

## Supporting Information

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

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**Pages:21, Table:1, Figures:17**

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## Table of contents

Table S1.....	3
Figure S1.....	4
Figure S2.....	5
Figure S3.....	6
Figure S4.....	7
Figure S5.....	8
Figure S6.....	9
Figure S7.....	10
Figure S8.....	10
Figure S9.....	11
Figure S10.....	12
Figure S11.....	13
Figure S12.....	14
Figure S13.....	15
Text S1.....	16
Text S2.....	17
Text S3.....	18
Figure S14.....	19
Figure S15.....	19
Figure S16.....	20
Figure S17.....	21

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

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#	Treatment	[PMS] <sub>0</sub> (mM)	[PDS] <sub>0</sub> (mM)	[Fe <sup>II</sup> <sub>aq</sub> ] <sub>0</sub> (mM)	[bicarbonate] <sub>0</sub> (mM)
1	PMS alone	0.04	0	0	0
2	Fe <sup>II</sup> <sub>aq</sub> - PMS	0.04	0	0.2	0
3	Fe <sup>II</sup> <sub>aq</sub> - PMS - bicarbonate	0.04	0	0.2	0.5
4	PDS alone	0	1.0	0	0
5	Fe <sup>II</sup> <sub>aq</sub> - PDS	0	1.0	2.0	0
6	Fe <sup>II</sup> <sub>aq</sub> - PDS - bicarbonate	0	1.0	2.0	5.0

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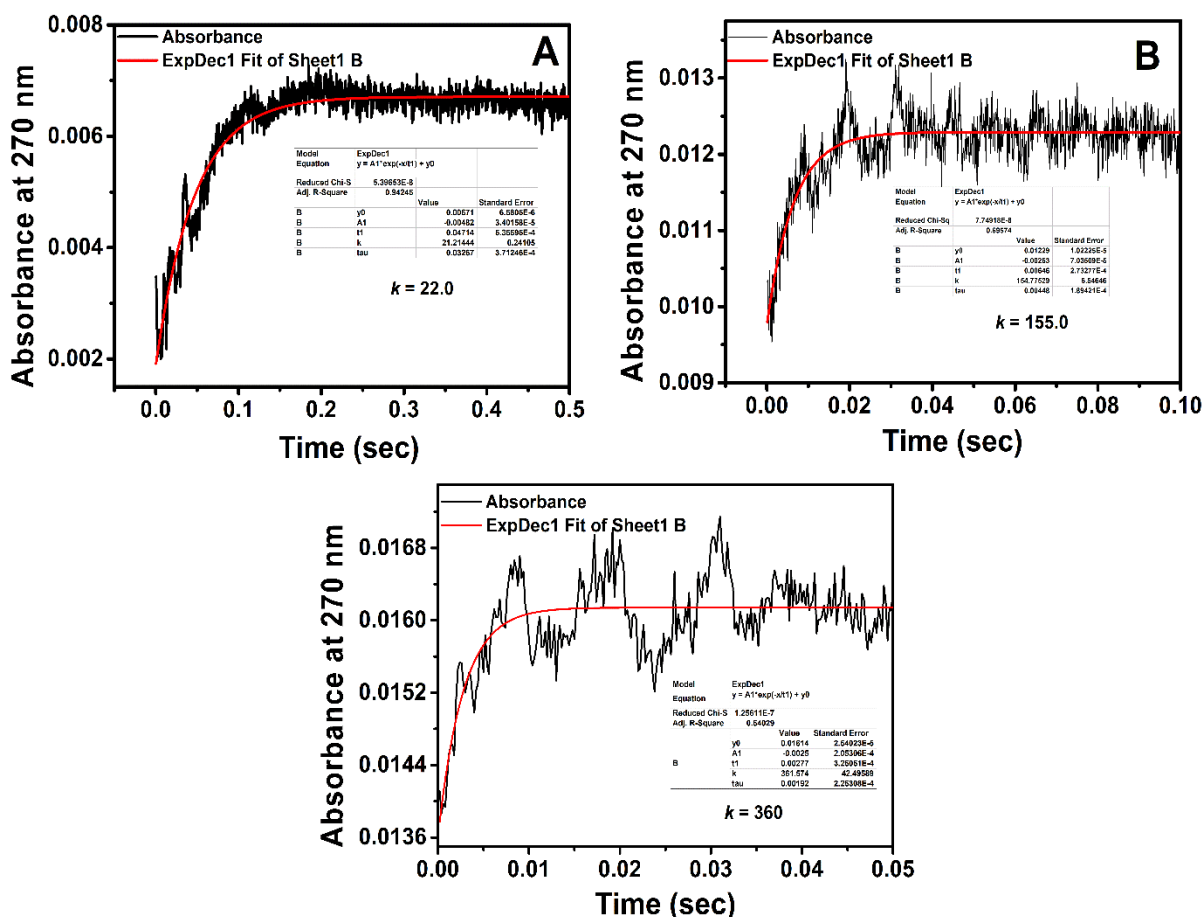
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114 **Figure S1.** Formation of Fe(III) as a function of time during the reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  with

115 PMS at different concentrations of PMS while keeping a constant low concentration of  $\text{HCO}_3^-$ .

116 (A) [PMS] = 0.05 mM, (B) [PMS] = 0.10 mM, and (C) [PMS] = 0.20 mM. (Experimental

117 initial concentrations in the Fenton solutions:  $[\text{Fe}^{II}] = 0.020$  mM,  $[\text{HCO}_3^-] = 0.50$  mM.

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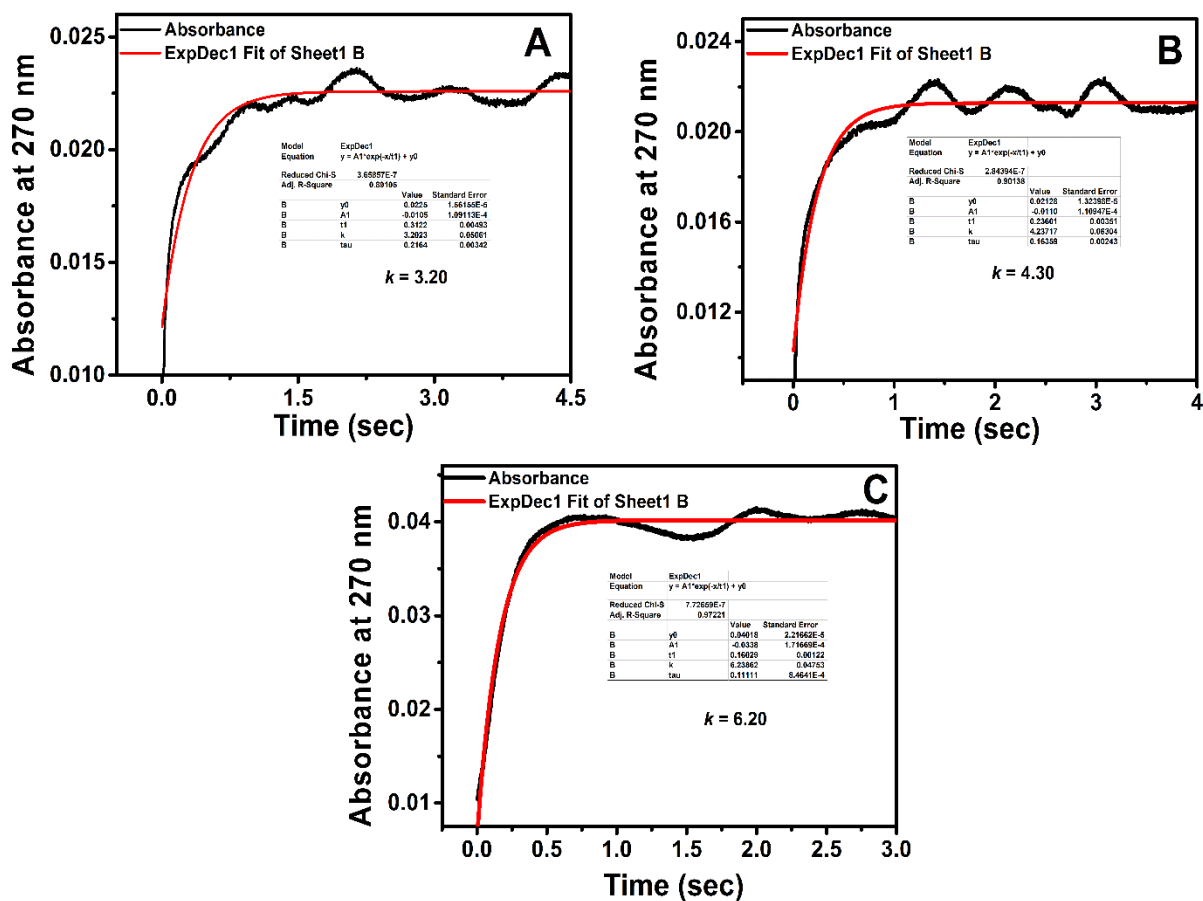
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128 **Figure S2.** Formation of Fe(III) as a function of time during the reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  with  
 129 PDS at different concentrations of PDS while keeping a constant concentration of  $\text{HCO}_3^-$ . (A)  
 130  $[\text{PDS}] = 1.0 \text{ mM}$ , (B)  $[\text{PDS}] = 2.0 \text{ mM}$ , and (C)  $[\text{PDS}] = 3.0 \text{ mM}$ . (Experimental initial  
 131 concentrations in the Fenton solutions:  $[\text{Fe}^{II}] = 0.10 \text{ mM}$ ,  $[\text{HCO}_3^-] = 8.0 \text{ mM}$ ).

