Supporting Information

Reaction of Fe^{II}_{aq} with Peroxymonosulfate and Peroxydisulfate in Presence of Bicarbonate: Formation of Fe^{IV}_{aq} and Carbonate Radical Anions

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Table S1. Six different setups used to determine the degradation efficiencies of SMX and SDM

#	Treatment	$[PMS]_0$ (mM)	$[PDS]_0$ (mM)	$[Fe^{II}_{aq}]_0$ (mM)	$[bicarbonate]_0$ (mM)
1	PMS alone	0.04	0	0	0
2	Fe^{II}_{aq} - PMS	0.04	0	0.2	0
3	Fe^{II}_{aq} – PMS - bicarbonate	0.04	0	0.2	0.5
4	PDS alone	0	1.0	0	0
5	Fe^{II}_{aq} - PDS	0	1.0	2.0	0
6	Fe^{II}_{aq} – PDS - bicarbonate	0	1.0	2.0	5.0

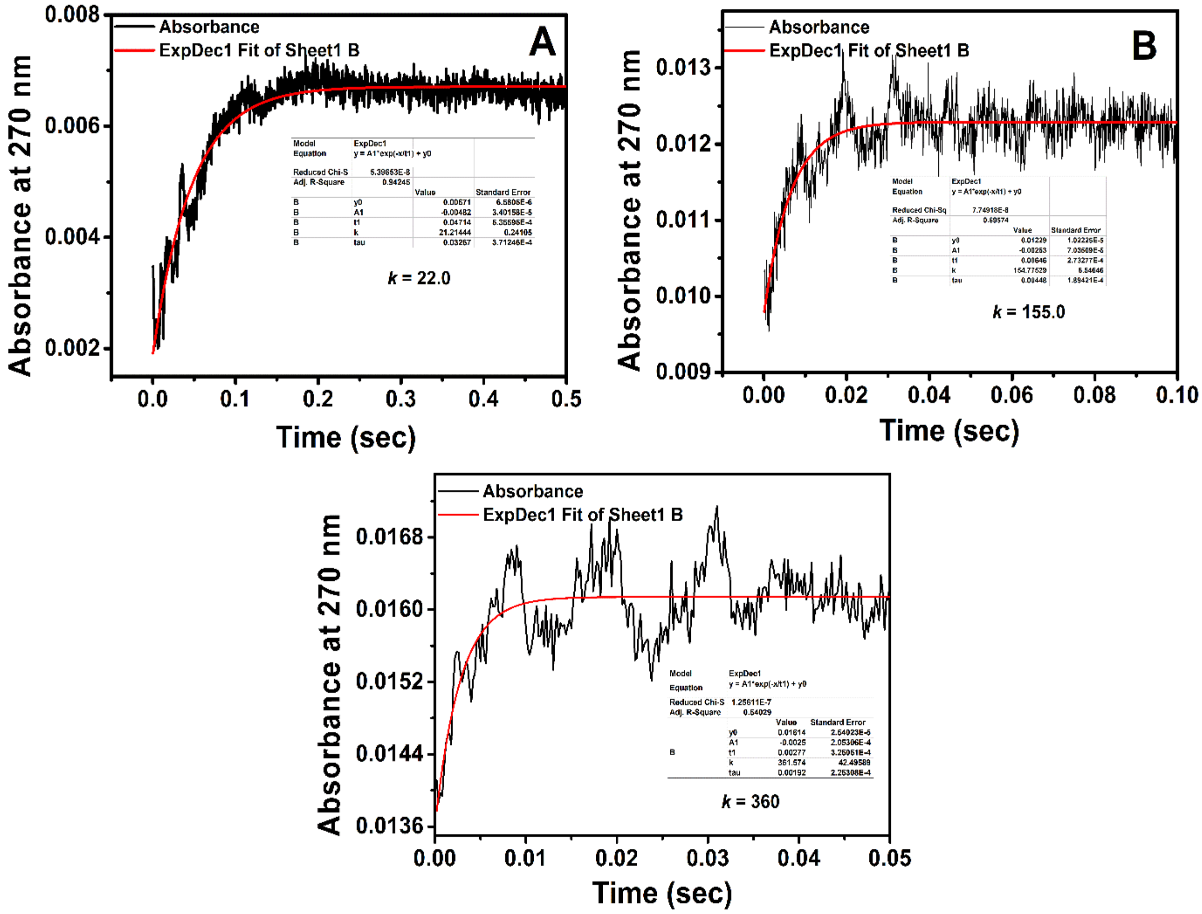

Figure S1. Formation of Fe(III) as a function of time during the reaction of $Fe(H_2O)_6^{2+}$ with PMS at different concentrations of PMS while keeping a constant low concentration of HCO_3^-. (**A**) [PMS] = 0.05 mM, (**B**) [PMS] = 0.10 mM, and (**C**) [PMS] = 0.20 mM. (Experimental initial concentrations in the Fenton solutions:)$[Fe^{II}]$ = 0.020 mM, $[HCO_3^-]$ = 0.50 mM.

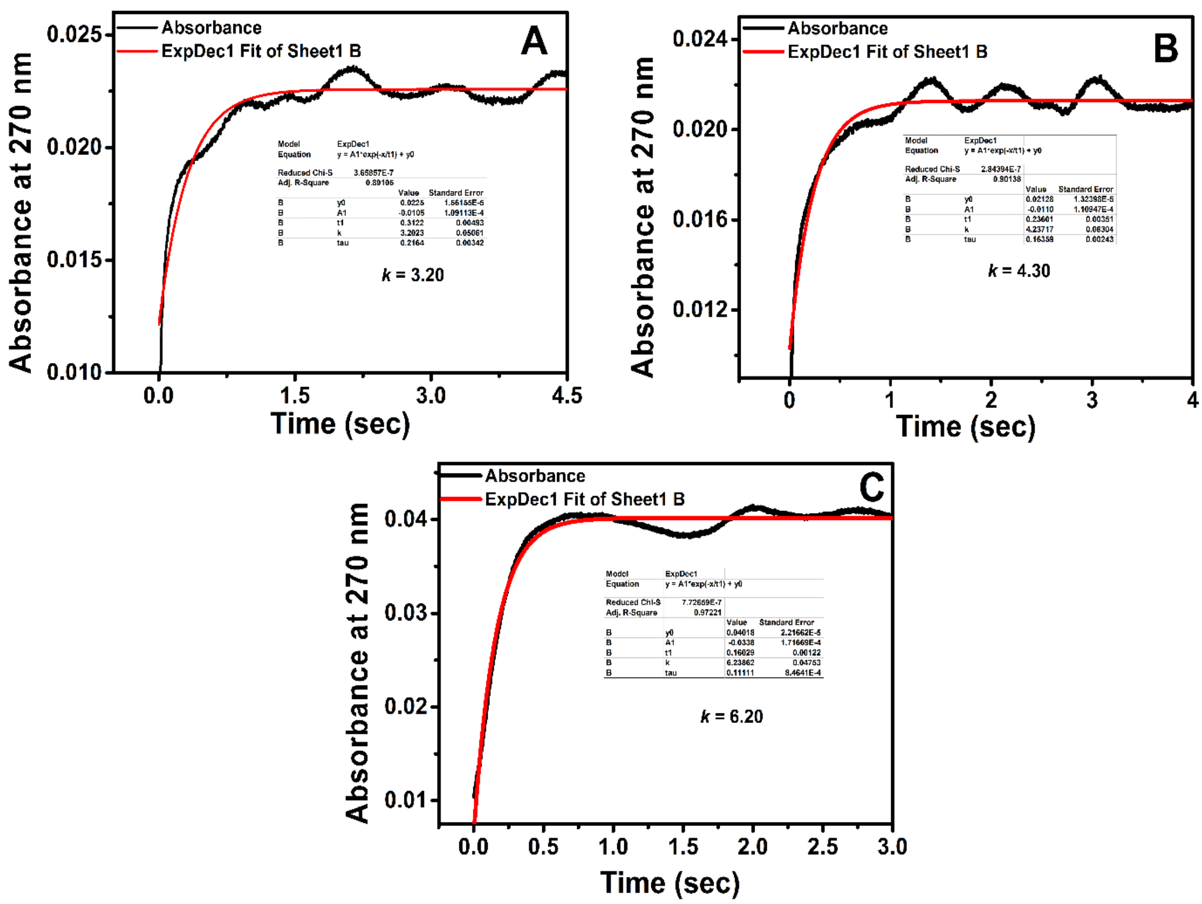

Figure S2. Formation of Fe(III) as a function of time during the reaction of $Fe(H_2O)_6^{2+}$ with PDS at different concentrations of PDS while keeping a constant concentration of HCO_3^-. (**A**) [PDS] = 1.0 mM, (**B**) [PDS] = 2.0 mM, and (**C**) [PDS] = 3.0 mM. (Experimental initial concentrations in the Fenton solutions: $[Fe^{II}]$ = 0.10 mM, $[HCO_3^-]$ = 8.0 mM).

