4^- + I_2O_2 + H_2O \xrightarrow{k_{29}} IO_3^- + 2HIO_2$	$r_{29} = k_{29}[IO_4^-][I_2O_2]$
(30)	$IO_4^- + I_2O_2 + H_2O \xrightarrow{k_{30}} 2IO_3^- + HOI + H^+$	$r_{30} = k_{30}[IO_4^-][I_2O_2]$
(31)	$IO_4^- + I^- + 2H^+ \xrightarrow{k_{31}} 2HIO_2$	$r_{31} = k_{31}[IO_4^-][I^-]$
(32)	$IO_4^- + I^- + H^+ \xrightarrow{k_{32}} IO_3^- + HOI$	$r_{32} = k_{32}[IO_4^-][I^-]$

No.	Step	Rate equation
(33)	$\text{IO}_4^- + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O} \xrightarrow{k_{33}} \text{I}_2 + 2\text{SO}_4^{2-} + 2\text{H}^+$	$r_{33}=k_{33}[\text{IO}_4^-][\text{S}_2\text{O}_3\text{I}^-]$
(34)	$\text{IO}_4^- + \text{S}_2\text{O}_3\text{I}^- + 2\text{H}_2\text{O} \xrightarrow{k_{34}} \text{HOI} + \text{I}^- + 2\text{SO}_4^{2-} + 3\text{H}^+$	$r_{34}=k_{34}[\text{IO}_4^-][\text{S}_2\text{O}_3\text{I}^-]$
(35)	$\text{IO}_4^- + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O} \xrightarrow{k_{35}} 2\text{HSO}_3^- + \text{I}_2\text{O}_2$	$r_{35}=k_{35}[\text{IO}_4^-][\text{S}_2\text{O}_3\text{I}^-]$
(36)	$\text{IO}_4^- + \text{S}_2\text{O}_3\text{I}^- + 2\text{H}_2\text{O} \xrightarrow{k_{36}} 2\text{HSO}_3^- + \text{HOI} + \text{HIO}_2$	$r_{36}=k_{36}[\text{IO}_4^-][\text{S}_2\text{O}_3\text{I}^-]$
(37)	$\text{IO}_4^- + \text{S}_2\text{O}_3\text{I}^- + 2\text{H}_2\text{O} \xrightarrow{k_{37}} 2\text{HSO}_3^- + \text{IO}_3^- + \text{I}^- + 2\text{H}^+$	$r_{37}=k_{37}[\text{IO}_4^-][\text{S}_2\text{O}_3\text{I}^-]$
(38)	$\text{IO}_4^- + \text{S}_2\text{O}_3\text{I}^- + \text{H}^+ + \text{H}_2\text{O} \xrightarrow{k_{38}} \text{S}_2\text{O}_3\text{OH}^- + 2\text{HIO}_2$	$r_{38}=k_{38}[\text{IO}_4^-][\text{S}_2\text{O}_3\text{I}^-]$
(39)	$\text{IO}_4^- + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O} \xrightarrow{k_{39}} \text{S}_2\text{O}_3\text{OH}^- + \text{IO}_3^- + \text{HOI}$	$r_{39}=k_{39}[\text{IO}_4^-][\text{S}_2\text{O}_3\text{I}^-]$
(40)	$2\text{S}_2\text{O}_3\text{OH}^- + \text{H}_2\text{O} \xrightarrow{k_{40}} \text{S}_2\text{O}_3^{2-} + 2\text{HSO}_3^- + 2\text{H}^+$	$r_{40}=k_{40}[\text{S}_2\text{O}_3\text{OH}^-]^2$
(41)	$\text{S}_2\text{O}_3\text{OH}^- + \text{HSO}_3^- \xrightarrow{k_{41}} \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + 2\text{H}^+$	$r_{41}=k_{41}[\text{S}_2\text{O}_3\text{OH}^-][\text{HSO}_3^-]$
(42)	$\text{S}_2\text{O}_3\text{OH}^- + \text{IO}_3^- + \text{H}_2\text{O} \xrightarrow{k_{42}} \text{I}^- + 2\text{SO}_4^{2-} + 3\text{H}^+$	$r_{42}=k_{42}[\text{S}_2\text{O}_3\text{OH}^-][\text{IO}_3^-]$
(43)	$\text{S}_2\text{O}_3\text{OH}^- + \text{IO}_3^- + \text{H}_2\text{O} \xrightarrow{k_{43}} 2\text{HSO}_3^- + \text{HIO}_2$	$r_{43}=k_{43}[\text{S}_2\text{O}_3\text{OH}^-][\text{IO}_3^-]$
(44)	$\text{S}_2\text{O}_3\text{OH}^- + \text{IO}_3^- \xrightarrow{k_{44}} \text{S}_2\text{O}_3^{2-} + \text{IO}_4^- + \text{H}^+$	$r_{44}=k_{44}[\text{S}_2\text{O}_3\text{OH}^-][\text{IO}_3^-]$
(45)	$\text{S}_2\text{O}_3\text{OH}^- + \text{HIO}_2 + \text{H}_2\text{O} \xrightarrow{k_{45}} 2\text{HSO}_3^- + \text{HOI} + \text{H}^+$	$r_{45}=k_{45}[\text{S}_2\text{O}_3\text{OH}^-][\text{HIO}_2]$
(46)	$\text{S}_2\text{O}_3\text{OH}^- + \text{HIO}_2 \xrightarrow{k_{46}} \text{S}_2\text{O}_3^{2-} + \text{IO}_3^- + 2\text{H}^+$	$r_{46}=k_{46}[\text{S}_2\text{O}_3\text{OH}^-][\text{HIO}_2]$
(47)	$\text{S}_2\text{O}_3\text{OH}^- + \text{HOI} + \text{H}_2\text{O} \xrightarrow{k_{47}} 2\text{HSO}_3^- + \text{I}^- + \text{H}^+$	$r_{47}=k_{47}[\text{S}_2\text{O}_3\text{OH}^-][\text{HOI}]$
(48)	$\text{S}_2\text{O}_3\text{OH}^- + \text{HOI} \xrightarrow{k_{48}} \text{S}_2\text{O}_3^{2-} + \text{HIO}_2 + \text{H}^+$	$r_{48}=k_{48}[\text{S}_2\text{O}_3\text{OH}^-][\text{HOI}]$
(49)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2 \xrightarrow{k_{49}} \text{HOI} + \text{S}_2\text{O}_3\text{I}^-$	$r_{49}=k_{49}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2]$
(50)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2 + 2\text{H}_2\text{O} \xrightarrow{k_{50}} 2\text{HSO}_3^- + 2\text{I}^- + 3\text{H}^+$	$r_{50}=k_{50}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2]$
(51)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2 + \text{H}_2\text{O} \xrightarrow{k_{51}} \text{S}_2\text{O}_3^{2-} + 2\text{HOI} + \text{H}^+$	$r_{51}=k_{51}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2]$
(52)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2 + \text{H}_2\text{O} \xrightarrow{k_{52}} \text{S}_2\text{O}_3^{2-} + \text{HIO}_2 + \text{I}^- + 2\text{H}^+$	$r_{52}=k_{52}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2]$
(53)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_3^- + \text{H}^+ \xrightarrow{k_{53}} \text{I}_2 + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O}$	$r_{53}=k_{53}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_3^-]$
(54)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_3^- \xrightarrow{k_{54}} \text{HOI} + \text{I}^- + \text{S}_2\text{O}_3\text{I}^-$	$r_{54}=k_{54}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_3^-]$
(55)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_3^- + 2\text{H}_2\text{O} \xrightarrow{k_{55}} 2\text{HSO}_3^- + 3\text{I}^- + 3\text{H}^+$	$r_{55}=k_{55}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_3^-]$
(56)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_3^- \xrightarrow{k_{56}} \text{S}_2\text{O}_3^{2-} + \text{I}_2 + \text{HOI}$	$r_{56}=k_{56}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_3^-]$
(57)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_3^- + \text{H}_2\text{O} \xrightarrow{k_{57}} \text{S}_2\text{O}_3^{2-} + 2\text{HOI} + \text{I}^- + \text{H}^+$	$r_{57}=k_{57}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_3^-]$
(58)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_3^- + \text{H}_2\text{O} \xrightarrow{k_{58}} \text{S}_2\text{O}_3^{2-} + \text{HIO}_2 + 2\text{I}^- + 2\text{H}^+$	$r_{58}=k_{58}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_3^-]$
(59)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{k_{59}} 2\text{I}^- + 2\text{SO}_4^{2-} + 5\text{H}^+$	$r_{59}=k_{59}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2\text{O}_2]$
(60)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2\text{O}_2 \xrightarrow{k_{60}} \text{IO}_3^- + \text{S}_2\text{O}_3\text{I}^- + \text{H}^+$	$r_{60}=k_{60}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2\text{O}_2]$
(61)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{61}} \text{HSO}_3^- + \text{I}_2 + \text{SO}_4^{2-} + 2\text{H}^+$	$r_{61}=k_{61}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2\text{O}_2]$
(62)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{k_{62}} 2\text{HSO}_3^- + 2\text{HOI} + \text{H}^+$	$r_{62}=k_{62}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2\text{O}_2]$
(63)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{k_{63}} 2\text{HSO}_3^- + \text{HIO}_2 + \text{I}^- + 2\text{H}^+$	$r_{63}=k_{63}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2\text{O}_2]$
(64)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{64}} \text{S}_2\text{O}_3^{2-} + 2\text{HIO}_2 + \text{H}^+$	$r_{64}=k_{64}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2\text{O}_2]$
(65)	$\text{S}_2\text{O}_3\text{OH}^- + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{65}} \text{S}_2\text{O}_3^{2-} + \text{IO}_3^- + \text{HOI} + 2\text{H}^+$	$r_{65}=k_{65}[\text{S}_2\text{O}_3\text{OH}^-][\text{I}_2\text{O}_2]$