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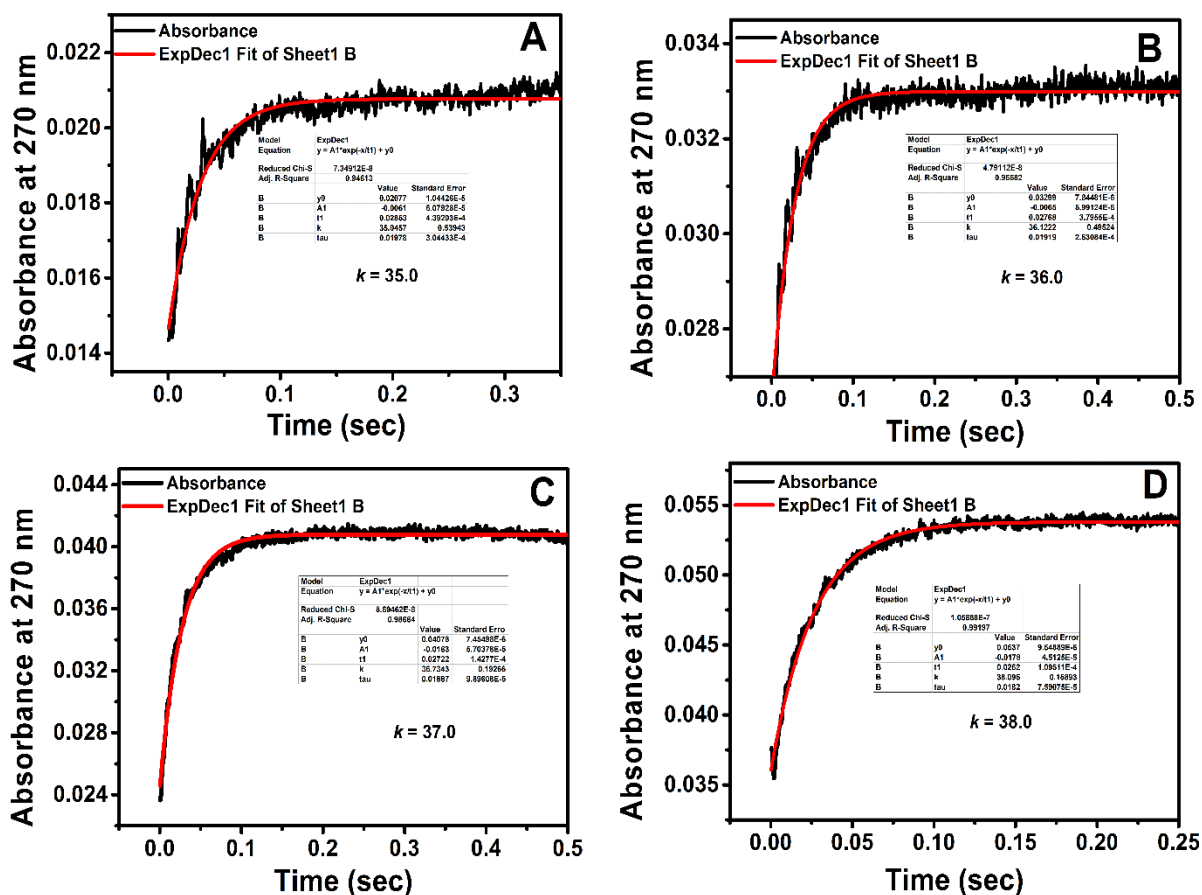
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140 **Figure S3.** Typical kinetic curves of the formation of Fe(III) during the reaction of  $Fe(H_2O)_6^{2+}$

141 with PMS at different concentrations of  $Fe^{II}_{aq}$  under a constant concentration of low  $HCO_3^-$ .

142 (A)  $[Fe^{II}_{aq}] = 0.02$  mM, (B)  $[Fe^{II}_{aq}] = 0.04$  mM, (C)  $[Fe^{II}_{aq}] = 0.06$  mM, and (D)  $[Fe^{II}_{aq}] = 0.08$

143 mM (Experimental initial concentrations in the Fenton solutions:  $[PMS] = 0.10$  mM and

144  $[HCO_3^-] = 0.30$  mM).

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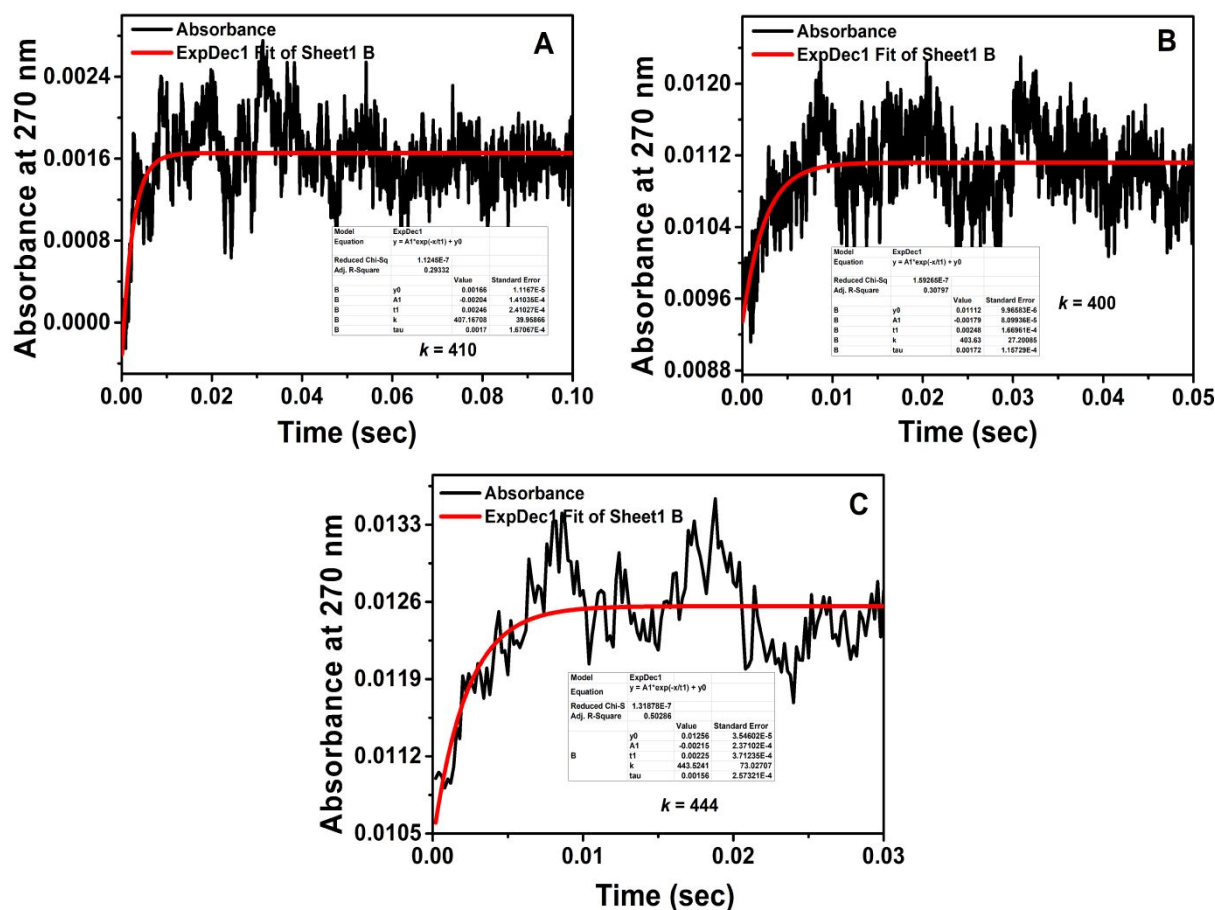
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154 **Figure S4.** Typical kinetic curves of the formation of Fe(III) during the reaction of Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>

155 with PMS at different concentrations of Fe<sup>II</sup><sub>aq</sub> under a constant concentration of high HCO<sub>3</sub><sup>-</sup>:

156 (A) [Fe<sup>II</sup><sub>aq</sub>] = 0.02 mM, (B) [Fe<sup>II</sup><sub>aq</sub>] = 0.04 mM and (C) [Fe<sup>II</sup><sub>aq</sub>] = 0.08 mM (Experimental initial

157 concentrations in the Fenton solutions: [PMS] = 0.10 mM and [HCO<sub>3</sub><sup>-</sup>] = 0.60 mM).