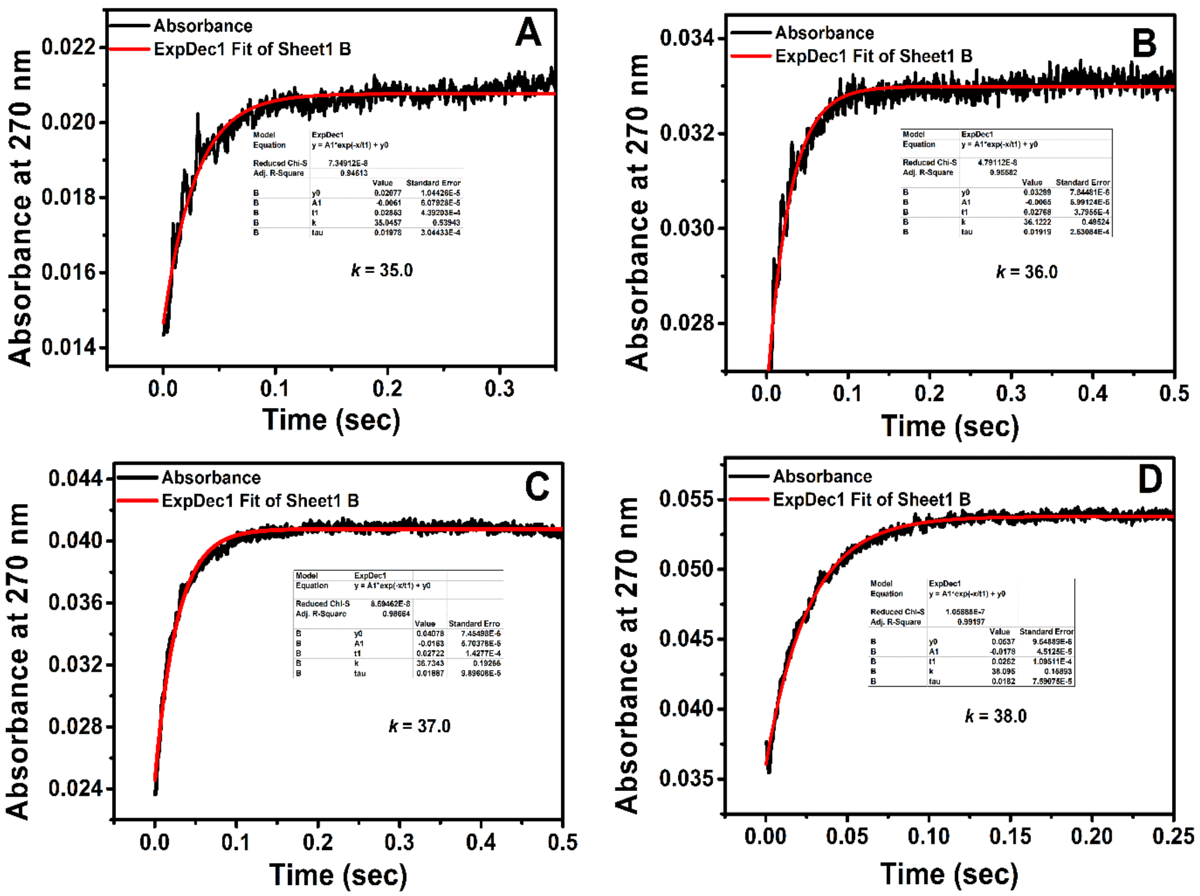

Figure S3. Typical kinetic curves of the formation of Fe(III) during the reaction of $Fe(H_2O)_6^{2+}$ with PMS at different concentrations of Fe^{II}_{aq} under a constant concentration of low HCO_3^-. (**A**) [Fe^{II}_{aq}= 0.02 mM, (**B**) [Fe^{II}_{aq}] = 0.04 mM, (**C**) [Fe^{II}_{aq}] = 0.06 mM, and (**D**) [Fe^{II}_{aq}] = 0.08 mM (Experimental initial concentrations in the Fenton solutions: [PMS] = 0.10 mM and [HCO_3^-]= 0.30 mM).

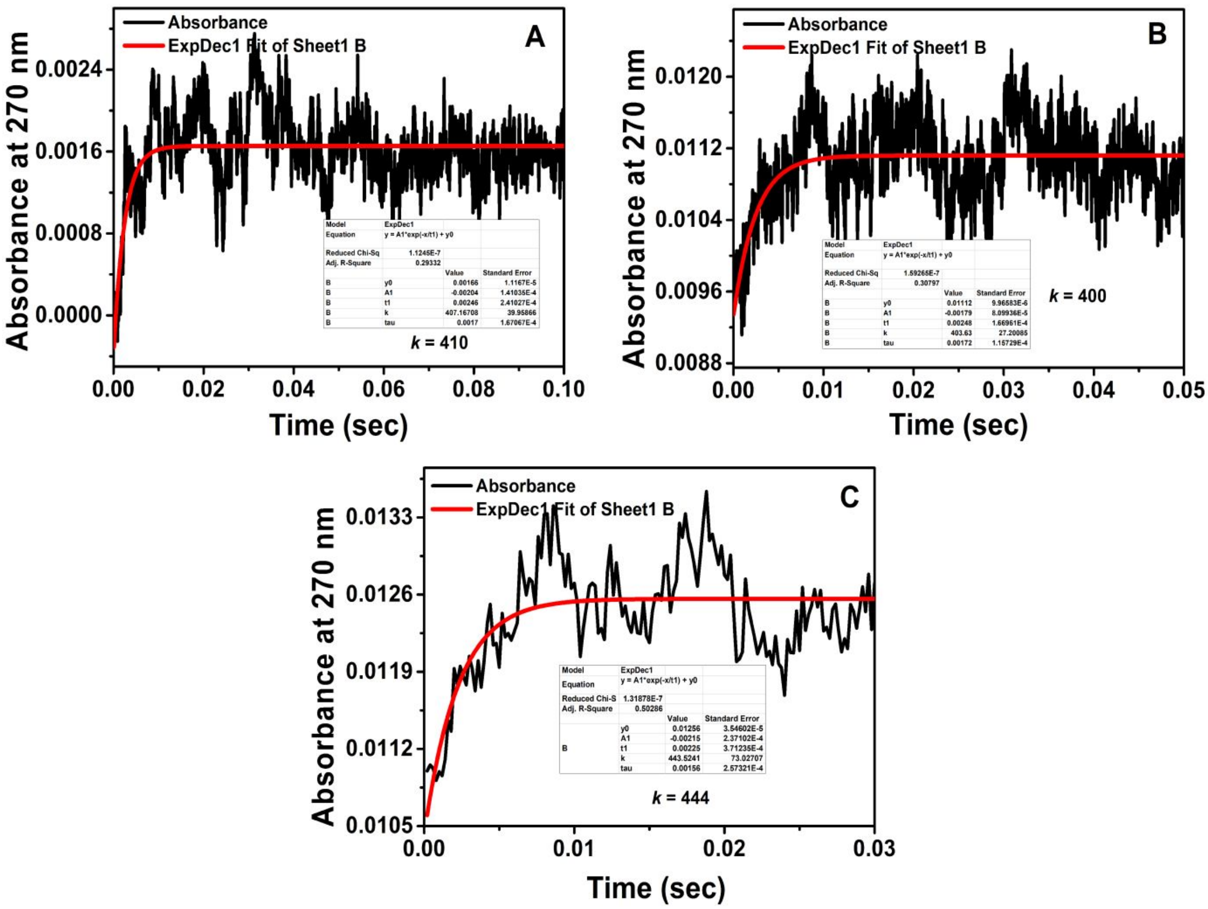

Figure S4. Typical kinetic curves of the formation of Fe(III) during the reaction of $Fe(H_2O)_6^{2+}$ with PMS at different concentrations of Fe^{II}_{aq} under a constant concentration of high HCO_3^-. (**A**) [Fe^{II}_{aq}= 0.02 mM, (**B**) [Fe^{II}_{aq}] = 0.04 mM and (**C**) [Fe^{II}_{aq}] = 0.08 mM (Experimental initial concentrations in the Fenton solutions: [PMS] = 0.10 mM and [HCO_3^-]= 0.60 mM).

