Supplementary Materials for:

Oxidations of Benzhydrazide and Phenylacetic Hydrazide by Hexachloroiridate(IV): Reaction Mechanism and Structure-Reactivity Relationship

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One supporting table (Table S1) and ten supporting figures (Figures S1-S10) are included in Supplementary Materials

Hydrazide	pH	$k'/M^{-1}s^{-1}$
BH	0.11	1.49 ± 0.05
	0.51	3.5 ± 0.1
	0.81	6.3 ± 0.2
	1.11	13.0 ± 0.3
	1.51	32.4 ± 0.8
	1.81	66.3 ± 1.3
	2.11	120 ± 4
	2.41	218 ± 6
	3.12	983 ± 30
	3.45	$(1.36 \pm 0.04) \ge 10^3$
	3.76	$(1.67 \pm 0.05) \ge 10^3$
	3.96	$(1.85 \pm 0.04) \ge 10^3$
	4.48	$(2.07 \pm 0.05) \ge 10^3$
	4.85	$(2.16 \pm 0.05) \ge 10^3$
	5.14	$(2.17 \pm 0.05) \ge 10^3$
	5.70	$(2.26 \pm 0.05) \ge 10^3$
	6.25	$(2.78 \pm 0.06) \ge 10^3$
	6.59	$(2.99 \pm 0.06) \ge 10^3$
	6.82	$(3.59 \pm 0.07) \ge 10^3$
	7.06	$(4.55 \pm 0.09) \ge 10^3$
	7.28	$(6.02 \pm 0.12) \ge 10^3$
	7.58	$(1.02 \pm 0.03) \ge 10^4$
	7.98	$(2.09 \pm 0.03) \ge 10^4$
	8.49	$(5.06 \pm 0.08) \ge 10^4$
	8.93	$(1.52 \pm 0.04) \ge 10^5$
	9.41	$(4.08 \pm 0.08) \ge 10^5$
	9.53	$(4.23 \pm 0.08) \ge 10^5$
	9.95	$(1.26 \pm 0.02) \ge 10^6$
	10.46	$(2.9 \pm 0.1) \ge 10^6$
РАН	0.16	0.50 ± 0.01
	0.41	1.01 ± 0.02
	0.81	2.30 ± 0.05
	1.11	5.5 ± 0.1

Table S1. Observed second-order rate constants k' for oxidations of BH and PAH by $[IrCl_6]^{2-}$ as a function of pH at 25.0 °C and 1.0 M ionic strength.

1.41	9.3 ± 0.2
1.81	20.8 ± 0.5
2.11	39.8 ± 0.9
2.41	71.3 ± 2.5
3.15	313 ± 6
3.48	411 ± 9
3.77	458 ± 9
4.03	516 ± 6
4.43	537 ± 7
4.82	580 ± 8
5.09	613 ± 9
5.74	630 ± 9
6.29	652 ± 9
6.55	768 ± 15
6.84	864 ± 16
7.30	$(1.06 \pm 0.02) \ge 10^3$
7.63	$(1.67 \pm 0.04) \ge 10^3$
8.46	$(3.73 \pm 0.07) \ge 10^3$
8.93	$(1.09 \pm 0.02) \ge 10^4$
9.41	$(3.02\pm0.06) \ge 10^4$
9.95	$(8.9 \pm 0.2) \ge 10^4$
10.46	$(2.25 \pm 0.04) \ge 10^5$
11.12	$(8.0 \pm 0.2) \ge 10^5$
11.78	$(3.10 \pm 0.06) \ge 10^6$





Benz(o)hydrazide (BH)

Phenylacetic hydrazide (PAH)

NH-NH₂



Isoniazid (Isonicotinic hydrazide, INH)

Nicotinic hydrazide (NH)



2-Furoic hydrazide (FH)

Figure S1. Structures of hydrazides including aryl hydrazides BH, INH, NH and FH.



Figure S2. Kinetic traces acquired from the data points in Figure 1 in the text. The solid curves were obtained from the best fits of the experimental data to Equation (1).



Figure S3. Spectrophotometric titration: absorbance at 488 nm for a series of reaction mixtures of $[IrCl_6]^{2-}$ with BH in which $[BH]_{tot}$ was changed from 0 to 0.40 mM and [Ir(IV)] = 0.40 mM was kept constant. Reaction medium: phosphate of pH 6.31 and $\mu = 1.0$ M. Reaction time: about 5 min for each of the mixtures at room temperature.



Figure S4. Spectrophotometric titration: absorbance at 488 nm for a series of reaction mixtures of $[IrCl_6]^{2-}$ with BH in which $[BH]_{tot}$ was changed from 0 to 0.40 mM and [Ir(IV)] = 0.40 mM was kept constant. Reaction medium: $[H^+] = 0.010$ M, and $\mu = 1.0$ M. Reaction time: about 2 h for each of the mixtures at room temperature.



Figure S5. Spectrophotometric titration: absorbance at 488 nm for a series of reaction mixtures of $[IrCl_6]^{2-}$ with PAH in which $[PAH]_{tot}$ was varied from 0 to 0.40 mM and [Ir(IV)] = 0.40 mM was retained constant. Reaction medium: phosphate buffer of pH 6.31 and $\mu = 1.0$ M. Reaction time: about 30 min for each of the mixtures at room temperature.



Figure S6. Spectrophotometric titration: absorbance at 488 nm for a series of reaction mixtures of $[IrCl_6]^{2-}$ with PAH in which $[PAH]_{tot}$ was varied from 0 to 0.40 mM and [Ir(IV)] = 0.40 mM was retained constant. Reaction medium: $[H^+] = 0.010$ M, and $\mu = 1.0$ M. Reaction time: about 2 h for each of the mixtures at room temperature.



Figure S7. (Top): BH species *versus* pH distribution diagram at 25.0 °C and $\mu = 1.0$ M, which was calculated by use of $pK_{a1} = 3.37$ and $pK_{a2} = 12.6$ in Table 2. (**Bottom**): Reactivity *versus* pH distribution diagram for the BH species in the reduction of $[IrCl_6]^{2-}$; the above pK_a values and $k_1 = 0.046$, $k_2 = 597$, and $k_3 = 1.47 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ in Table 1 were utilized in the calculations. Species I – III of BH are described in Figure 7.



Figure S8. (**Top**): PAH species *versus* pH distribution diagram at 25.0 °C and $\mu = 1.0$ M, which was calculated by use of $pK_{a1} = 3.24$ and $pK_{a2} = 11.7$ in Table 2. (**Bottom**): Reactivity *versus* pH distribution diagram for the PAH species in the reduction of $[IrCl_6]^{2-}$; the above pK_a values and $k_1 = 0$, $k_2 = 157$, and $k_3 = 1.19 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ in Table 1 were utilized in the calculations. Species I – III of PAH are described in Figure 7.



Figure S9. (Top): Linear plots of k_{obsd} versus [BH]_{tot} in a buffer of pH 5.10. (Bottom): Eyring plot of the rate-determining step described by k_2 in the oxidation of BH by [IrCl₆]^{2–}.



Figure S10. (Top): Linear plots of k_{obsd} versus [PAH]_{tot} in a buffer of pH 5.74. (Bottom): Eyring plot of the rate-determining step described by k_2 in the oxidation of PAH by [IrCl₆]^{2–}.