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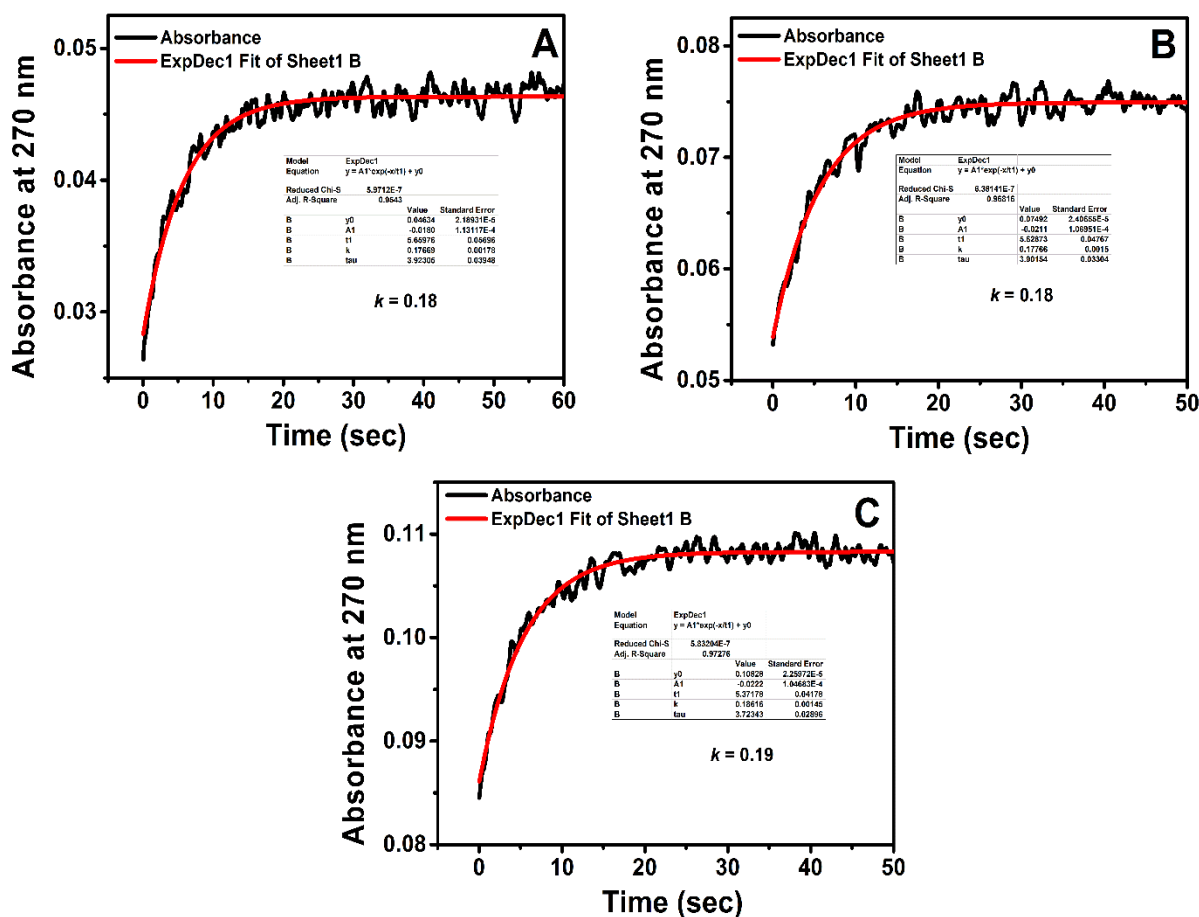
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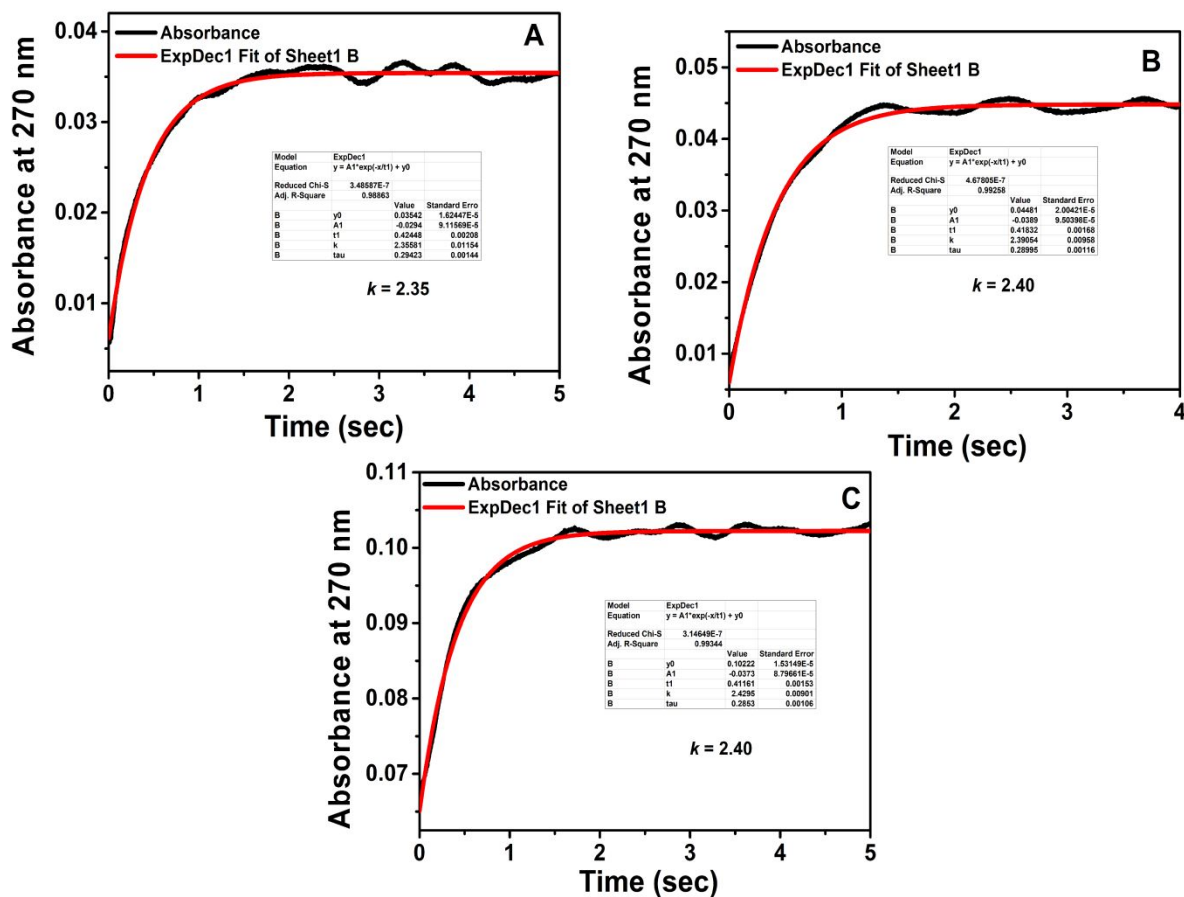
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 169 **Figure S5.** Typical kinetic curves of the formation of Fe(III) during the reaction of Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>  
 170 with PDS at different concentrations of Fe<sup>II</sup><sub>aq</sub> under a constant concentration of low HCO<sub>3</sub><sup>-</sup>.  
 171 (A) [Fe<sup>II</sup><sub>aq</sub>] = 0.10 mM, (B) [Fe<sup>II</sup><sub>aq</sub>] = 0.20 mM, and (C) [Fe<sup>II</sup><sub>aq</sub>] = 0.40 mM Fe<sup>II</sup><sub>aq</sub>. (Experimental  
 172 initial concentrations in the Fenton solutions: [PDS] = 1.0 mM, [HCO<sub>3</sub><sup>-</sup>] = 2.0 mM)

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184 **Figure S6.** Typical kinetic curves of the formation of  $Fe(III)$  during the reaction of  $Fe(H_2O)_6^{2+}$

185 with PDS at different concentrations of  $Fe^{II}_{aq}$  under a constant concentration of high  $HCO_3^-$ .