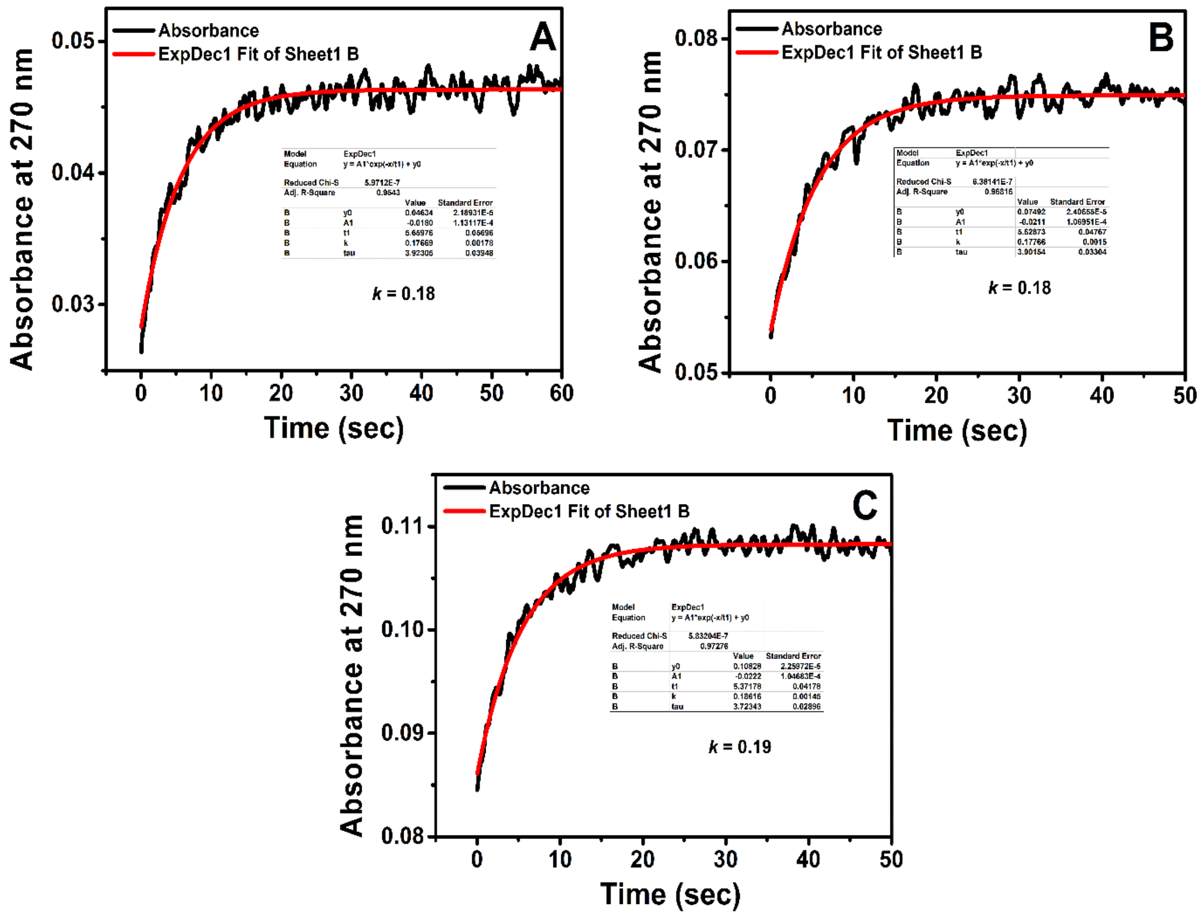

Figure S5. Typical kinetic curves of the formation of Fe(III) during the reaction of $Fe(H_2O)_6^{2+}$ with PDS at different concentrations of Fe^{II}_{aq} under a constant concentration of low HCO_3^-. (**A**) [Fe^{II}_{aq}] = 0.10 mM, (**B**) [Fe^{II}_{aq}] = 0.20 mM, and (**C**) [Fe^{II}_{aq}] = 0.40 mM Fe^{II}_{aq}. (Experimental initial concentrations in the Fenton solutions: [PDS] = 1.0 mM, [HCO_3^-] = 2.0 mM)

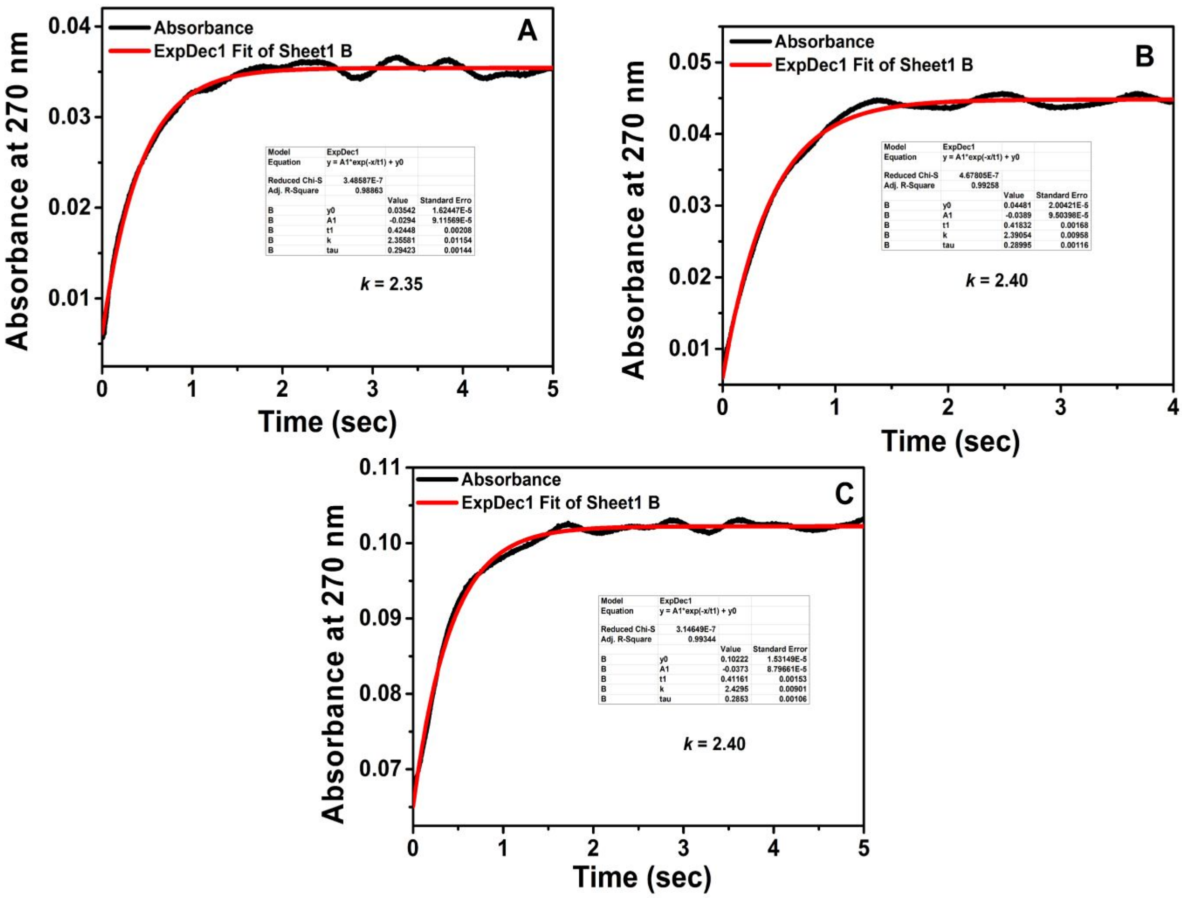

Figure S6. Typical kinetic curves of the formation of Fe(III) during the reaction of $Fe(H_2O)_6^{2+}$ with PDS at different concentrations of Fe^{II}_{aq} under a constant concentration of high HCO_3^-. (**A**) $[Fe^{II}_{aq}]$ = 0.10 mM, (**B**) $[Fe^{II}_{aq}]$ = 0.20 mM, and (**C**) $[Fe^{II}_{aq}]$ = 0.40 mM Fe^{II}_{aq}. (Experimental initial concentrations in the Fenton solutions: [PDS] = 1.0 mM, $[HCO_3^-]$ = 5.0 mM)