No.	Step	Rate equation
(66)	$S_2O_3OH^- + I_2O_2 + H_2O \xrightarrow{k_{66}} S_2O_3^{2-} + IO_4^- + I^- + 3H^+$	$r_{66}=k_{66}[S_2O_3OH^-][I_2O_2]$
(67)	$S_2O_3OH^- + I^- + H^+ \xrightarrow{k_{67}} S_2O_3I^- + H_2O$	$r_{67}=k_{67}[S_2O_3OH^-][I^-]$
(68)	$S_2O_3OH^- + I^- \xrightarrow{k_{68}} S_2O_3^{2-} + HOI$	$r_{68}=k_{68}[S_2O_3OH^-][I^-]$
(69)	$S_2O_3OH^- + S_2O_3I^- \xrightarrow{k_{69}} S_4O_6^{2-} + HOI$	$r_{69}=k_{69}[S_2O_3OH^-][S_2O_3I^-]$
(70)	$S_2O_3OH^- + S_2O_3I^- + 2H_2O \xrightarrow{k_{70}} S_2O_3^{2-} + 2HSO_3^- + I^- + 3H^+$	$r_{70}=k_{70}[S_2O_3OH^-][S_2O_3I^-]$
(71)	$S_2O_3OH^- + S_2O_3I^- + H_2O \xrightarrow{k_{71}} 2S_2O_3^{2-} + HIO_2 + 2H^+$	$r_{71}=k_{71}[S_2O_3OH^-][S_2O_3I^-]$
(72)	$HSO_3^- + IO_3^- \xrightarrow{k_{72}} HIO_2 + SO_4^{2-}$	$r_{72}=k_{72}[HSO_3^-][IO_3^-]$
(73)	$HSO_3^- + HIO_2 \xrightarrow{k_{73}} HOI + SO_4^{2-} + H^+$	$r_{73}=k_{73}[HSO_3^-][HIO_2]$
(74)	$HSO_3^- + HOI \xrightarrow{k_{74}} I^- + SO_4^{2-} + 2H^+$	$r_{74}=k_{74}[HSO_3^-][HOI]$
(75)	$HSO_3^- + I_2 + H_2O \xrightarrow{k_{75}} 2I^- + SO_4^{2-} + 3H^+$	$r_{75}=k_{75}[HSO_3^-][I_2]$
(76)	$HSO_3^- + I_2O_2 + H_2O \xrightarrow{k_{76}} 2HOI + SO_4^{2-} + H^+$	$r_{76}=k_{76}[HSO_3^-][I_2]$
(77)	$HSO_3^- + I_2O_2 + H_2O \xrightarrow{k_{77}} HIO_2 + I^- + SO_4^{2-} + 2H^+$	$r_{77}=k_{77}[HSO_3^-][I_2O_2]$
(78)	$HSO_3^- + S_2O_3I^- + H_2O \xrightarrow{k_{78}} S_2O_3^{2-} + I^- + SO_4^{2-} + 3H^+$	$r_{78}=k_{78}[HSO_3^-][S_2O_3I^-]$
(79)	$IO_3^- + HIO_2 \xrightarrow{k_{79}} IO_4^- + HOI$	$r_{79}=k_{79}[IO_3^-][HIO_2]$
(80)	$IO_3^- + HOI + H^+ \xrightarrow{k_{80}} 2HIO_2$	$r_{80}=k_{80}[IO_3^-][HOI]$
(81)	$IO_3^- + HOI \xrightarrow{k_{81}} IO_4^- + I^- + H^+$	$r_{81}=k_{81}[IO_3^-][HOI]$
(82)	$IO_3^- + I_2O_2 + H^+ + H_2O \xrightarrow{k_{82}} 3HIO_2$	$r_{82}=k_{82}[IO_3^-][I_2O_2]$
(83)	$IO_3^- + I_2O_2 + H_2O \xrightarrow{k_{83}} IO_4^- + 2HOI$	$r_{83}=k_{83}[IO_3^-][I_2O_2]$
(84)	$IO_3^- + I^- + 2H^+ \xrightarrow{k_{84}} I_2O_2 + H_2O$	$r_{84}=k_{84}[IO_3^-][I^-]$
(85)	$IO_3^- + I^- + 2H^+ \xrightarrow{k_{85}} HIO_2 + HOI$	$r_{85}=k_{85}[IO_3^-][I^-]$
(86)	$IO_3^- + S_2O_3I^- + 2H_2O \xrightarrow{k_{86}} 2I^- + 2SO_4^{2-} + 4H^+$	$r_{86}=k_{86}[IO_3^-][S_2O_3I^-]$
(87)	$IO_3^- + S_2O_3I^- + 2H_2O \xrightarrow{k_{87}} 2HSO_3^- + 2HOI$	$r_{87}=k_{87}[IO_3^-][S_2O_3I^-]$
(88)	$IO_3^- + S_2O_3I^- + H^+ \xrightarrow{k_{88}} S_2O_3OH^- + I_2O_2$	$r_{88}=k_{88}[IO_3^-][S_2O_3I^-]$
(89)	$IO_3^- + S_2O_3I^- + H^+ + H_2O \xrightarrow{k_{89}} S_2O_3OH^- + HIO_2 + HOI$	$r_{89}=k_{89}[IO_3^-][S_2O_3I^-]$
(90)	$IO_3^- + S_2O_3I^- + H_2O \xrightarrow{k_{90}} S_2O_3^{2-} + 2HIO_2$	$r_{90}=k_{90}[IO_3^-][S_2O_3I^-]$
(91)	$IO_3^- + S_2O_3I^- + H_2O \xrightarrow{k_{91}} S_2O_3^{2-} + IO_4^- + I^- + 2H^+$	$r_{91}=k_{91}[IO_3^-][S_2O_3I^-]$
(92)	$2HIO_2 \xrightarrow{k_{92}} IO_3^- + HOI + H^+$	$r_{92}=k_{92}[HIO_2]^2$
(93)	$HIO_2 + HOI \xrightarrow{k_{93}} I_2O_2$	$r_{93}=k_{93}[HIO_2][HOI]$
(94)	$HIO_2 + HOI \xrightarrow{k_{94}} IO_3^- + I^- + 2H^+$	$r_{94}=k_{94}[HIO_2][HOI]$
(95)	$HIO_2 + I_2 \xrightarrow{k_{95}} I_2O_2 + I^- + H^+$	$r_{95}=k_{95}[HIO_2][I_2]$
(96)	$HIO_2 + I_2 + H_2O \xrightarrow{k_{96}} 3HOI$	$r_{96}=k_{96}[HIO_2][I_2]$
(97)	$HIO_2 + I_2 + H_2O \xrightarrow{k_{97}} IO_3^- + 2I^- + 3H^+$	$r_{97}=k_{97}[HIO_2][I_2]$
(98)	$HIO_2 + I_3^- \xrightarrow{k_{98}} I_2O_2 + 2I^- + H^+$	$r_{98}=k_{98}[HIO_2][I_2]$