186 (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

187 initial concentrations in the Fenton solutions:  $[PDS] = 1.0$  mM,  $[HCO_3^-] = 5.0$  mM)

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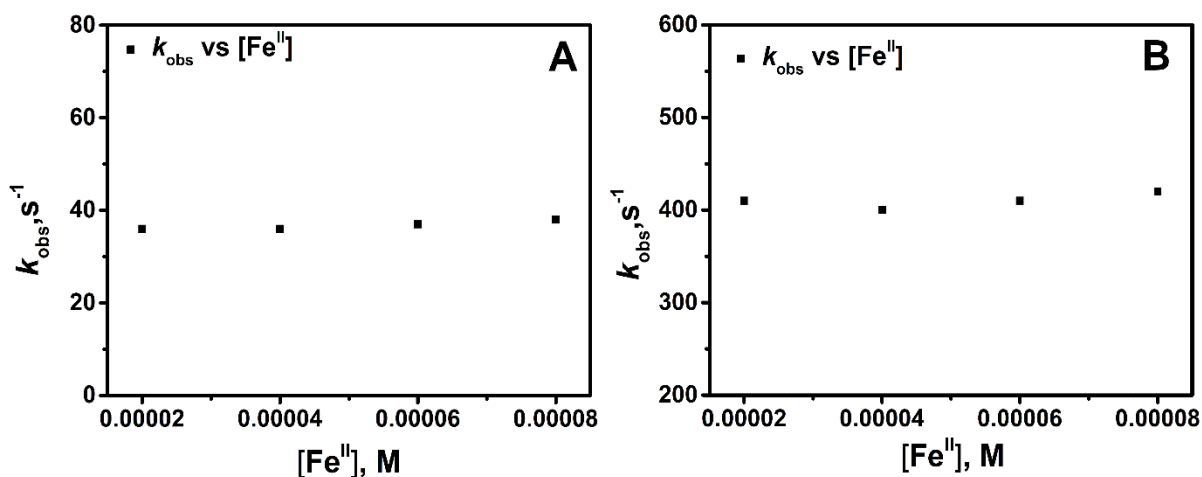
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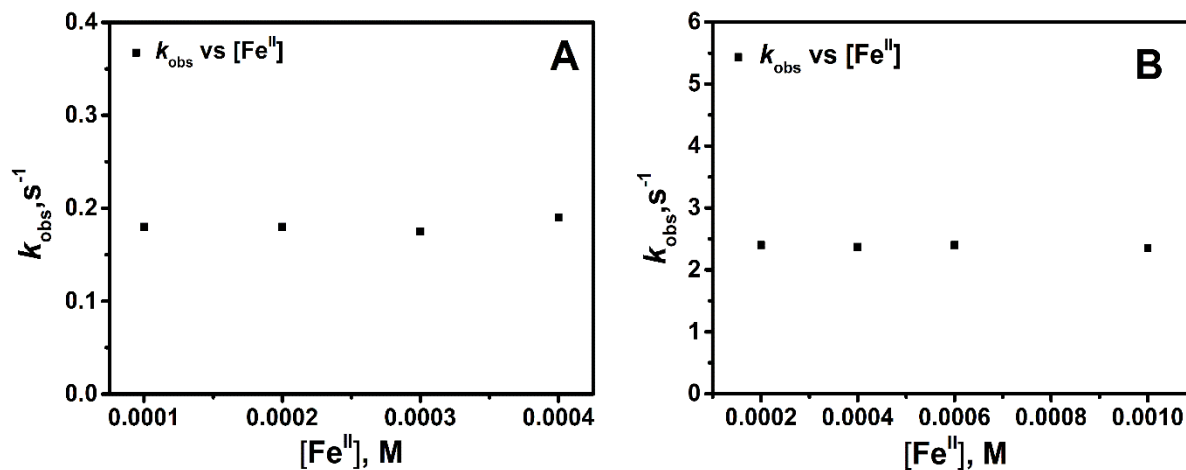
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202 **Figure S7.** Dependence of  $k_{\text{obs}}$  at pH 7.40 on the concentrations of  $\text{Fe}^{\text{II}}_{\text{aq}}$ , at a constant

203 concentration of PMS (A)  $[\text{HCO}_3^-] = 0.30 \text{ mM}$  (Low  $[\text{HCO}_3^-]$ ) and (B)  $[\text{HCO}_3^-] = 0.60 \text{ mM}$

204 (High  $[\text{HCO}_3^-]$ ). Here in both cases,  $[\text{PMS}] = 0.10 \text{ mM}$

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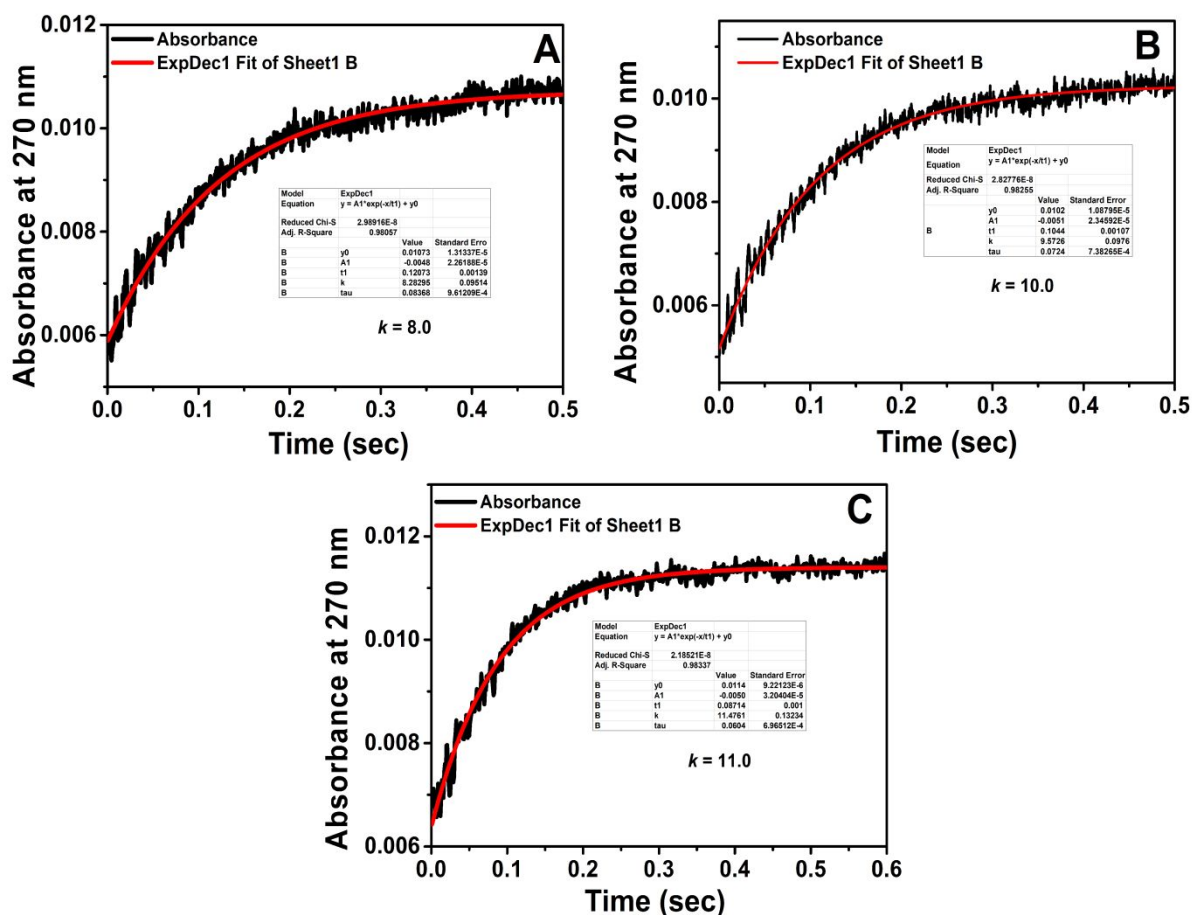
207 **Figure S8.** Dependence of  $k_{\text{obs}}$  at pH 7.40 on the concentrations of  $\text{Fe}^{\text{II}}_{\text{aq}}$ , at a constant

208 concentration of PDS (A)  $[\text{HCO}_3^-] = 2.0 \text{ mM}$  (Low  $[\text{HCO}_3^-]$ ) and (B)  $[\text{HCO}_3^-] = 5.0 \text{ mM}$  (High

209  $[\text{HCO}_3^-]$ ). Here in both cases,  $[\text{PDS}] = 1.0 \text{ mM}$

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213 **Figure S9.** Kinetic curves of the formation of Fe(III) during the reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  with  
 214 PMS in the absence of bicarbonate at different pH's (A) pH = 5.80, (B) pH = 7.0 and (C) pH  
 215 = 8.40. (Experimental initial concentrations in the Fenton solutions:  $[\text{PMS}] = 0.20 \text{ mM}$ ,  $[\text{Fe}^{\text{II}}_{\text{aq}}]$   
 216 =  $0.020 \text{ mM}$ )