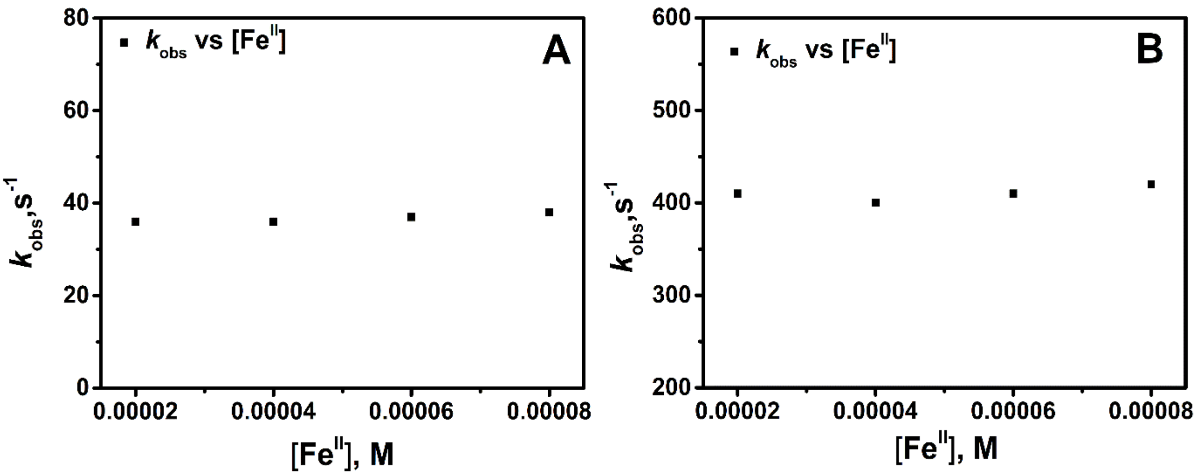

Figure S7. Dependence of k_{obs} at pH 7.40 on the concentrations of Fe^{II}_{aq}, at a constant concentration of PMS **(A)** [HCO_3^-] = 0.30 mM (Low [HCO_3^-]) and **(B)** [HCO_3^-] = 0.60 mM (High [HCO_3^-]). Here in both cases, [PMS] = 0.10 mM

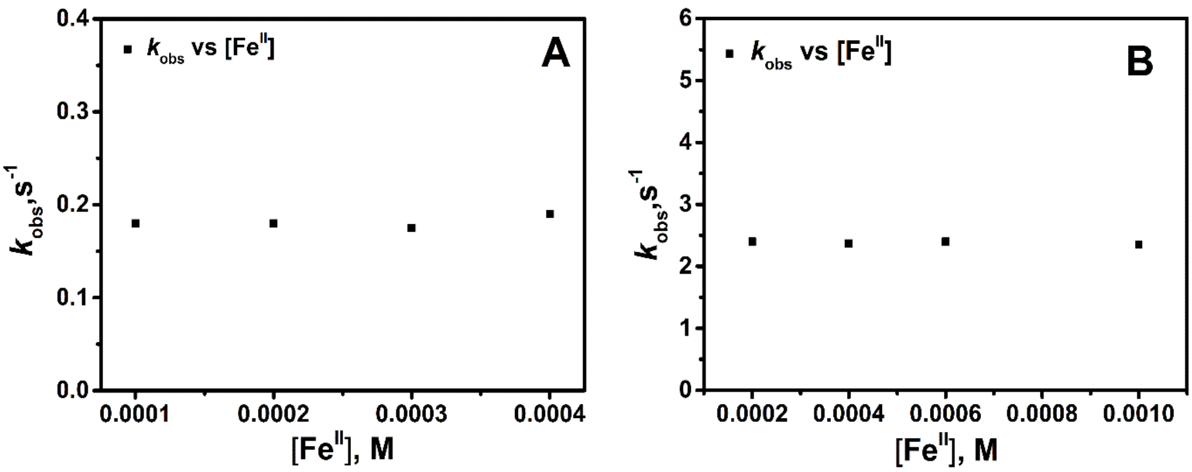

Figure S8. Dependence of k_{obs} at pH 7.40 on the concentrations of Fe^{II}_{aq}, at a constant concentration of PDS **(A)** [HCO_3^-] = 2.0 mM (Low [HCO_3^-]) and **(B)** [HCO_3^-] = 5.0 mM (High [HCO_3^-]). Here in both cases, [PDS] = 1.0 mM

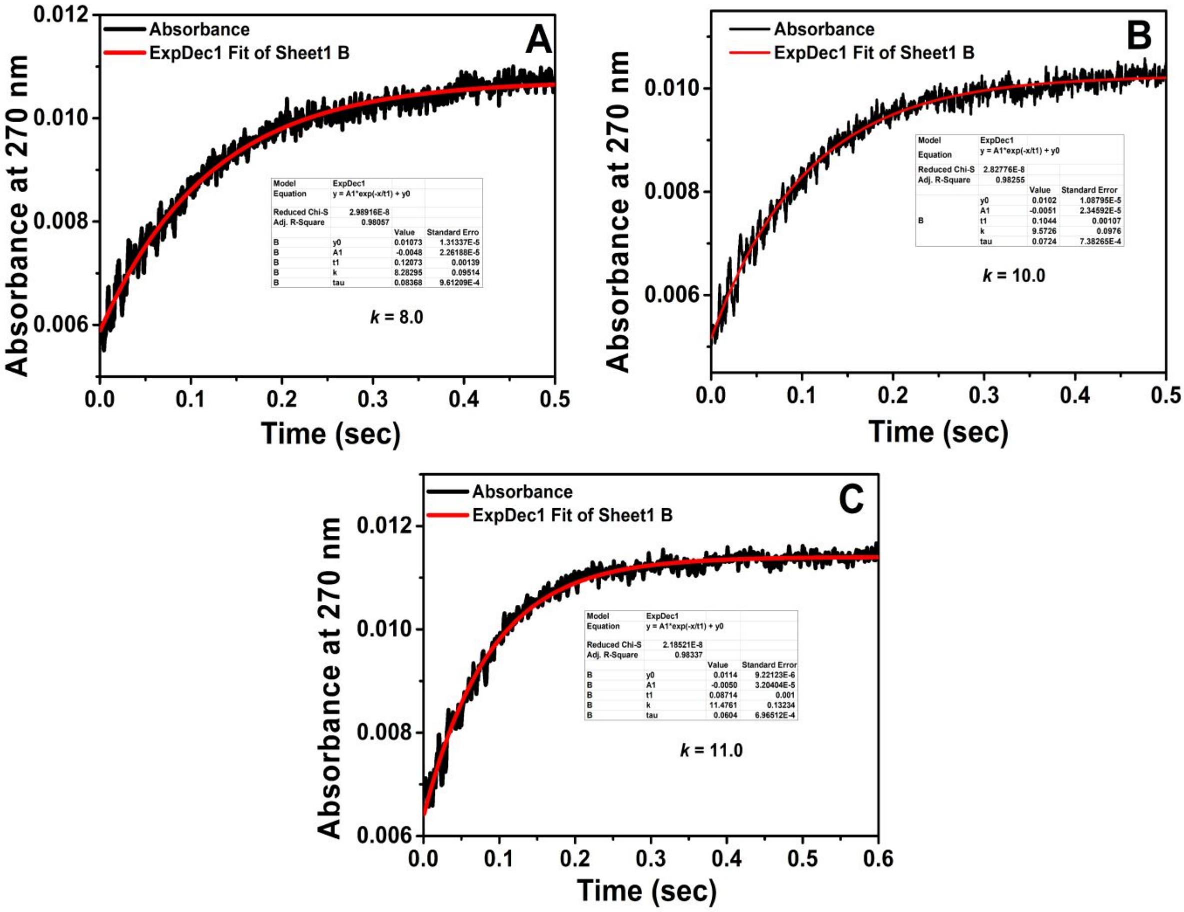

Figure S9. Kinetic curves of the formation of Fe(III) during the reaction of $Fe(H_2O)_6^{2+}$ with PMS in the absence of bicarbonate at different pH's (A) pH = 5.80, (B) pH = 7.0 and (C) pH = 8.40. (Experimental initial concentrations in the Fenton solutions: [PMS] = 0.20 mM, $[Fe^{II}_{aq}]$ = 0.020 mM)