No.	Step	Rate equation
(99)	$\text{HIO}_2 + \text{I}_3^- + \text{H}^+ \xrightarrow{k_{99}} 2\text{HOI} + \text{I}_2$	$r_{99}=k_{99}[\text{HIO}_2][\text{I}_3^-]$
(100)	$\text{HIO}_2 + \text{I}_3^- + \text{H}_2\text{O} \xrightarrow{k_{100}} 3\text{HOI} + \text{I}^-$	$r_{100}=k_{100}[\text{HIO}_2][\text{I}_3^-]$
(101)	$\text{HIO}_2 + \text{I}_3^- + \text{H}_2\text{O} \xrightarrow{k_{101}} \text{IO}_3^- + 3\text{I}^- + 3\text{H}^+$	$r_{101}=k_{101}[\text{HIO}_2][\text{I}_3^-]$
(102)	$\text{HIO}_2 + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{102}} \text{IO}_3^- + 2\text{HOI} + \text{H}^+$	$r_{102}=k_{102}[\text{HIO}_2][\text{I}_2\text{O}_2]$
(103)	$\text{HIO}_2 + \text{I}_2\text{O}_2 \xrightarrow{k_{103}} \text{IO}_4^- + \text{I}_2 + \text{H}^+$	$r_{103}=k_{103}[\text{HIO}_2][\text{I}_2\text{O}_2]$
(104)	$\text{HIO}_2 + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{104}} \text{IO}_4^- + \text{HOI} + \text{I}^- + 2\text{H}^+$	$r_{104}=k_{104}[\text{HIO}_2][\text{I}_2\text{O}_2]$
(105)	$\text{HIO}_2 + \text{I}^- + \text{H}^+ \xrightarrow{k_{105}} 2\text{HOI}$	$r_{105}=k_{105}[\text{HIO}_2][\text{I}^-]$
(106)	$\text{HIO}_2 + \text{S}_2\text{O}_3\text{I}^- + 2\text{H}_2\text{O} \xrightarrow{k_{106}} \text{HSO}_3^- + 2\text{I}^- + \text{SO}_4^{2-} + 3\text{H}^+$	$r_{106}=k_{106}[\text{HIO}_2][\text{S}_2\text{O}_3\text{I}^-]$
(107)	$\text{HIO}_2 + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O} \xrightarrow{k_{107}} 2\text{HSO}_3^- + \text{I}_2 + \text{H}^+$	$r_{107}=k_{107}[\text{HIO}_2][\text{S}_2\text{O}_3\text{I}^-]$
(108)	$\text{HIO}_2 + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O} \xrightarrow{k_{108}} \text{S}_2\text{O}_3\text{OH}^- + 2\text{HOI}$	$r_{108}=k_{108}[\text{HIO}_2][\text{S}_2\text{O}_3\text{I}^-]$
(109)	$\text{HIO}_2 + \text{S}_2\text{O}_3\text{I}^- \xrightarrow{k_{109}} \text{S}_2\text{O}_3^{2-} + \text{I}_2\text{O}_2 + \text{H}^+$	$r_{109}=k_{109}[\text{HIO}_2][\text{S}_2\text{O}_3\text{I}^-]$
(110)	$\text{HIO}_2 + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O} \xrightarrow{k_{110}} \text{S}_2\text{O}_3^{2-} + \text{IO}_3^- + \text{I}^- + \text{H}^+$	$r_{110}=k_{110}[\text{HIO}_2][\text{S}_2\text{O}_3\text{I}^-]$
(111)	$2\text{HOI} \xrightarrow{k_{111}} \text{HIO}_2 + \text{I}^- + \text{H}^+$	$r_{111}=k_{111}[\text{HOI}]^2$
(112)	$\text{HOI} + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{112}} 2\text{HIO}_2 + \text{I}^- + \text{H}^+$	$r_{112}=k_{112}[\text{HOI}][\text{I}_2\text{O}_2]$
(113)	$\text{HOI} + \text{I}_2\text{O}_2 \xrightarrow{k_{113}} \text{IO}_3^- + \text{I}_2 + \text{H}^+$	$r_{113}=k_{113}[\text{HOI}][\text{I}_2\text{O}_2]$
(114)	$\text{HOI} + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{114}} 2\text{HIO}_2 + \text{I}^- + \text{H}^+$	$r_{114}=k_{114}[\text{HOI}][\text{I}_2\text{O}_2]$
(115)	$\text{HOI} + \text{I}^- + \text{H}^+ \xrightarrow{k_{115}} \text{I}_2 + \text{H}_2\text{O}$	$r_{115}=k_{115}[\text{HOI}][\text{I}^-]$
(116)	$\text{HOI} + \text{S}_2\text{O}_3\text{I}^- + 2\text{H}_2\text{O} \xrightarrow{k_{116}} 2\text{HSO}_3^- + 2\text{I}^- + 3\text{H}^+$	$r_{116}=k_{116}[\text{HOI}][\text{S}_2\text{O}_3\text{I}^-]$
(117)	$\text{HOI} + \text{S}_2\text{O}_3\text{I}^- \xrightarrow{k_{117}} \text{S}_2\text{O}_3\text{OH}^- + \text{I}_2$	$r_{117}=k_{117}[\text{HOI}][\text{S}_2\text{O}_3\text{I}^-]$
(118)	$\text{HOI} + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O} \xrightarrow{k_{118}} \text{S}_2\text{O}_3^{2-} + \text{HIO}_2 + \text{I}^- + 2\text{H}^+$	$r_{118}=k_{118}[\text{HOI}][\text{S}_2\text{O}_3\text{I}^-]$
(119)	$\text{I}_2 + \text{I}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{k_{119}} 4\text{HOI}$	$r_{119}=k_{119}[\text{I}_2][\text{I}_2\text{O}_2]$
(120)	$\text{I}_2 + \text{I}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{k_{120}} 2\text{HIO}_2 + 2\text{I}^- + 2\text{H}^+$	$r_{120}=k_{120}[\text{I}_2][\text{I}_2\text{O}_2]$
(121)	$\text{I}_2 + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{121}} \text{IO}_3^- + \text{I}_3^- + 2\text{H}^+$	$r_{121}=k_{121}[\text{I}_2][\text{I}_2\text{O}_2]$
(122)	$\text{I}_2 + \text{I}_2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{k_{122}} \text{IO}_4^- + 3\text{I}^- + 4\text{H}^+$	$r_{122}=k_{122}[\text{I}_2][\text{I}_2\text{O}_2]$
(123)	$\text{I}_2 + \text{I}^- \xrightarrow{k_{123}} \text{I}_3^-$	$r_{123}=k_{123}[\text{I}_2][\text{I}^-]$
(124)	$\text{I}_2 + \text{S}_2\text{O}_3\text{I}^- + 3\text{H}_2\text{O} \xrightarrow{k_{124}} 2\text{HSO}_3^- + 3\text{I}^- + 4\text{H}^+$	$r_{124}=k_{124}[\text{I}_2][\text{S}_2\text{O}_3\text{I}^-]$
(125)	$\text{I}_2 + \text{S}_2\text{O}_3\text{I}^- + \text{H}_2\text{O} \xrightarrow{k_{125}} \text{S}_2\text{O}_3\text{OH}^- + \text{I}_3^- + \text{H}^+$	$r_{125}=k_{125}[\text{I}_2][\text{S}_2\text{O}_3\text{I}^-]$
(126)	$\text{I}_2 + \text{S}_2\text{O}_3\text{I}^- + 2\text{H}_2\text{O} \xrightarrow{k_{126}} \text{S}_2\text{O}_3^{2-} + 2\text{HOI} + \text{I}^- + 2\text{H}^+$	$r_{126}=k_{126}[\text{I}_2][\text{S}_2\text{O}_3\text{I}^-]$
(127)	$\text{I}_2 + \text{S}_2\text{O}_3\text{I}^- + 2\text{H}_2\text{O} \xrightarrow{k_{127}} \text{S}_2\text{O}_3^{2-} + \text{HIO}_2 + 2\text{I}^- + 3\text{H}^+$	$r_{127}=k_{127}[\text{I}_2][\text{S}_2\text{O}_3\text{I}^-]$
(128)	$\text{I}_3^- + \text{I}_2\text{O}_2 + \text{H}^+ + \text{H}_2\text{O} \xrightarrow{k_{128}} 3\text{HOI} + \text{I}_2$	$r_{128}=k_{128}[\text{I}_3^-][\text{I}_2\text{O}_2]$
(129)	$\text{I}_3^- + \text{I}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{k_{129}} 4\text{HOI} + \text{I}^-$	$r_{129}=k_{129}[\text{I}_3^-][\text{I}_2\text{O}_2]$
(130)	$\text{I}_3^- + \text{I}_2\text{O}_2 + \text{H}^+ \xrightarrow{k_{130}} \text{HIO}_2 + 2\text{I}_2$	$r_{130}=k_{130}[\text{I}_3^-][\text{I}_2\text{O}_2]$
(131)	$\text{I}_3^- + \text{I}_2\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{k_{131}} \text{IO}_4^- + 4\text{I}^- + 4\text{H}^+$	$r_{131}=k_{131}[\text{I}_3^-][\text{I}_2\text{O}_2]$