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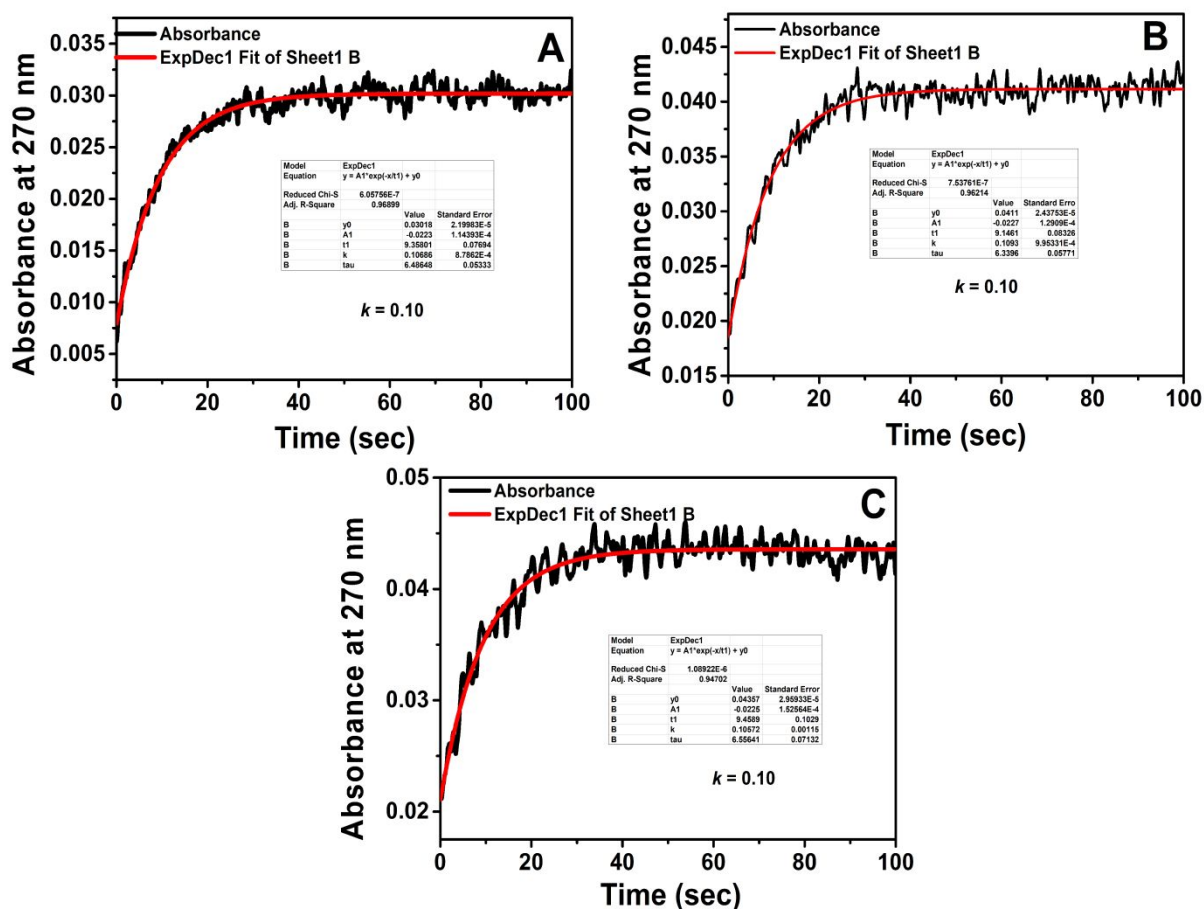
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227 **Figure S10.** Kinetic curves of the formation of Fe(III) during the reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  with  
 228 PDS in the absence of bicarbonate at different pH's (A) pH = 5.80, (B) pH = 7.0 and (C) pH  
 229 = 8.40. (Experimental initial concentrations in the Fenton solutions:  $[\text{PDS}] = 1.0 \text{ mM}$ ,  $[\text{Fe}^{\text{II}}_{\text{aq}}]$   
 230 = 0.10 mM)

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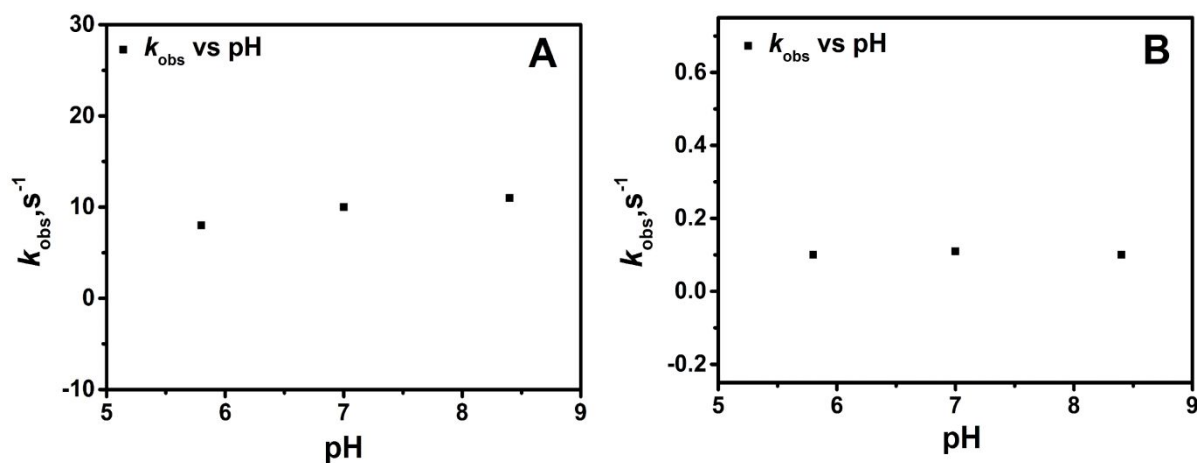
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239 **Figure S11.** Dependence of  $k_{\text{obs}}$  on the pH in the absence of bicarbonate at a constant

240 concentration of (A) PMS ( $[\text{PMS}] = 0.20 \text{ mM}$ ,  $[\text{Fe}^{\text{II}}_{\text{aq}}] = 0.020 \text{ mM}$ ) and (B) PDS ( $[\text{PDS}] =$

241  $1.0 \text{ mM}$ ,  $[\text{Fe}^{\text{II}}_{\text{aq}}] = 0.10 \text{ mM}$ )

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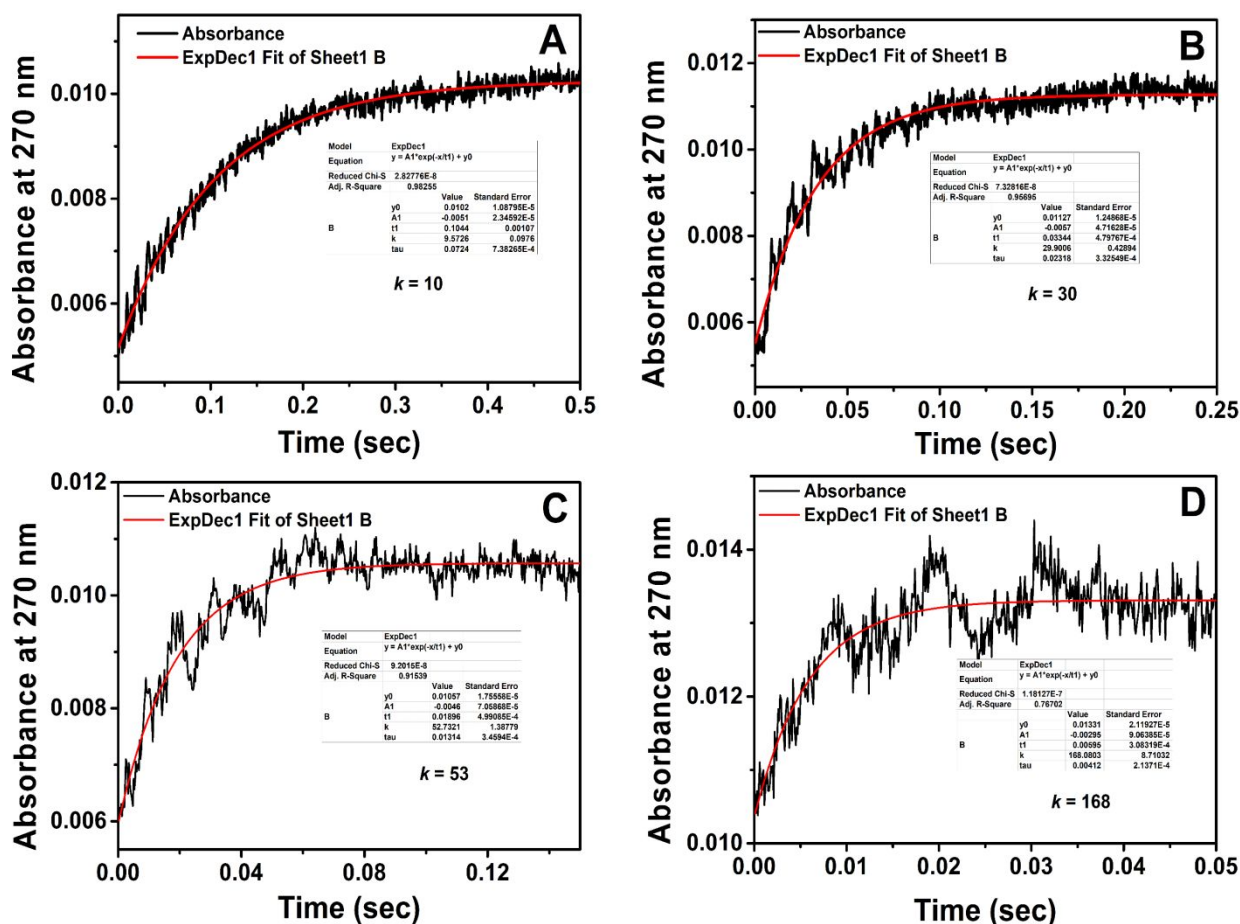
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258 **Figure S12.** Typical kinetic curve of the reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  with PMS in presence of excess