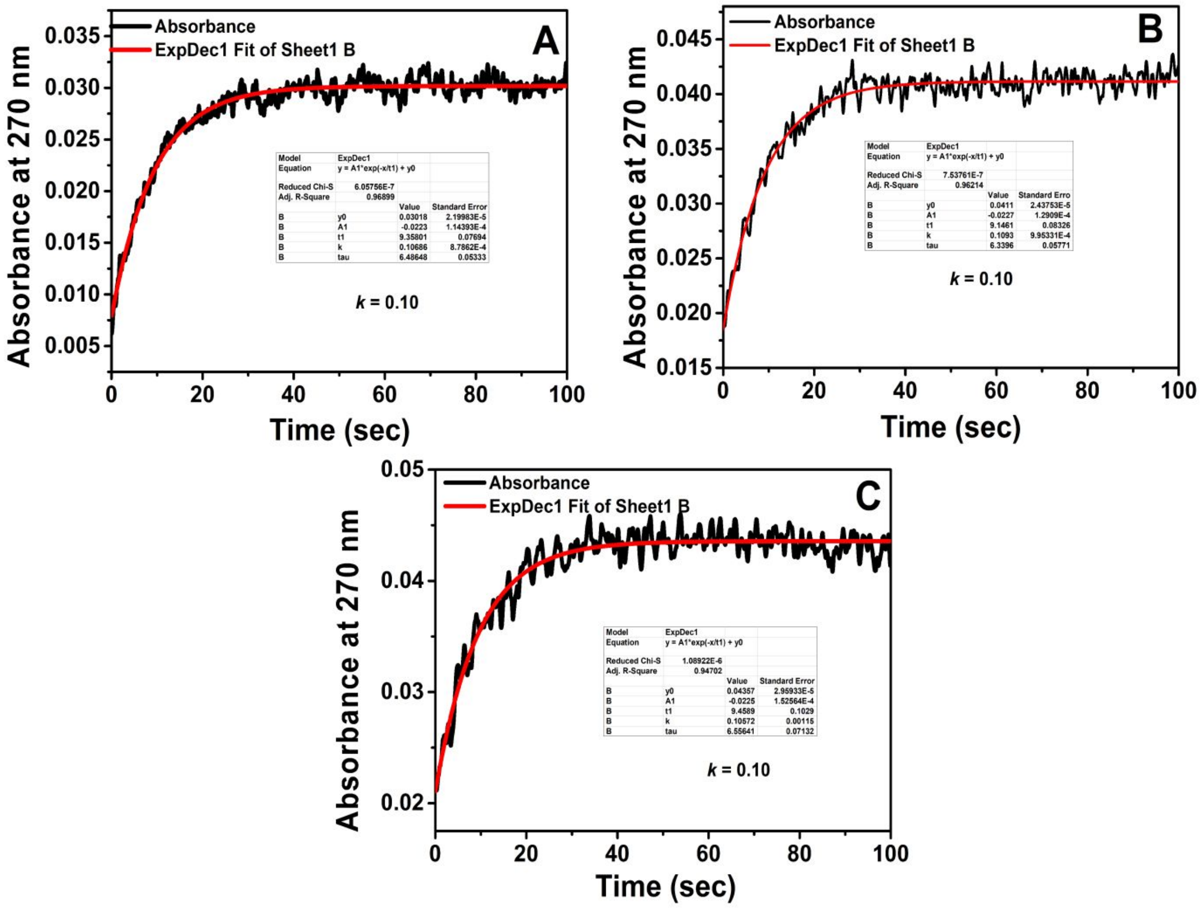

Figure S10. Kinetic curves of the formation of Fe(III) during the reaction of $Fe(H_2O)_6^{2+}$ with PDS in the absence of bicarbonate at different pH's (A) pH = 5.80, (B) pH = 7.0 and (C) pH = 8.40. (Experimental initial concentrations in the Fenton solutions: [PDS] = 1.0 mM, [Fe^{II}_{aq}] = 0.10 mM)

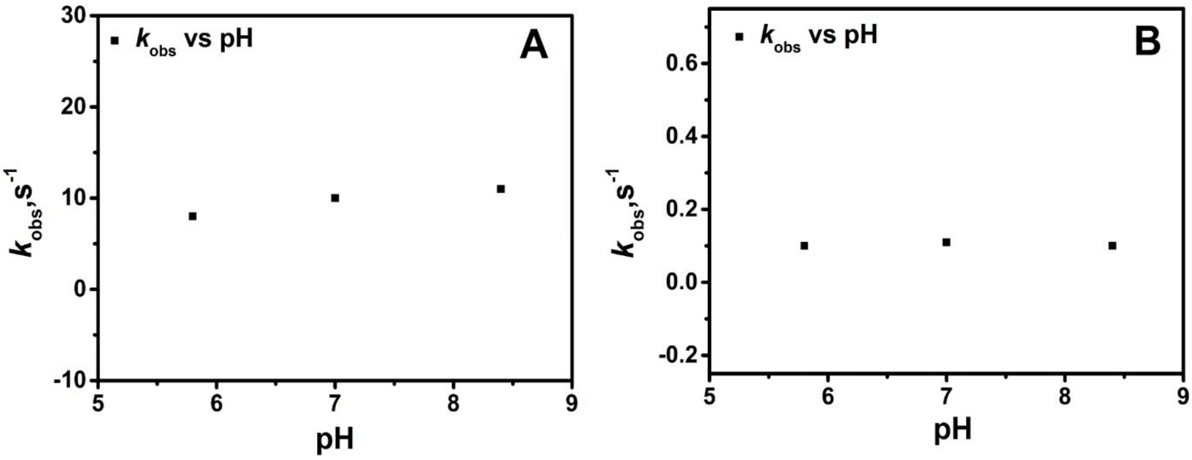

Figure S11. Dependence of k_{obs} on the pH in the absence of bicarbonate at a constant concentration of (**A**) PMS ([PMS] = 0.20 mM, [Fe^{II}_{aq}] = 0.020 mM) and (**B**) PDS ([PDS] = 1.0 mM, [Fe^{II}_{aq}] = 0.10 mM)