No.	Step	Rate equation
(132)	$I_3^- + I_2O_2 + 3H_2O \xrightarrow{k_{132}} 2HSO_3^- + 4I^- + 4H^+$	$r_{132} = k_{132}[I_3^-][I_2O_2]$
(133)	$I_3^- + I_2O_2 \xrightarrow{k_{133}} S_2O_3^{2-} + 2I_2$	$r_{133} = k_{133}[I_3^-][I_2O_2]$
(134)	$2I_2O_2 + 2H_2O \xrightarrow{k_{134}} 3HIO_2 + I^- + H^+$	$r_{134} = k_{134}[I_2O_2]^2$
(135)	$2I_2O_2 + 2H_2O \xrightarrow{k_{135}} IO_3^- + 3HOI + H^+$	$r_{135} = k_{135}[I_2O_2]^2$
(136)	$I_2O_2 + I^- + H^+ + H_2O \xrightarrow{k_{136}} 3HOI$	$r_{136} = k_{136}[I_2O_2][I^-]$
(137)	$I_2O_2 + I^- + H^+ \xrightarrow{k_{137}} HIO_2 + I_2$	$r_{137} = k_{137}[I_2O_2][I^-]$
(138)	$I_2O_2 + S_2O_3I^- + 3H_2O \xrightarrow{k_{138}} 3I^- + 2SO_4^{2-} + 6H^+$	$r_{138} = k_{138}[I_2O_2][S_2O_3I^-]$
(139)	$I_2O_2 + S_2O_3I^- + 2H_2O \xrightarrow{k_{139}} HSO_3^- + I_3^- + SO_4^{2-} + 3H^+$	$r_{139} = k_{139}[I_2O_2][S_2O_3I^-]$
(140)	$I_2O_2 + S_2O_3I^- + 2H_2O \xrightarrow{k_{140}} S_2O_3OH^- + 3HOI$	$r_{140} = k_{140}[I_2O_2][S_2O_3I^-]$
(141)	$I_2O_2 + S_2O_3I^- + H_2O \xrightarrow{k_{141}} S_2O_3OH^- + HIO_2 + I_2$	$r_{141} = k_{141}[I_2O_2][S_2O_3I^-]$
(142)	$I_2O_2 + S_2O_3I^- + 2H_2O \xrightarrow{k_{142}} S_2O_3OH^- + IO_3^- + 2I^- + 3H^+$	$r_{142} = k_{142}[I_2O_2][S_2O_3I^-]$
(143)	$I^- + S_2O_3I^- \xrightarrow{k_{143}} S_2O_3^{2-} + I_2$	$r_{143} = k_{143}[I^-][S_2O_3I^-]$
(144)	$2S_2O_3I^- \xrightarrow{k_{144}} S_4O_6^{2-} + I_2$	$r_{144} = k_{144}[S_2O_3I^-]^2$
(145)	$2S_2O_3I^- + H_2O \xrightarrow{k_{145}} S_4O_6^{2-} + HOI + I^- + H^+$	$r_{145} = k_{145}[S_2O_3I^-]^2$
(146)	$2S_2O_3I^- + 3H_2O \xrightarrow{k_{146}} S_2O_3^{2-} + 2HSO_3^- + 2I^- + 4H^+$	$r_{146} = k_{146}[S_2O_3I^-]^2$
(147)	$2S_2O_3I^- + H_2O \xrightarrow{k_{147}} S_2O_3^{2-} + S_2O_3OH^- + I_2 + H^+$	$r_{147} = k_{147}[S_2O_3I^-]^2$
(148)	$2S_2O_3I^- + 2H_2O \xrightarrow{k_{148}} 2S_2O_3^{2-} + HIO_2 + I^- + 3H^+$	$r_{148} = k_{148}[S_2O_3I^-]^2$
(149)	$S_4O_6^{2-} + I_2 \xrightarrow{k_{149}} I^- + S_4O_6I^-$	$r_{149} = k_{149}[S_4O_6^{2-}][I_2]$
(150)	$I^- + S_4O_6I^- \xrightarrow{k_{150}} S_4O_6^{2-} + S_4O_6I^-$	$r_{150} = k_{150}[I^-][S_4O_6I^-]$
(151)	$S_4O_6I^- + H_2O \xrightarrow{k_{151}} S_2O_3I^- + S_2O_3OH^- + H^+$	$r_{151} = k_{151}[S_4O_6I^-]$
(152)	$I^- + S_4O_6I^- \xrightarrow{k_{152}} 2S_2O_3I^-$	$r_{152} = k_{152}[I^-][S_4O_6I^-]$
(153)	$IO_4^- + S_4O_6I^- + 2H_2O \xrightarrow{k_{153}} 2HSO_3^- + IO_3^- + S_2O_3I^- + 2H^+$	$r_{153} = k_{153}[IO_4^-][S_4O_6I^-]$
(154)	$IO_4^- + S_4O_6I^- + 4H_2O \xrightarrow{k_{154}} 4HSO_3^- + 2HOI + 2H^+$	$r_{154} = k_{154}[IO_4^-][S_4O_6I^-]$