259 PMS taken by stopped flow instrument with different concentration of (A) 0 mM  $\text{HCO}_3^-$  (B)

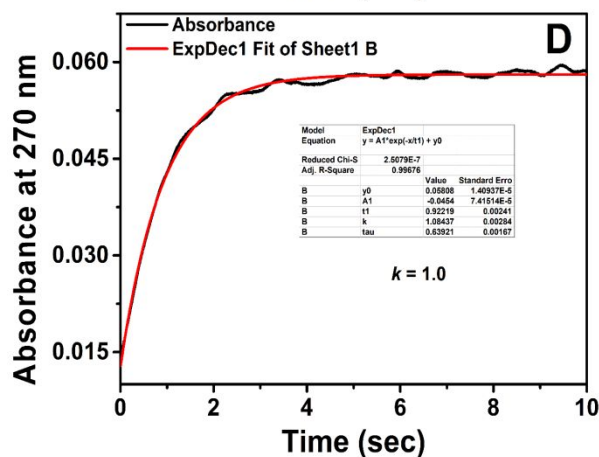
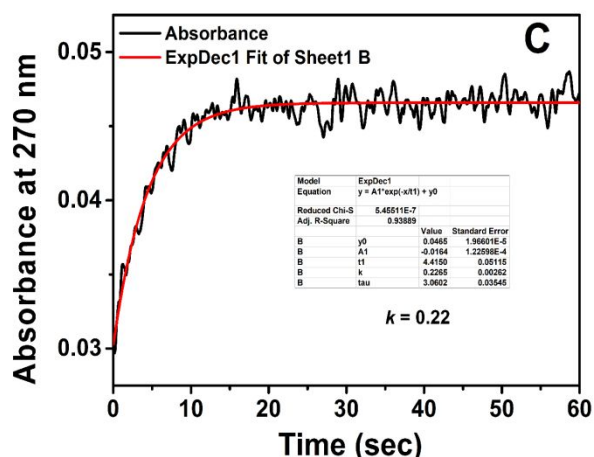
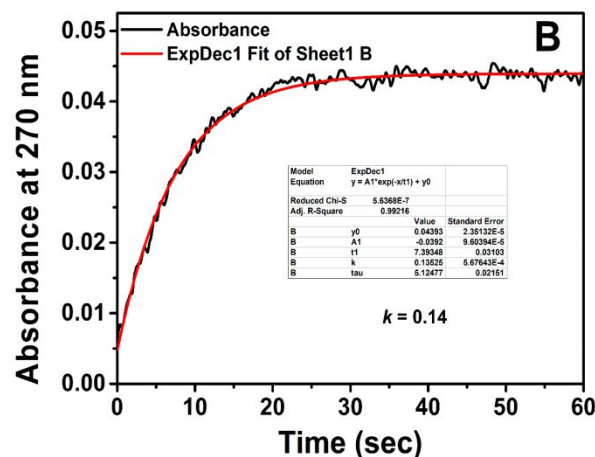
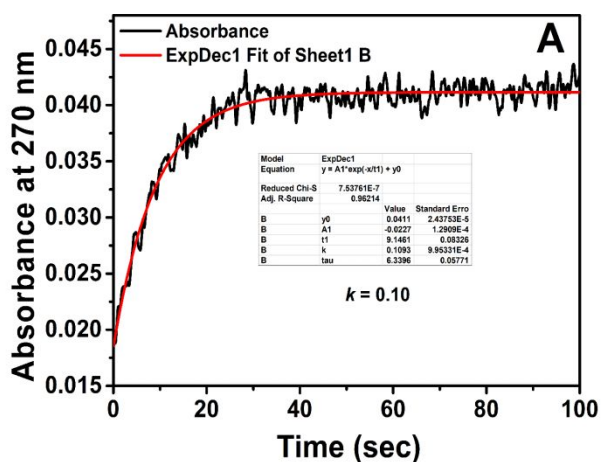
260 0.10 mM  $\text{HCO}_3^-$  (C) 0.20 mM  $\text{HCO}_3^-$  and (D) 0.40 mM  $\text{HCO}_3^-$ . The initial concentrations in

261 the Fenton solutions are  $[\text{Fe}^{\text{II}}] = 0.020$  mM,  $[\text{PMS}] = 0.20$  mM. The data of the conventional

262 spectrophotometric measurements were analyzed graphically, and the  $k$  values were

263 determined by fitting single exponential curves to the absorbance vs. time plots.

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267 **Figure S13.** Typical kinetic curve of the reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  with PDS in presence of excess  
 268 PDS taken by stopped flow instrument with different concentration of (A) 0 mM  $\text{HCO}_3^-$  (B)  
 269 1.0 mM  $\text{HCO}_3^-$  (C) 2.0 mM  $\text{HCO}_3^-$  and (D) 3.0 mM  $\text{HCO}_3^-$ . The initial concentrations in the  
 270 Fenton solutions are  $[\text{Fe}^{\text{II}}] = 0.10$  mM,  $[\text{PDS}] = 1.0$  mM.

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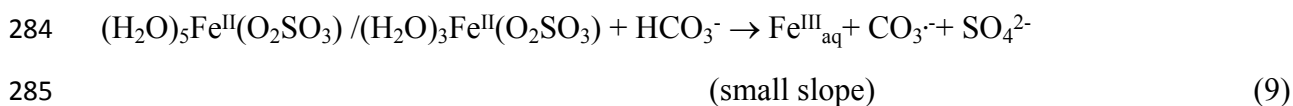
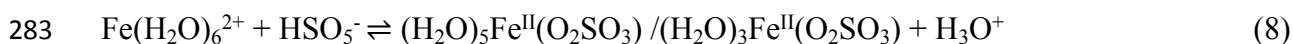
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280 **Text S1:**

281 ***Mechanism I:***

282 ***Small slope***



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

288 
$$\text{rate} = k_9 [(\text{H}_2\text{O})_5\text{Fe}^{\text{II}}(\text{O}_2\text{SO}_3) / (\text{H}_2\text{O})_3\text{Fe}^{\text{II}}(\text{O}_2\text{SO}_3)] [\text{HCO}_3^-] \quad (9'')$$

289 Since  $(\text{H}_2\text{O})_5\text{Fe}^{\text{II}}(\text{O}_2\text{SO}_3) / (\text{H}_2\text{O})_3\text{Fe}^{\text{II}}(\text{O}_2\text{SO}_3)$  is an intermediate, from eqtn (8),

290 
$$k_8 [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HSO}_5^-] = k_{-8} [(\text{H}_2\text{O})_5\text{Fe}^{\text{II}}(\text{O}_2\text{SO}_3) / (\text{H}_2\text{O})_3\text{Fe}^{\text{II}}(\text{O}_2\text{SO}_3)] \quad (8'')$$

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

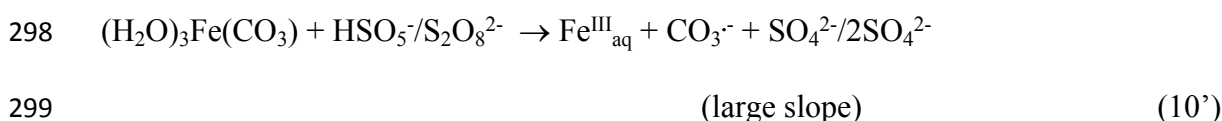
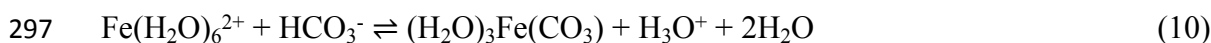
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$$[(\text{H}_2\text{O})_5\text{Fe}^{\text{II}}(\text{O}_2\text{SO}_3) / (\text{H}_2\text{O})_3\text{Fe}^{\text{II}}(\text{O}_2\text{SO}_3)] = K_8 [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HSO}_5^-]$$

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

294 
$$\text{rate} = k_9 K_8 [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HSO}_5^-] [\text{HCO}_3^-]$$

295

296 ***Large slope***



300 The overall rate law of this reaction is as follows:

301 
$$r = k_{10} [(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)] [\text{HSO}_5^- / \text{S}_2\text{O}_8^{2-}] \quad (10'')$$

302 Here,  $(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)$  is the intermediate formed. Rearranging the equilibrium rate equation

303 (10), the  $[(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)]$  is given by,

304 
$$[(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)] = K_{10} [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-]$$

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

306 
$$\text{rate} = k_{10} K_{10} [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-] [\text{HSO}_5^- / \text{S}_2\text{O}_8^{2-}]$$