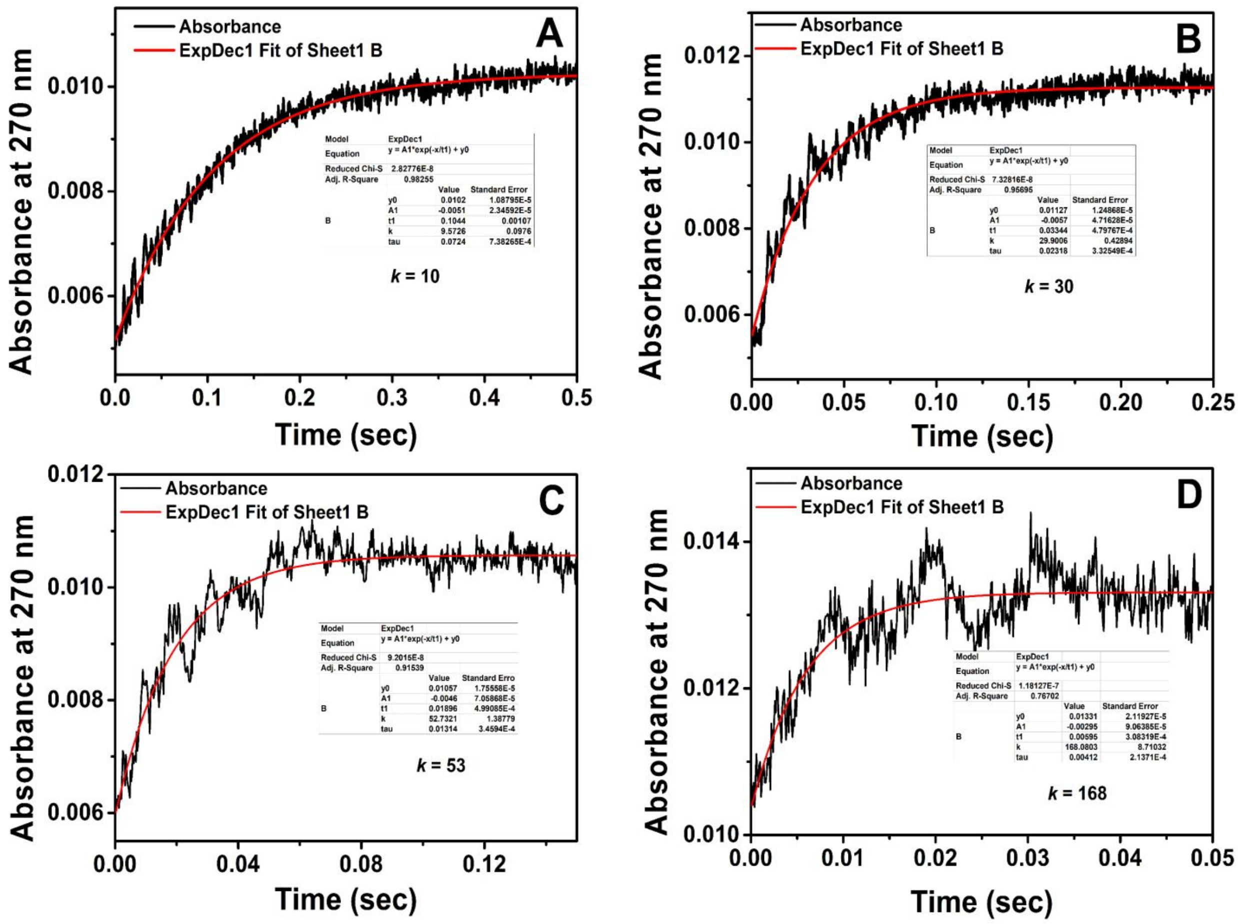

Figure S12. Typical kinetic curve of the reaction of $Fe(H_2O)_6^{2+}$ with PMS in presence of excess PMS taken by stopped flow instrument with different concentration of (A) 0 mM HCO_3^- (B) 0.10 mM HCO_3^- (C) 0.20 mM HCO_3^- and (D) 0.40 mM HCO_3^- .The initial concentrations in the Fenton solutions are [Fe^{II}] = 0.020 mM, [PMS] = 0.20 mM. The data of the conventional spectrophotometric measurements were analyzed graphically, and the *k* values were determined by fitting single exponential curves to the absorbance *vs*. time plots.

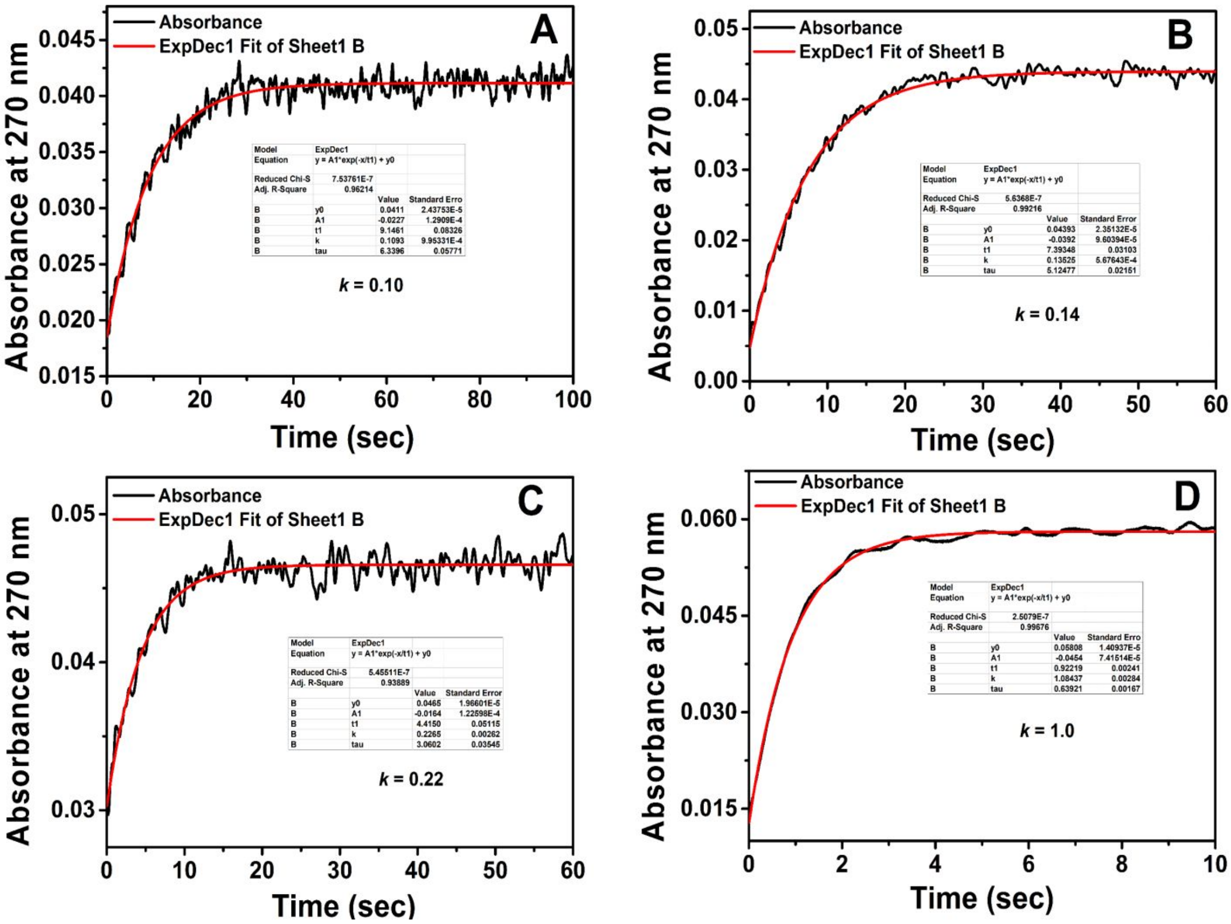

Figure S13. Typical kinetic curve of the reaction of $Fe(H_2O)_6^{2+}$ with PDS in presence of excess PDS taken by stopped flow instrument with different concentration of (**A**) 0 mM HCO_3^- (**B**) 1.0 mM HCO_3^- (**C**) 2.0 mM HCO_3^- and (**D**) 3.0 mM HCO_3^- .The initial concentrations in the Fenton solutions are $[Fe^{II}]$ = 0.10 mM, [PDS] = 1.0 mM.

Text S1:

Mechanism I:

Small slope

$Fe(H_2O)_6^{2+} + HSO_5^- \rightleftharpoons (H_2O)_5Fe^{II}(O_2SO_3)$ /$(H_2O)_3Fe^{II}(O_2SO_3) + H_3O^+$ (8)

$(H_2O)_5Fe^{II}(O_2SO_3)$ /$(H_2O)_3Fe^{II}(O_2SO_3) + HCO_3^- \rightarrow Fe^{III}_{aq} + CO_3^{\cdot -} + SO_4^{2-}$

(small slope) (9)

Since the rate determining step (rds) is Eq. (9), the overall rate law for this reaction is as follows:

rate = $k_9\, [(H_2O)_5Fe^{II}(O_2SO_3)$ /$(H_2O)_3Fe^{II}(O_2SO_3)]\, [HCO_3^-]$ (9'')

Since $(H_2O)_5Fe^{II}(O_2SO_3)$ /$(H_2O)_3Fe^{II}(O_2SO_3)$ is an intermediate, from eqtn (8),

$k_8\, [Fe(H_2O)_6^{2+}]\, [HSO_5^-] = k_{-8}\, [(H_2O)_5Fe^{II}(O_2SO_3)$ /$(H_2O)_3Fe^{II}(O_2SO_3)]$ (8'')

This equation may also be written in the following alternative way,

$[(H_2O)_5Fe^{II}(O_2SO_3)$ /$(H_2O)_3Fe^{II}(O_2SO_3)] = K_8\, [Fe(H_2O)_6^{2+}]\, [HSO_5^-]$

Eq. (9'') may be rewritten as,

rate = $\mathbf{k_9\, K_8\, [Fe(H_2O)_6^{2+}]\, [HSO_5^-]\, [HCO_3^-]}$

Large slope

$Fe(H_2O)_6^{2+} + HCO_3^- \rightleftharpoons (H_2O)_3Fe(CO_3) + H_3O^+ + 2H_2O$ (10)

$(H_2O)_3Fe(CO_3) + HSO_5^-/S_2O_8^{2-} \rightarrow Fe^{III}_{aq} + CO_3^{\cdot -} + SO_4^{2-}/2SO_4^{2-}$

(large slope) (10')

The overall rate law of this reaction is as follows:

$r = k_{10'}\, [(H_2O)_3Fe(CO_3)]\, [HSO_5^-/S_2O_8^{2-}]$ (10'')