Figure S1: Reproducibility of the measured curves in parallel runs in four different cases. Red and green dots indicate the independently measured kinetic curves at the same initial conditions. The solid blue lines belong to the fitted kinetic curves

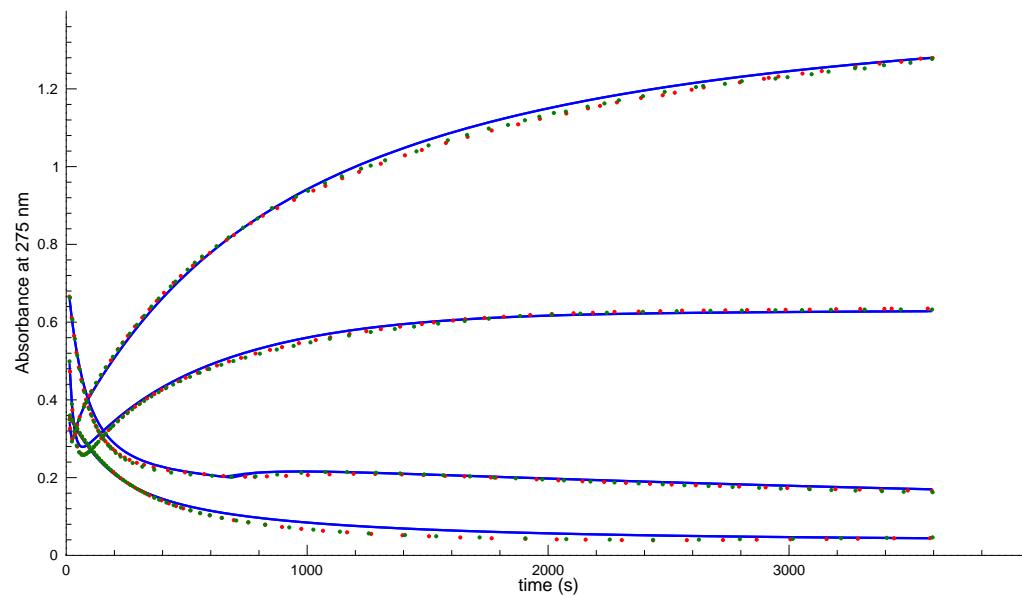


Figure S2: Measured (dots) and calculated (solid lines) absorbances at different initial thiosulfate concentration at pH=5.55 and $[IO_4^-]_0=2.0$ mM $[S_2O_3^{2-}]_0$ /mM=1.0 (black), 1.5 (blue), 3.0 (green), 4.0 (red), 6.0 (cyan), 6.67 (yellow), 10.0 (orange), 12.0 (magenta), 16.0 (purple), 20.0 (grey).