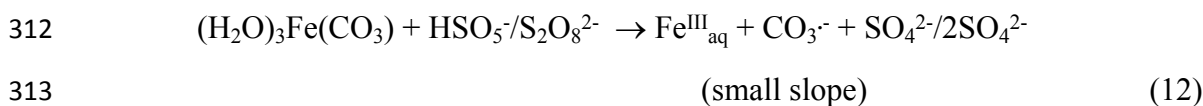
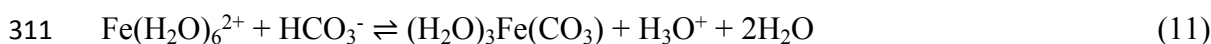
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308 **Text S2**

309 ***Mechanism II:***

310 ***Small slope***



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

315  $r = k_{12} [(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)] [\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}]$  (12')

316 Here,  $(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)$  is an intermediate

317 From (11),

318  $r_{\text{forward}} = r_{\text{backward}}$

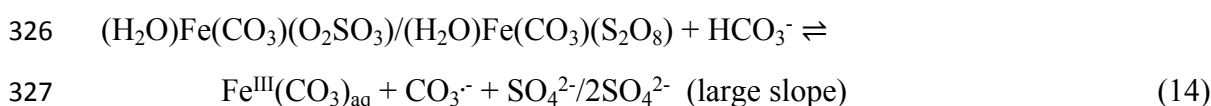
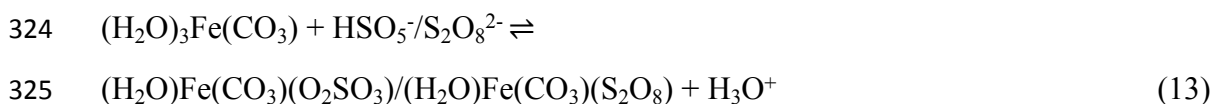
319  $k_{11} [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-] = k_{-11} [(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)]$  (12'')

320  $[(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)] = K_{11} [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-]$

321 Rearrange the Eq. (12') by substituting the value for  $[(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)]$ ,

322 **rate =  $k_{12} K_{11} [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-] [\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}]$**

323 ***Large slope***



328 Overall rate is as followed:

329  $r = k_{14} [(\text{H}_2\text{O})\text{Fe}(\text{CO}_3)(\text{O}_2\text{SO}_3)/(\text{H}_2\text{O})\text{Fe}(\text{CO}_3)(\text{S}_2\text{O}_8)] [\text{HCO}_3^-]$  (14')

330 Here  $(\text{H}_2\text{O})\text{Fe}(\text{CO}_3)(\text{O}_2\text{SO}_3)/(\text{H}_2\text{O})\text{Fe}(\text{CO}_3)(\text{S}_2\text{O}_8)$  is an intermediate

331 Hence, from Eq. (13)

332  $[(\text{H}_2\text{O})\text{Fe}(\text{CO}_3)(\text{O}_2\text{SO}_3)/(\text{H}_2\text{O})\text{Fe}(\text{CO}_3)(\text{S}_2\text{O}_8)] = K_{13} [(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)] [\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}]$   
 333 (14'')

334 Substitute the  $[(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)]$  and  $[(\text{H}_2\text{O})\text{Fe}(\text{CO}_3)(\text{O}_2\text{SO}_3)/(\text{H}_2\text{O})\text{Fe}(\text{CO}_3)(\text{S}_2\text{O}_8)]$  in (14')

335 **rate =  $k_{14} K_{13} K_{11} [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-]^2 [\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}]$**

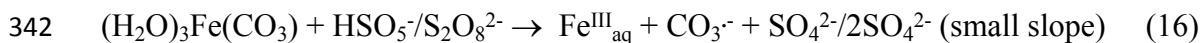
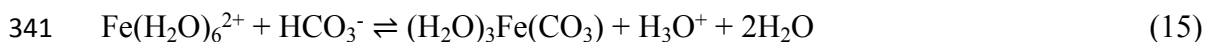
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338 **Text S3**

339 ***Mechanism III:***

340 ***Small slope***



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

344  $r = k_{16} [(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)] [\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}]$  (16')

345 From (15),

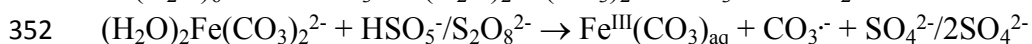
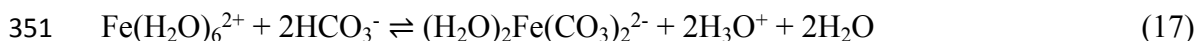
346  $[(\text{H}_2\text{O})_3\text{Fe}(\text{CO}_3)] = K_{15}[\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-]$

347 Eq. (16') may be rewritten as,

348 **rate =  $k_{16}K_{15}[\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-] [\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}]$**

349

350 ***Large slope***



354 Overall rate law (rds (18)) will be

355  $r = k_{18}[(\text{H}_2\text{O})_2\text{Fe}(\text{CO}_3)_2^{2-}] [\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}]$  (18')

356 From (17),

357  $[(\text{H}_2\text{O})_2\text{Fe}(\text{CO}_3)_2^{2-}] = k_{17} [\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-]^2 / k_{-17}$

358 Eq. (18') may be rewritten as,

359 **rate =  $k_{18}K_{17}[\text{Fe}(\text{H}_2\text{O})_6^{2+}] [\text{HCO}_3^-]^2 [\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}]$**

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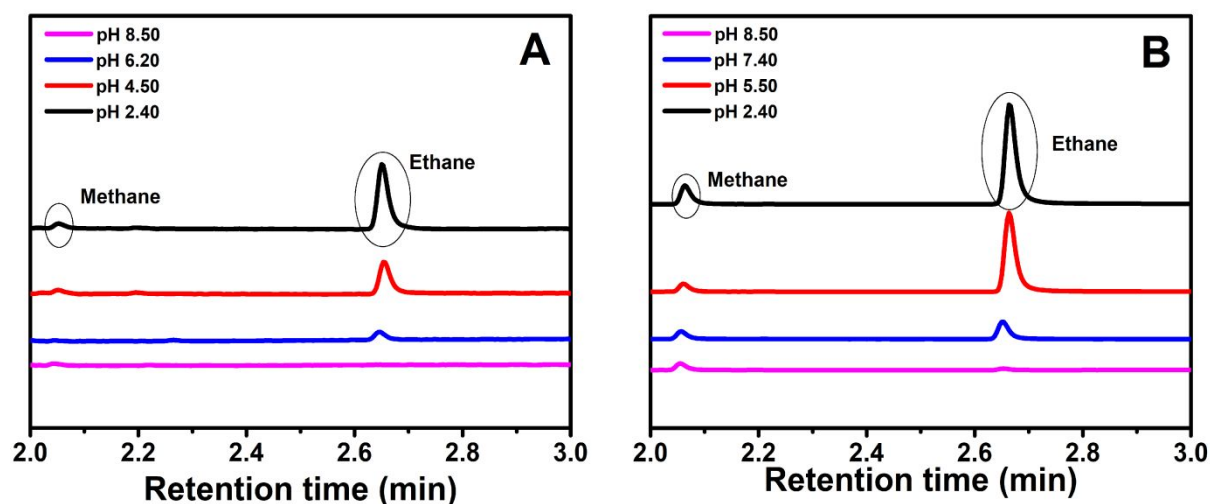
364