Here, $(H_2O)_3Fe(CO_3)$ is the intermediate formed. Rearranging the equilibrium rate equation (10), the $[(H_2O)_3Fe(CO_3)]$ is given by,

$[(H_2O)_3Fe(CO_3)] = K_{10}\, [Fe(H_2O)_6^{2+}]\, [HCO_3^-]$

The overall rate of this reaction can be expressed by rearranging the Eq. (10'') as

rate = $\mathbf{k_{10'}\, K_{10}\, [Fe(H_2O)_6^{2+}]\, [HCO_3^-]\, [HSO_5^-/S_2O_8^{2-}]}$

<u>Text S2</u>

Mechanism II:

Small slope

$Fe(H_2O)_6^{2+} + HCO_3^- \rightleftharpoons (H_2O)_3Fe(CO_3) + H_3O^+ + 2H_2O$ (11)

$(H_2O)_3Fe(CO_3) + HSO_5^-/S_2O_8^{2-} \rightarrow Fe^{III}_{aq} + CO_3^{\cdot-} + SO_4^{2-}/2SO_4^{2-}$

(small slope) (12)

The overall rate law for this reaction (rds = (12)) is as follows

$r = k_{12}\,[(H_2O)_3Fe(CO_3)]\,[HSO_5^-/S_2O_8^{2-}]$ (12')

Here, $(H_2O)_3Fe(CO_3)$ is an intermediate

From (11),

$r_{forward} = r_{backward}$

$k_{11}\,[Fe(H_2O)_6^{2+}]\,[HCO_3^-] = k_{-11}\,[(H_2O)_3Fe(CO_3)]$ (12'')

$[(H_2O)_3Fe(CO_3)] = K_{11}[Fe(H_2O)_6^{2+}]\,[HCO_3^-]$

Rearrange the Eq. (12') by substituting the value for $[(H_2O)_3Fe(CO_3)]$,

rate = $\mathbf{k_{12}\,K_{11}\,[Fe(H_2O)_6^{2+}]\,[HCO_3^-]\,[HSO_5^-/S_2O_8^{2-}]}$

Large slope

$(H_2O)_3Fe(CO_3) + HSO_5^-/S_2O_8^{2-} \rightleftharpoons$

$(H_2O)Fe(CO_3)(O_2SO_3)/(H_2O)Fe(CO_3)(S_2O_8) + H_3O^+$ (13)

$(H_2O)Fe(CO_3)(O_2SO_3)/(H_2O)Fe(CO_3)(S_2O_8) + HCO_3^- \rightleftharpoons$

$Fe^{III}(CO_3)_{aq} + CO_3^{\cdot-} + SO_4^{2-}/2SO_4^{2-}$ (large slope) (14)

Overall rate is as followed:

$r = k_{14}\,[(H_2O)Fe(CO_3)(O_2SO_3)/(H_2O)Fe(CO_3)(S_2O_8)]\,[HCO_3^-]$ (14')

Here $(H_2O)Fe(CO_3)(O_2SO_3)/(H_2O)Fe(CO_3)(S_2O_8)$ is an intermediate

Hence, from Eq. (13)

$[(H_2O)Fe(CO_3)(O_2SO_3)/(H_2O)Fe(CO_3)(S_2O_8)] = K_{13}\,[(H_2O)_3Fe(CO_3)]\,[HSO_5^-/S_2O_8^{2-}]$

(14'')

Substitute the $[(H_2O)_3Fe(CO_3)]$ and $[(H_2O)Fe(CO_3)(O_2SO_3)/(H_2O)Fe(CO_3)(S_2O_8)]$ in (14')

rate = $\mathbf{k_{14}K_{13}K_{11}\,[Fe(H_2O)_6^{2+}]\,[HCO_3^-]^2\,[HSO_5^-/S_2O_8^{2-}]}$

Text S3

Mechanism III:

Small slope

$Fe(H_2O)_6^{2+} + HCO_3^- \rightleftharpoons (H_2O)_3Fe(CO_3) + H_3O^+ + 2H_2O$ (15)

$(H_2O)_3Fe(CO_3) + HSO_5^-/S_2O_8^{2-} \rightarrow Fe^{III}_{aq} + CO_3^{\cdot -} + SO_4^{2-}/2SO_4^{2-}$ (small slope) (16)

The overall rate law for this reaction (rds (16)) is as follows:

$r = k_{16} [(H_2O)_3Fe(CO_3)] [HSO_5^-/S_2O_8^{2-}]$ (16')

From (15),

$[(H_2O)_3Fe(CO_3)] = K_{15}[Fe(H_2O)_6^{2+}] [HCO_3^-]$

Eq. (16') may be rewritten as,

rate = $\mathbf{k_{16}K_{15}[Fe(H_2O)_6^{2+}] [HCO_3^-] [HSO_5^-/S_2O_8^{2-}]}$

Large slope

$Fe(H_2O)_6^{2+} + 2HCO_3^- \rightleftharpoons (H_2O)_2Fe(CO_3)_2^{2-} + 2H_3O^+ + 2H_2O$ (17)

$(H_2O)_2Fe(CO_3)_2^{2-} + HSO_5^-/S_2O_8^{2-} \rightarrow Fe^{III}(CO_3)_{aq} + CO_3^{\cdot -} + SO_4^{2-}/2SO_4^{2-}$

(large slope) (18)

Overall rate law (rds (18)) will be

$r = k_{18}[(H_2O)_2Fe(CO_3)_2^{2-}] [HSO_5^-/S_2O_8^{2-}]$ (18')

From (17),

$[(H_2O)_2Fe(CO_3)_2^{2-}] = k_{17} [Fe(H_2O)_6^{2+}] [HCO_3^-]^2 / k_{-17}$

Eq. (18') may be rewritten as,

rate = $\mathbf{k_{18}K_{17}[Fe(H_2O)_6^{2+}] [HCO_3^-]^2 [HSO_5^-/S_2O_8^{2-}]}$

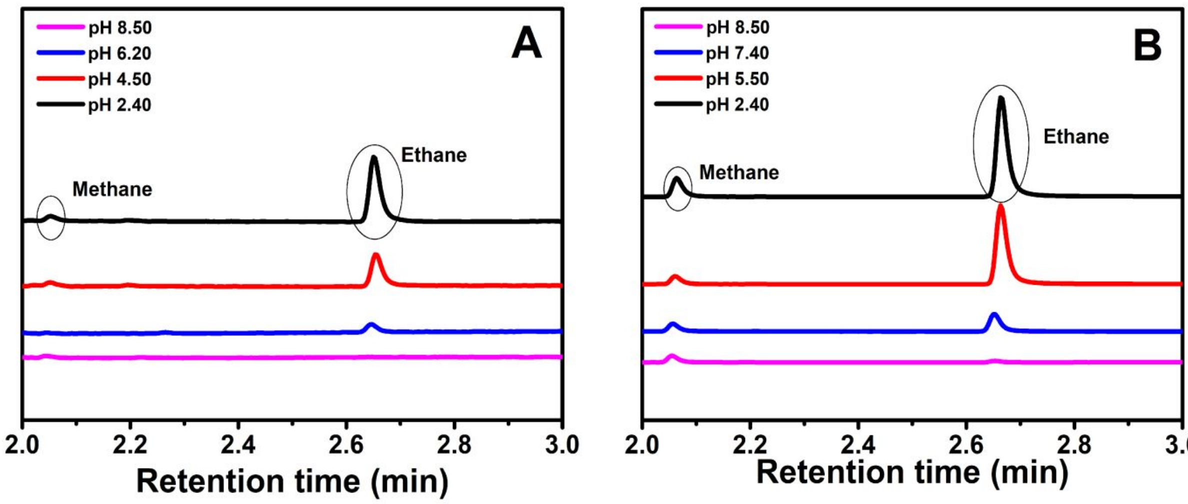

Figure S14. GC determination of methane and ethane with FID detector at four different pH in the absence of HCO_3^- after the Fenton reaction of (**A**) Fe^{2+} and HSO_5^- and (**B**) Fe^{2+} and $S_2O_8^{2-}$ in presence of excess Fe^{II}_{aq} and $(CH_3)_2SO$. $[Fe^{II}] = 0.50$ mM, $[HSO_5^-/S_2O_8^{2-}] = 0.10$ mM, $[(CH_3)_2SO] = 25.0$ mM.