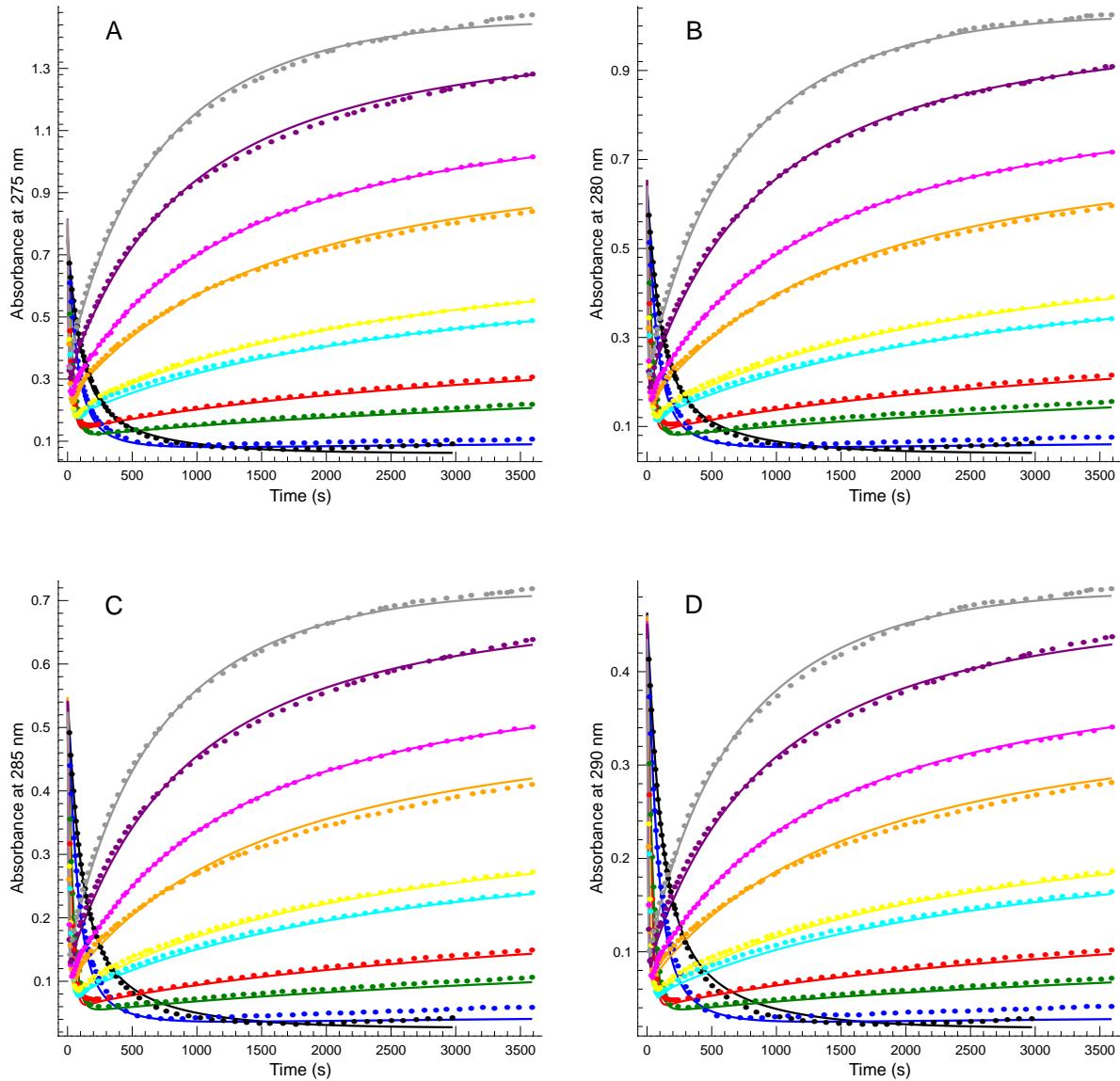


Figure S3: Measured (dots) and calculated (solid lines) absorbances at different initial thiosulfate concentration at pH=5.10 and $[IO_4^-]_0=2.0$ mM $[S_2O_3^{2-}]_0$ /mM=0.5 (black), 1.0 (blue), 1.5 (green), 2.0 (red), 3.0 (dark grey), 4.0 (cyan), 6.0 (brown), 6.67 (yellow), 8.0 (orange), 10.0 (magenta), 12.0 (purple), 16.0 (light gray).

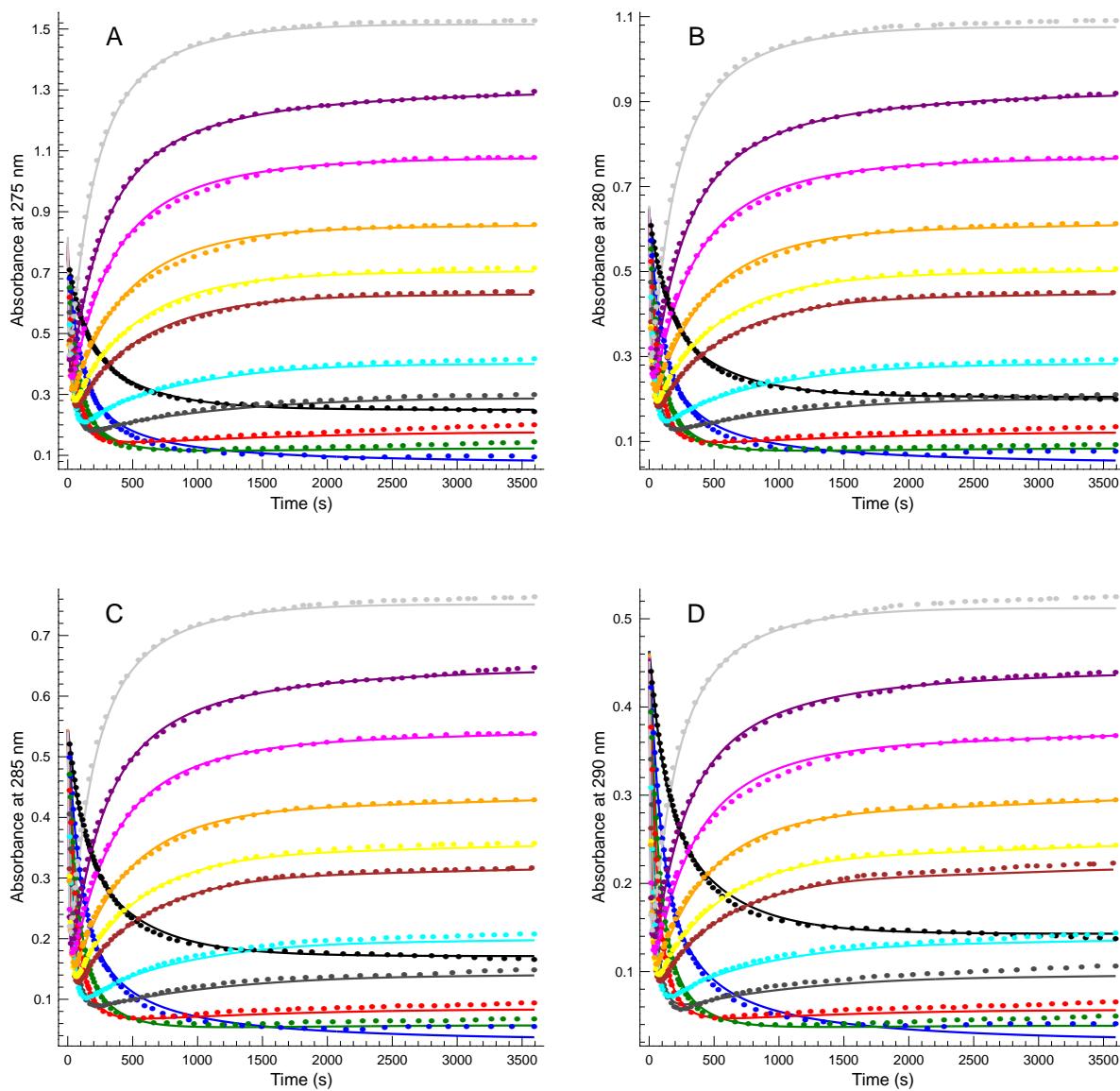


Figure S4: Measured (dots) and calculated (solid lines) absorbances at different initial periodate concentration at pH=5.10 and $[S_2O_3^{2-}]_0=0.5$ mM $[IO_4^-]_0/mM=4.8$ (black), 4.0 (blue), 3.0 (green), 2.0 (red), 1.0 (yellow), 0.5 (cyan), 0.25 (magenta), 0.083 (orange).

