

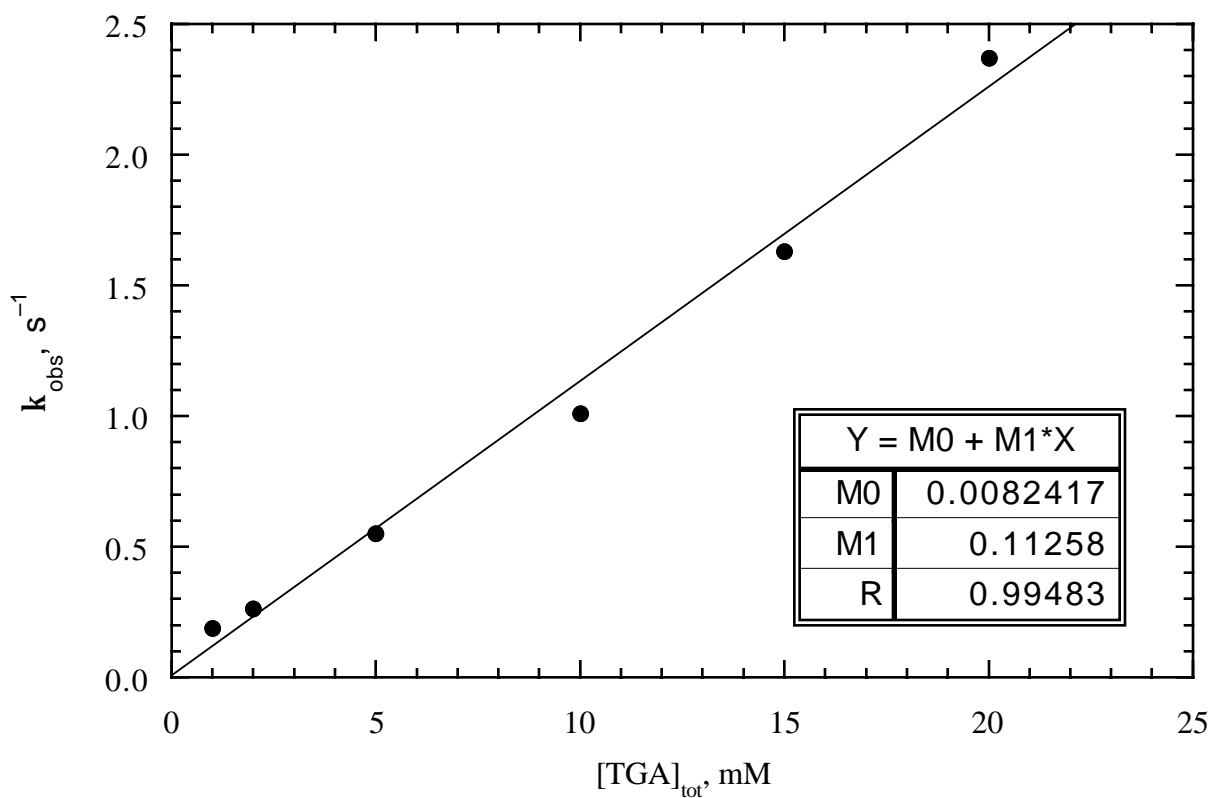
## Supplementary Material

**Table S-1.** Pseudo-first-order rate constants for the oxidation of TGA by  $[\text{IrCl}_6]^{2-}$ .

[TGA] <sub>0</sub> , M	[Ir(IV)] <sub>0</sub> , mM	[bathophen], mM	buffer	$\mu$ , M	pH	$k_{\text{obs}}$ , s <sup>-1</sup>
0.02	0.1	0.10	acetate	0.12	4.61	4.78
0.02	0.1	0.4	acetate	0.12	4.57	2.67
0.02	0.1	0.7	acetate	0.12	4.58	2.25
0.02	0.1	1.0	acetate	0.12	4.56	1.92
$1 \times 10^{-2}$	0.01	1.0	acetate	0.11	4.75	1.11
$1 \times 10^{-2}$	0.02	1.0	acetate	0.11	4.71	1.05
$1 \times 10^{-2}$	0.04	1.0	acetate	0.11	4.72	1.05
$1 \times 10^{-2}$	0.06	1.0	acetate	0.11	4.70	1.08
$1 \times 10^{-2}$	0.08	1.0	acetate	0.11	4.68	1.10
$1 \times 10^{-2}$	0.1	1.0	acetate	0.11	4.68	1.13
$1 \times 10^{-3}$	0.1	1.0	acetate	0.10	4.57	0.189
$2 \times 10^{-3}$	0.1	1.0	acetate	0.10	4.53	0.264
$5 \times 10^{-3}$	0.1	1.0	acetate	0.11	4.54	0.553
$1 \times 10^{-2}$	0.1	1.0	acetate	0.11	4.56	1.01
$1.5 \times 10^{-2}$	0.1	1.0	acetate	0.12	4.57	1.63
$2.0 \times 10^{-2}$	0.1	1.0	acetate	0.12	4.60	2.37
$1 \times 10^{-3}$	0.02	5	perchlorate	0.10	2.5	0.015
$1 \times 10^{-3}$	0.02	5	perchlorate	0.10	2.80	0.0285
$1 \times 10^{-3}$	0.02	5	perchlorate	0.10	3.21	0.056
$1 \times 10^{-2}$	0.1	1.0	perchlorate	0.11	3.18	0.321
$1 \times 10^{-2}$	0.1	1.0	perchlorate	0.11	3.33	0.370
$1 \times 10^{-2}$	0.1	1.0	perchlorate	0.11	3.48	0.432

$1 \times 10^{-2}$	0.1	1.0	perchlorate	0.11	3.60	0.489
$1 \times 10^{-2}$	0.1	1.0	perchlorate	0.11	3.77	0.589
$1 \times 10^{-2}$	0.1	1.0	perchlorate	0.10	3.97	0.707
$5 \times 10^{-3}$	0.1	1.0	perchlorate	0.10	3.74	0.362
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	3.81	0.402
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	4.09	0.464
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	4.29	0.519