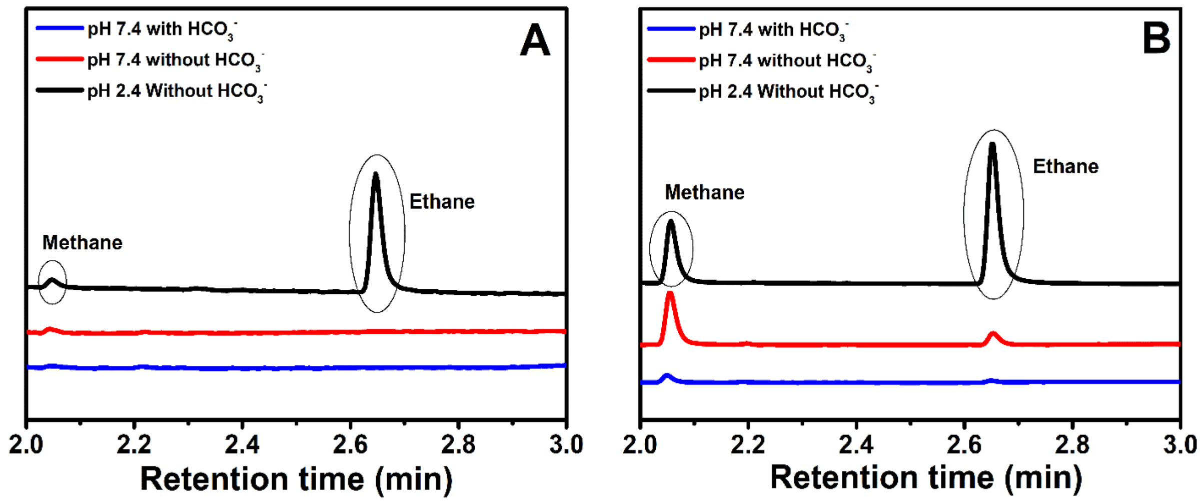

Figure S15. GC determination of methane and ethane with FID detector at pH 2.2 and at neutral pH in the absence and presence of HCO_3^- after the Fenton reaction of (**A**) Fe^{2+} and HSO_5^- and (**B**) Fe^{2+} and $S_2O_8^{2-}$ in presence of excess Fe^{II}_{aq} and $(CH_3)_2SO$. $[Fe^{II}] = 0.50$ mM, $[HSO_5^-/S_2O_8^{2-}] = 0.10$ mM, $[(CH_3)_2SO] = 25.0$ mM, $[HCO_3^-] = 3.0$ mM.

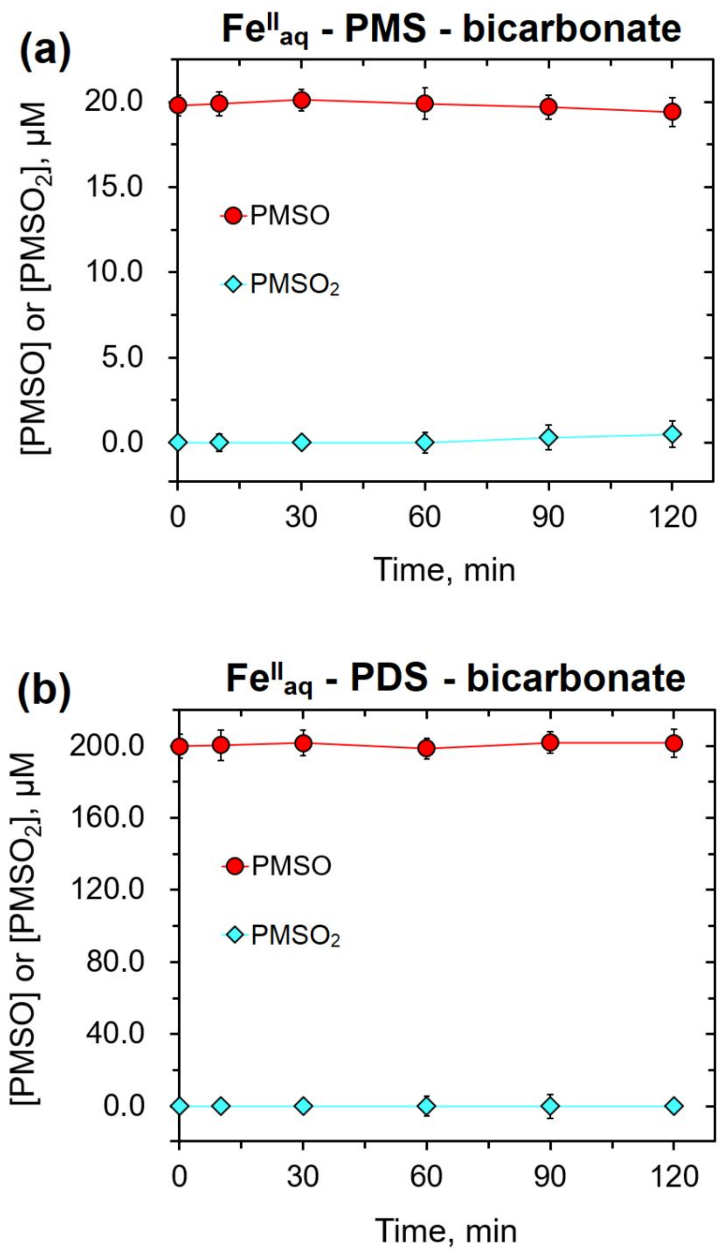

Figure S16. The changes in concentrations of PMSO and $PMSO_2$ in the **(a)** Fe^{II}_{aq} - PMS and **(b)** Fe^{II}_{aq} - PDS systems in presence of high bicarbonate concentrations (Initial pH = 7.0. The PMS system: $[PMS]_0$ = 0.04 mM; $[Fe^{II}_{aq}]_0$ = 0.2 mM; $[bicarbonate]_0$ = 20.0 mM; $[PMSO]_0$ = 20.0 μM. The PDS system: $[PMS]_0$ = 1.0 mM; $[Fe^{II}_{aq}]_0$ = 2.0 mM; $[bicarbonate]_0$ = 200.0 mM; $[PMSO]_0$ = 200.0 μM)).

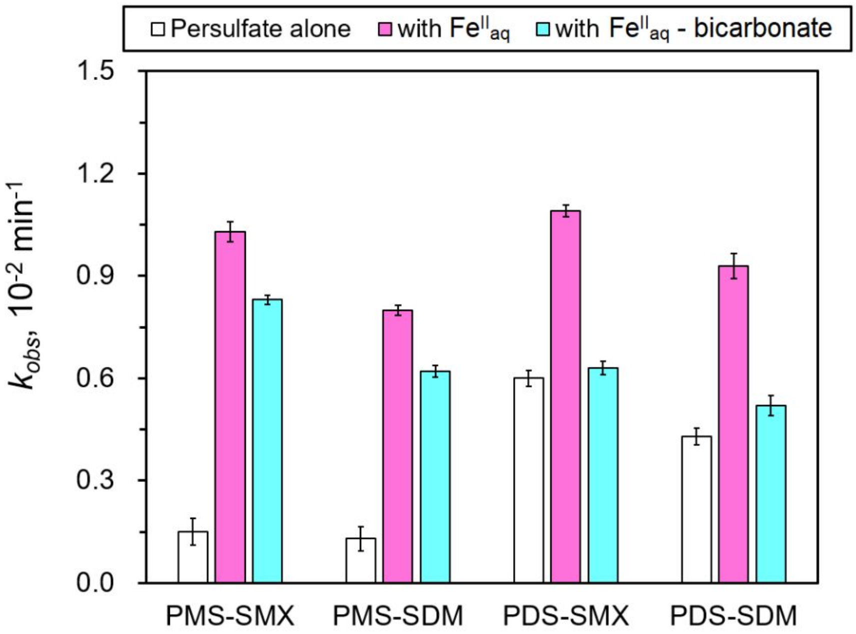

Figure S17. The pseudo-first-order rate constants of the degradation of SMX and SDM by different persulfate systems ($[SMX]_0 = [SDM]_0 = 5.0$ μM; initial pH = 7.0. The PMS system: $[PMS]_0 = 0.04$ mM; $[Fe^{II}_{aq}]_0 = 0.2$ mM; $[bicarbonate]_0 = 0.5$ mM. The PDS system: $[PDS]_0 = 1.0$ mM; $[Fe^{II}_{aq}]_0 = 2.0$ mM; $[bicarbonate]_0 = 5.0$ mM.).