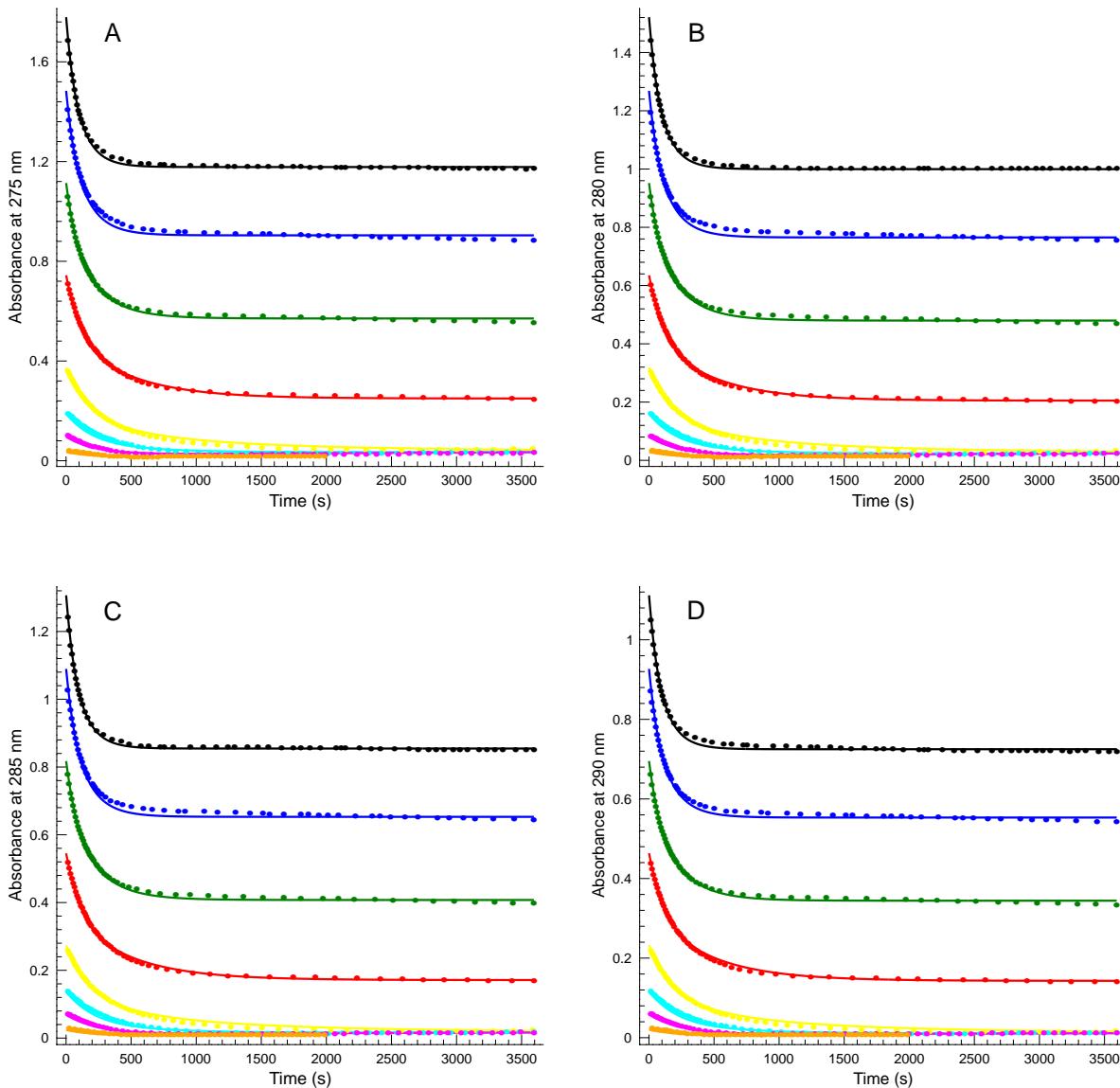


Figure S5: Measured (dots) and calculated (solid lines) absorbances at different initial periodate concentration at pH=4.65 and $[S_2O_3^{2-}]_0=0.5$ mM $[IO_4^-]_0/mM=4.8$ (black), 4.0 (blue), 3.0 (green), 2.0 (red), 1.0 (yellow), 0.75 (magenta), 0.5 (cyan), 0.25 (orange).

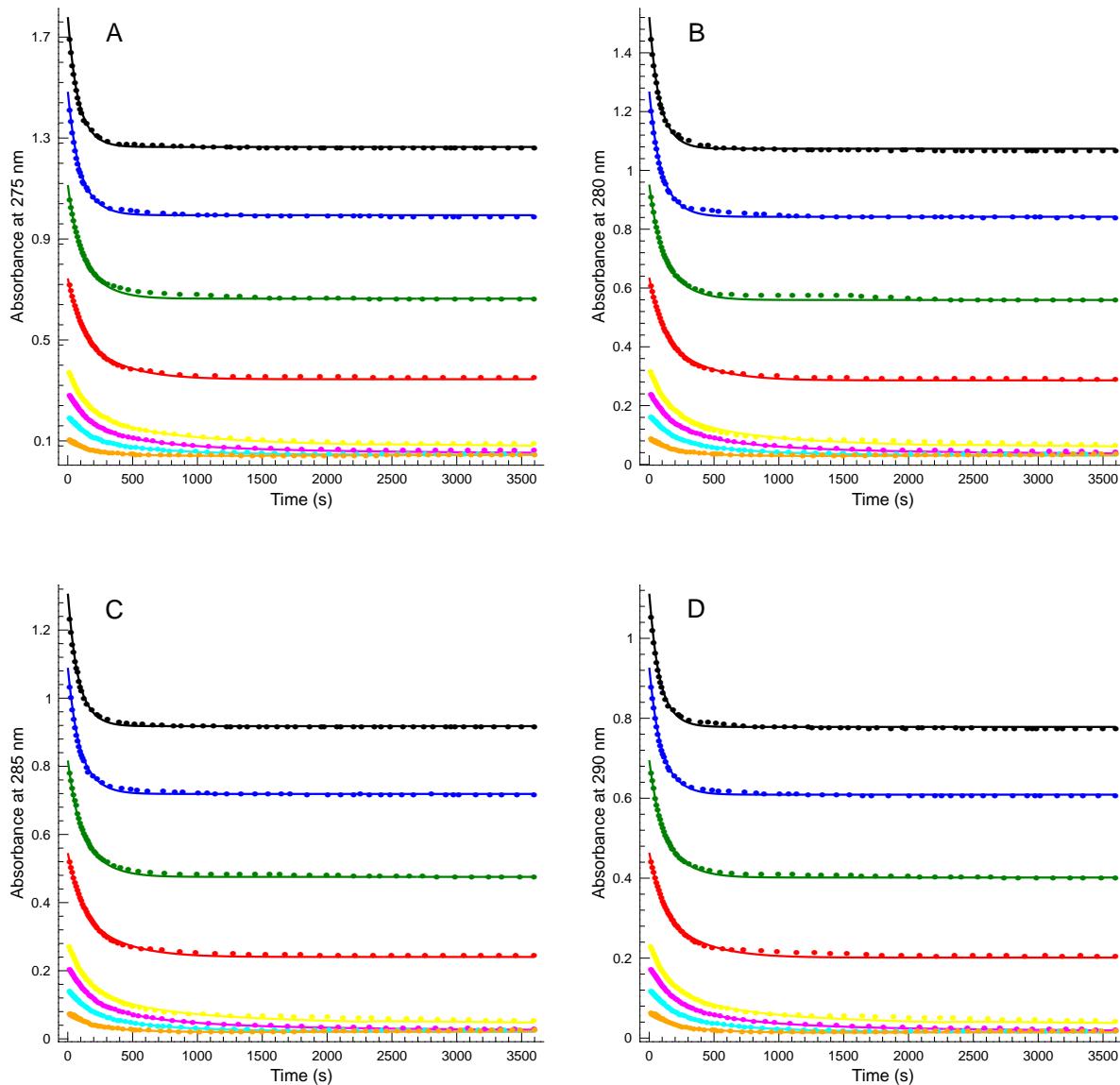
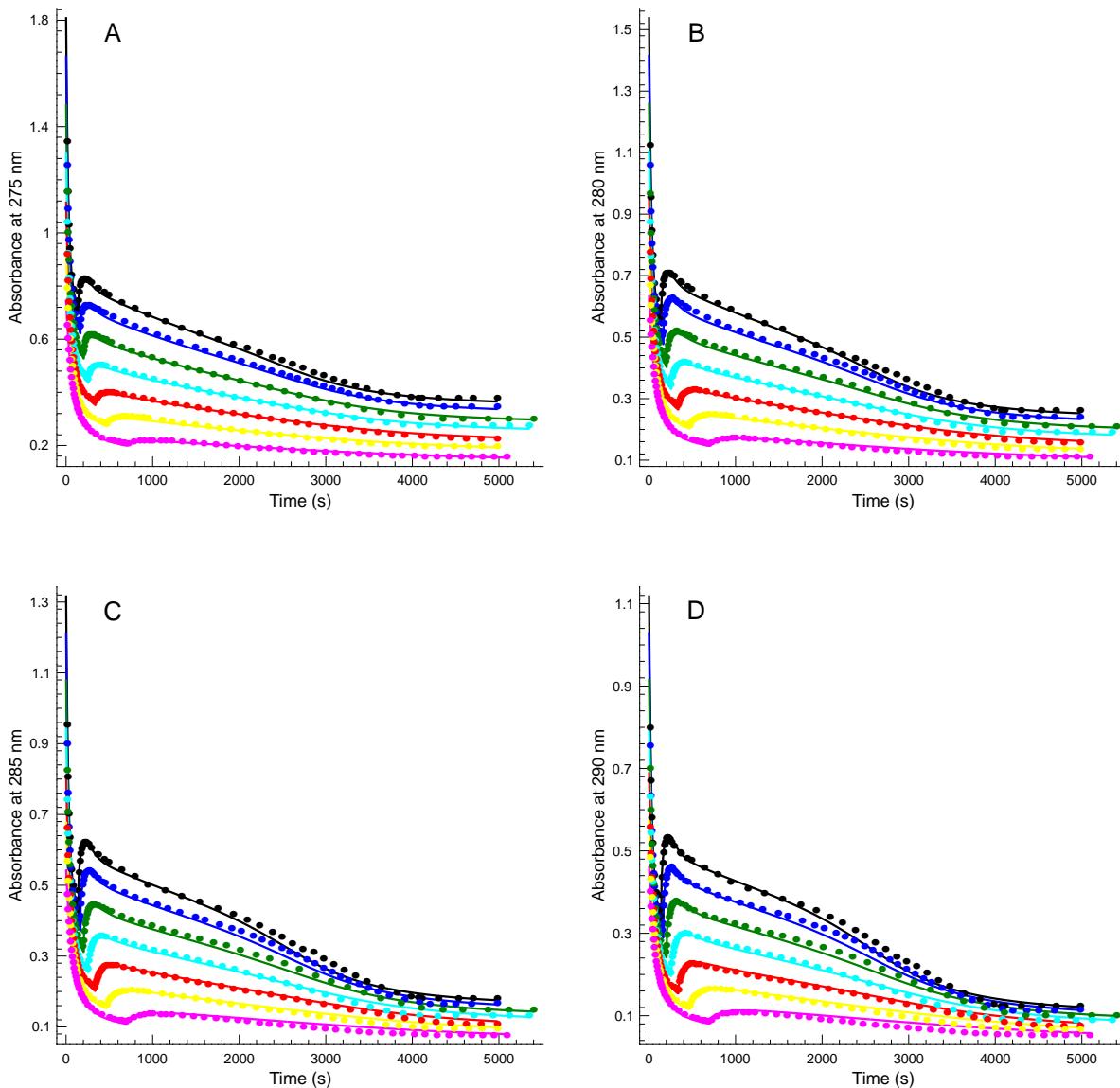