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	4.49	0.579
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	4.63	0.84
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	4.70	0.73
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	4.89	0.78
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	5.12	0.92
$5 \times 10^{-3}$	0.1	1.0	acetate	0.10	5.43	1.37
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.21	5.56	1.47
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.22	5.59	3.36
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.23	6.08	6.43
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.25	6.53	15.9
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.27	6.90	36.5
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.28	7.17	57.7
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.25	6.73	16.84
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.26	6.76	24.6
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.27	6.96	37.03
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.28	7.20	64.8
$5 \times 10^{-3}$	0.1	1.0	phosphate	0.29	7.52	137
$2 \times 10^{-4}$	0.02	1.0	borate	0.10	8.60	38.4
$2 \times 10^{-4}$	0.02	1.0	borate	0.10	8.62	40.2
$2 \times 10^{-4}$	0.02	1.0	borate	0.10	8.78	50.3

$2 \times 10^{-4}$	0.02	1.0	borate	0.10	8.93	67.8
$2 \times 10^{-4}$	0.02	1.0	borate	0.10	9.08	88.0
$2 \times 10^{-4}$	0.02	1.0	borate	0.10	9.23	113



**Figure S-1.** Dependence of the pseudo-first-order rate constant ( $k_{\text{obs}}$ ) on  $[\text{TGA}]_{\text{tot}}$ . The slope of the line is  $113 \text{ M}^{-1} \text{ s}^{-1}$ .  $[\text{Ir(IV)}]_0 = 1 \times 10^{-4} \text{ M}$ ,  $[\text{bathophen}] = 1 \times 10^{-3} \text{ M}$ , NaOAc-HOAc buffer ( $\mu = 0.10 \text{ M}$ ),  $\text{pH} = 4.53 \sim 4.60$ , and  $[\text{TGA}]_0 = 1 \times 10^{-3} \sim 2 \times 10^{-2} \text{ M}$ .