365

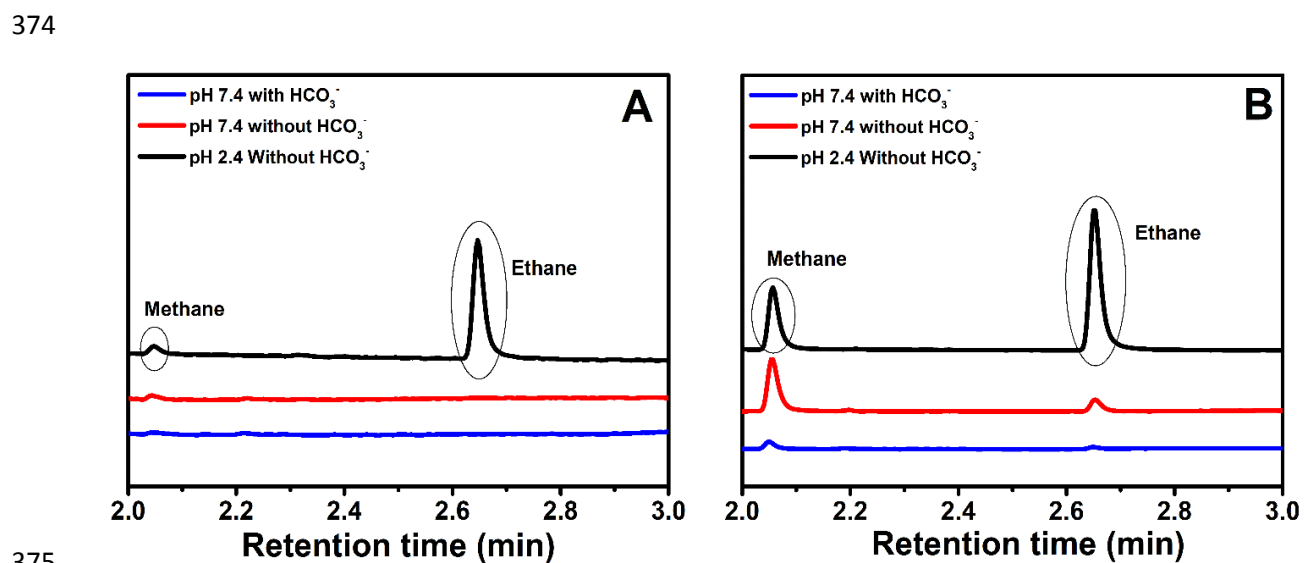
366

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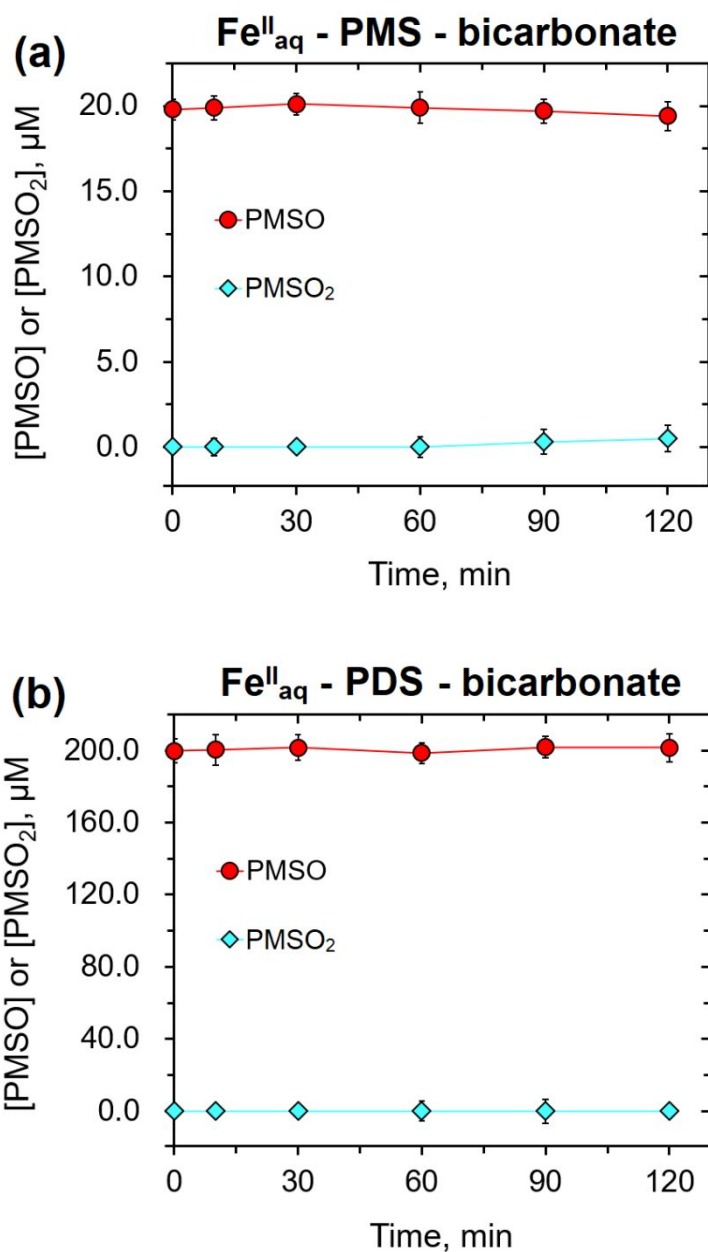
368



369  
 370 **Figure S14.** GC determination of methane and ethane with FID detector at four different pH  
 371 in the absence of  $\text{HCO}_3^-$  after the Fenton reaction of (A)  $\text{Fe}^{2+}$  and  $\text{HSO}_5^-$  and (B)  $\text{Fe}^{2+}$  and  
 372  $\text{S}_2\text{O}_8^{2-}$  in presence of excess  $\text{Fe}^{\text{II}}_{\text{aq}}$  and  $(\text{CH}_3)_2\text{SO}$ .  $[\text{Fe}^{\text{II}}] = 0.50 \text{ mM}$ ,  $[\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}] = 0.10 \text{ mM}$ ,  
 373  $[(\text{CH}_3)_2\text{SO}] = 25.0 \text{ mM}$ .



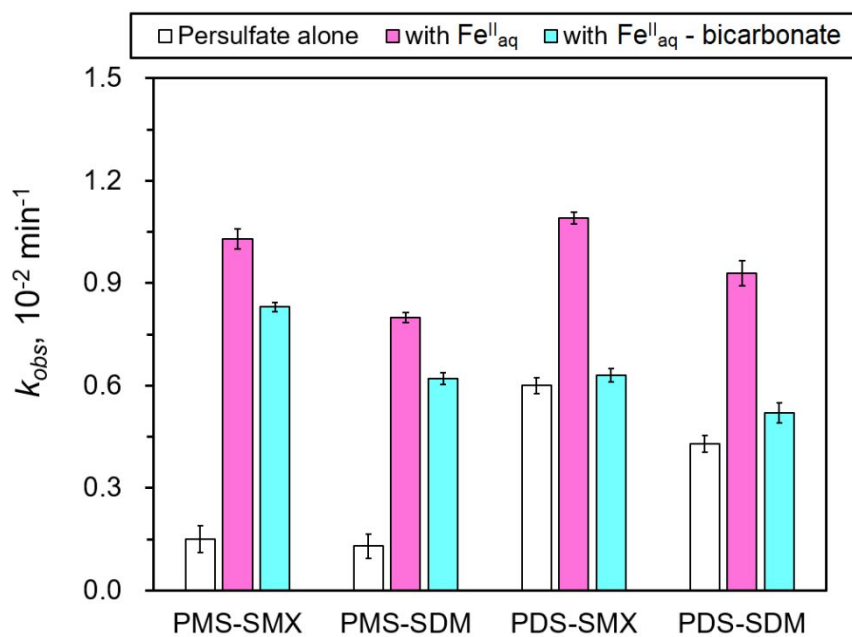
375  
 376 **Figure S15.** GC determination of methane and ethane with FID detector at pH 2.2 and at neutral  
 377 pH in the absence and presence of  $\text{HCO}_3^-$  after the Fenton reaction of (A)  $\text{Fe}^{2+}$  and  $\text{HSO}_5^-$  and  
 378 (B)  $\text{Fe}^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$  in presence of excess  $\text{Fe}^{\text{II}}_{\text{aq}}$  and  $(\text{CH}_3)_2\text{SO}$ .  $[\text{Fe}^{\text{II}}] = 0.50 \text{ mM}$ ,  $[\text{HSO}_5^-/\text{S}_2\text{O}_8^{2-}] = 0.10 \text{ mM}$ ,  
 379  $[(\text{CH}_3)_2\text{SO}] = 25.0 \text{ mM}$ ,  $[\text{HCO}_3^-] = 3.0 \text{ mM}$ .  
 380



381

382 **Figure S16.** The changes in concentrations of PMSO and PMSO<sub>2</sub> in the (a)  $\text{Fe}^{\text{II}}_{\text{aq}}$  - PMS and  
 383 (b)  $\text{Fe}^{\text{II}}_{\text{aq}}$  - PDS systems in presence of high bicarbonate concentrations (Initial pH = 7.0. The  
 384 PMS system:  $[\text{PMS}]_0 = 0.04 \text{ mM}$ ;  $[\text{Fe}^{\text{II}}_{\text{aq}}]_0 = 0.2 \text{ mM}$ ;  $[\text{bicarbonate}]_0 = 20.0 \text{ mM}$ ;  $[\text{PMSO}]_0 =$   
 385  $20.0 \mu\text{M}$ . The PDS system:  $[\text{PMS}]_0 = 1.0 \text{ mM}$ ;  $[\text{Fe}^{\text{II}}_{\text{aq}}]_0 = 2.0 \text{ mM}$ ;  $[\text{bicarbonate}]_0 = 200.0 \text{ mM}$ ;  
 386  $[\text{PMSO}]_0 = 200.0 \mu\text{M}$ )).

387



388

389 **Figure S17.** The pseudo-first-order rate constants of the degradation of SMX and SDM by  
 390 different persulfate systems ( $[\text{SMX}]_0 = [\text{SDM}]_0 = 5.0 \mu\text{M}$ ; initial pH = 7.0. The PMS system:  
 391  $[\text{PMS}]_0 = 0.04 \text{ mM}$ ;  $[\text{Fe}^{\text{II}}_{\text{aq}}]_0 = 0.2 \text{ mM}$ ;  $[\text{bicarbonate}]_0 = 0.5 \text{ mM}$ . The PDS system:  $[\text{PDS}]_0 =$   
 392  $1.0 \text{ mM}$ ;  $[\text{Fe}^{\text{II}}_{\text{aq}}]_0 = 2.0 \text{ mM}$ ;  $[\text{bicarbonate}]_0 = 5.0 \text{ mM}$ ).

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