

## Supporting Information

### Transition Metal Ion-Assisted Photochemical Generation of Alkyl Halides and Hydrocarbons from Carboxylic Acids

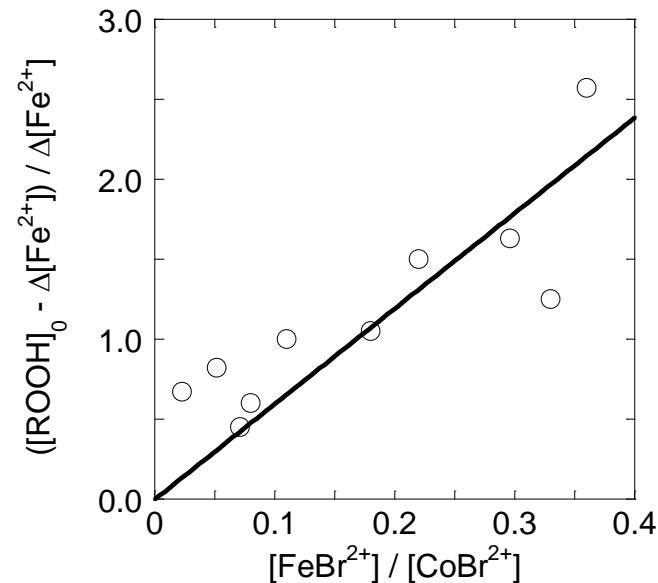
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**Fig. S1.** Plot of product ratios  $[\text{ROOH}]_{\text{tot}} - \Delta[\text{Fe}^{2+}] / \Delta[\text{Fe}^{2+}]$  vs.  $[\text{FeBr}^{2+}] / [(\text{NH}_3)_5\text{CoBr}^{2+}]$  according to eq 15 for the  $\cdot\text{CH}_3/\text{FeBr}^{2+}$  reaction

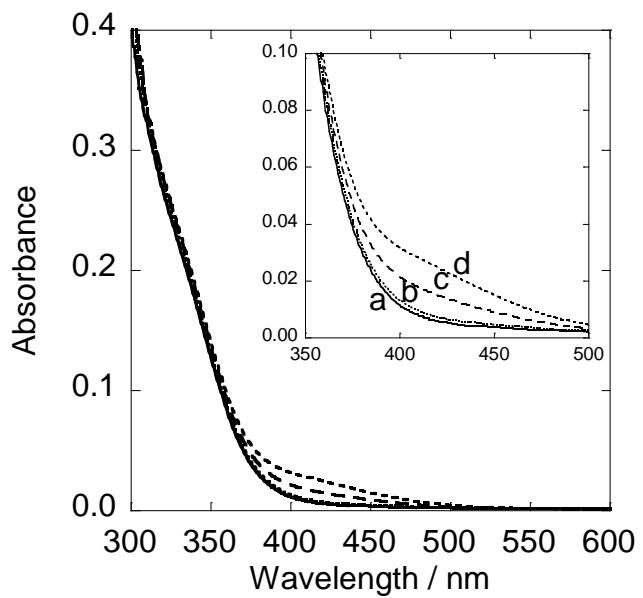
**Fig. S2.** UV-vis absorption spectra of  $\text{Fe}^{3+}/\text{C}_2\text{H}_5\text{CO}_2\text{H}/\text{Br}^-$

**Fig. S3.** UV-vis absorption spectra of  $\text{Fe}^{3+}/\text{C}_2\text{H}_5\text{CO}_2\text{H}/\text{Cl}^-$

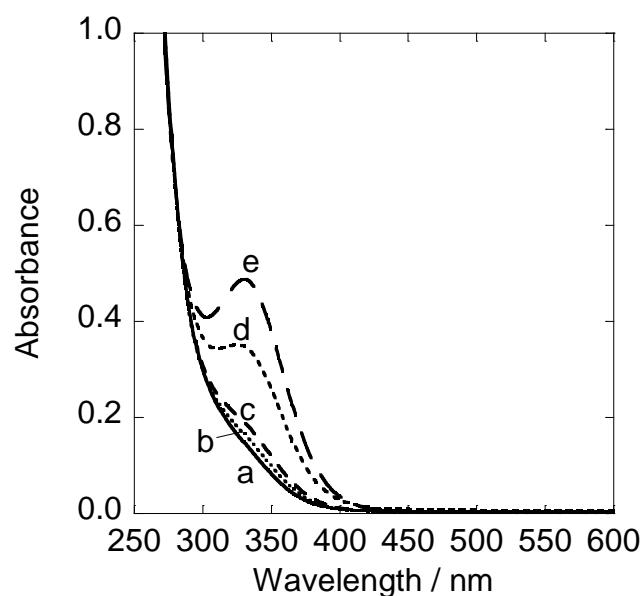


**Figure S1.** Plot of product ratios  $[\text{ROOH}]_0 - \Delta[\text{Fe}^{2+}] / \Delta[\text{Fe}^{2+}]$  vs.  $[\text{FeBr}^{2+}] / [(\text{NH}_3)_5\text{CoBr}^{2+}]$  according to eq 15. R =  $(\text{CH}_3)_3\text{C}$ . Concentrations: 0.57 – 0.62 mM  $\text{Fe}^{2+}$ , 0.47 – 0.50 mM  $(\text{CH}_3)_3\text{COOH}$ , 0.10 – 0.23 mM  $\text{FeBr}^{2+}$ , and 0.5 – 2.2 mM  $(\text{NH}_3)_5\text{CoBr}^{2+}$ .

The plotted concentrations of  $\text{FeBr}^{2+}$  and  $(\text{NH}_3)_5\text{CoBr}^{2+}$  are the averages for each run.



**Figure S2.** UV-vis absorption spectra (0.1 cm path length) of 7.1 mM Fe<sup>3+</sup> + 55 mM propionic acid + 5 mM Br<sup>-</sup> (a), + 10 mM Br<sup>-</sup> (b), + 50 mM Br<sup>-</sup> (c), 100 mM Br<sup>-</sup> (d). pH = 1.85 at pH = 1.85 and  $\mu$  = 0.2 M.



**Figure S3.** UV-vis absorption spectra (0.1 cm path length) of 7.1 mM  $\text{Fe}^{3+}$  + 55 mM propionic acid (a), + 5 mM  $\text{Cl}^-$  (b), + 10 mM  $\text{Cl}^-$  (c), + 50 mM  $\text{Cl}^-$  (d), and 100 mM  $\text{Cl}^-$  (e) at  $\text{pH} = 1.85$  and  $\mu = 0.2 \text{ M}$ .