Figure S6: Measured (dots) and calculated (solid lines) absorbances at constant $[IO_4^-]_0/[S_2O_3^{2-}]_0=4:3$ ratio and at pH=4.65. $[IO_4^-]_0/\text{mM}=4.9$ (black), 4.5 (blue), 4.0 (green), 3.5 (cyan), 3.0 (red), 2.5 (yellow), 2.0 (magenta).



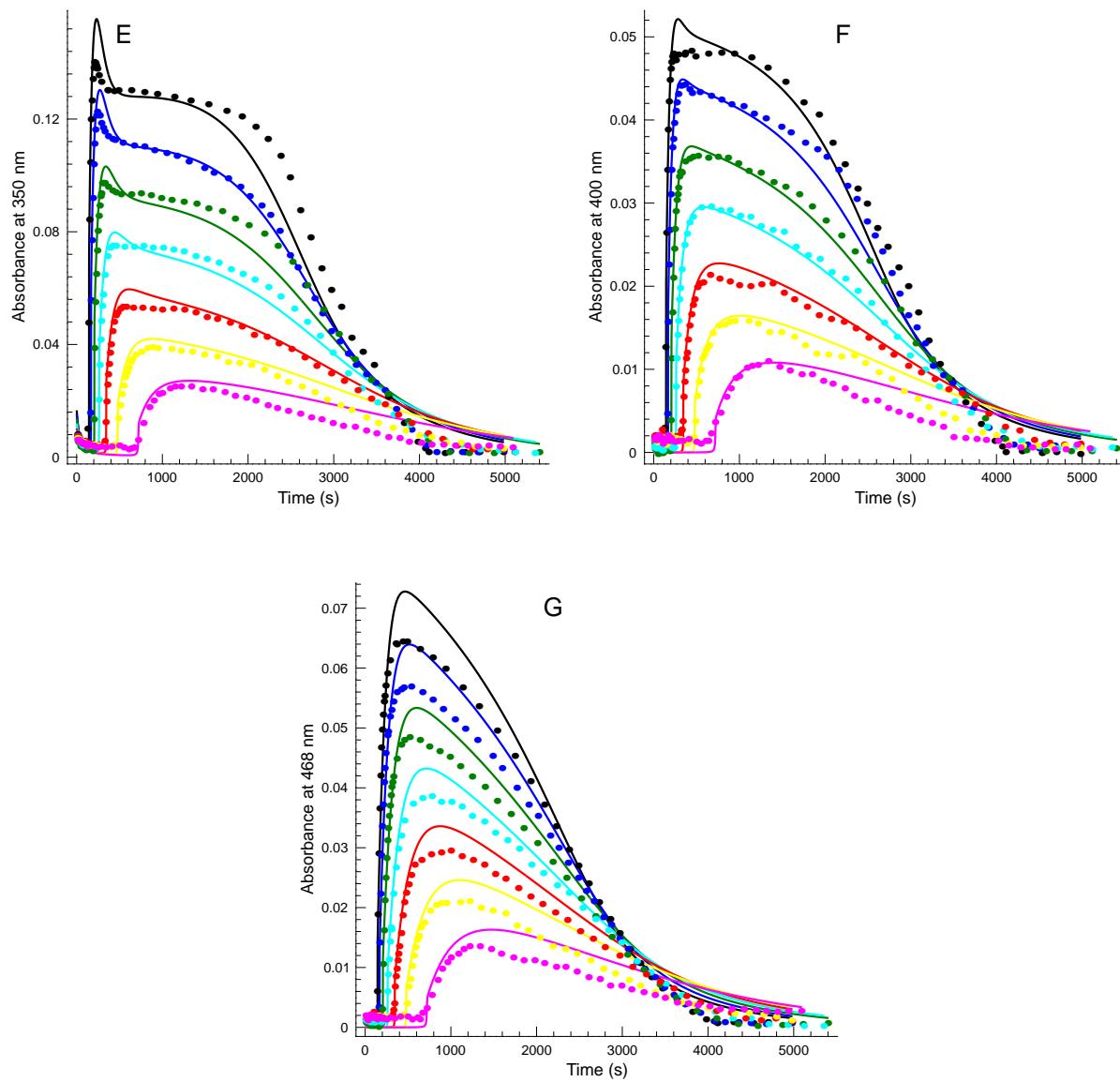


Figure S7: Measured (dots) and calculated (solid lines) absorbances at constant $[IO_4^-]_0/[S_2O_3^{2-}]_0=1.54:1$ ratio and at pH=4.65. $[IO_4^-]_0/\text{mM}=5.0$ (black), 4.5 (blue), 4.0 (green), 3.5 (cyan), 3.0 (red), 2.0 (magenta).

