

Trace Water Affects Tris(pentafluorophenyl)borane Catalytic Activity in the Piers-Rubinsztajn Reaction

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Supporting Information

Table S1 System Parameters used on the Karl-Fischer Titrator – measurement of trace water in B(C₆F₅)₃ solutions and PR reagent solutions (RS).

	BCF	RS		BCF	RS
Sample Parameters			Control Parameters		
Minimum (g)	0	0	Current (μA)	2	2
Maximum (g)	2.000	5.000	End Point (mV)	100	100
Entry	during	before	Generation speed	fast	Normal
Mixing Parameters			Termination Parameters		
Speed (%)	40	40	Max time (s)	300	300
Mix time (s)	10	15	Drift stop	Relative	Relative
Auto Start	No	No	Drift (μg min ⁻¹)	3	3

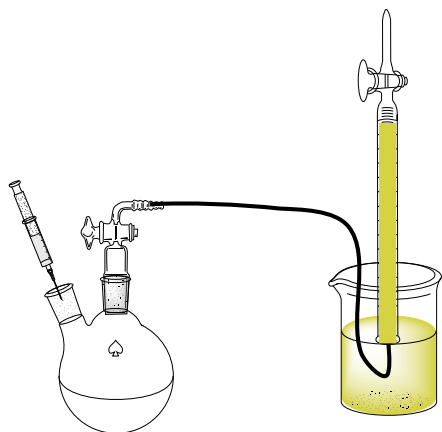


Figure S1 Apparatus to measure rate of gas evolution.

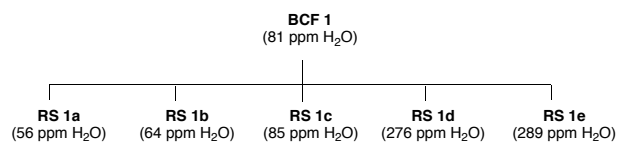


Table 1
Figure S3

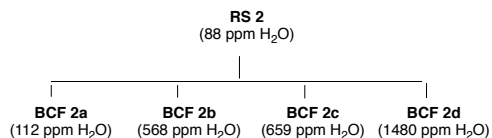


Table 2
Figure 5
(Sigma-Aldrich BCF)

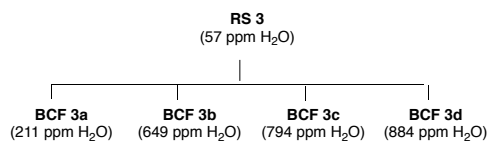


Table 2
Figure 5
(Alfa-Aesar BCF)

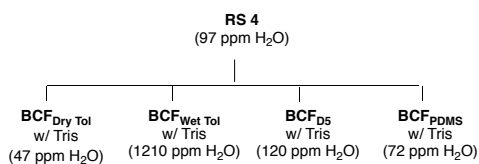


Table 3

Figure S2 PR Reaction Flow Chart – different numbers represent different stock solutions where different letters designate different water concentrations of the same (numbered) solution

Table S2 PR reaction times (with error) when [H₂O]_{BCF} in catalyst solution is held constant and [H₂O]_{RS} in reagent solution is varied (Table 1 expanded).

Solution	BCF1	RS1a	RS1b	RS1c	RS1d	RS1e
[H ₂ O] (ppm)	81	54	54	80	280	316
KF	76	57	69	85	264	293
	85	56	68	90	284	256
Average [H ₂ O] (ppm)	81	56	64	85	276	289
Error (ppm)	3	1	5	3	6	17
PR Reaction Time (s)	N/A	28.4	29.5	28.2	31.3	32.7
	N/A	31.7	30.2	30.8	30.2	32.4
	N/A	29.9	31.2	34.6	34.6	34.1
Average time (s)	N/A	30.0	30.3	31.2	32.0	33.1
Error (s)	N/A	1.0	0.5	1.9	1.3	0.5

Table S3 PR induction and reaction times when the $[H_2O]_{RS}$ in a model reagent solution is held constant and the $[H_2O]_{BCF}$ in the catalyst solution (Sigma-Aldrich $B(C_6F_5)_3$) varies (Table 2 expanded).

Solution	RS2	BCF2a	BCF2b	BCF 2c	BCF 2d
[H ₂ O] (ppm)	79	112	567	687	1426
KF readings	105	103	554	648	1523
	80	120	582	642	1491
Average [H ₂ O] (ppm)	88	112	568	659	1480
Error (ppm)	8	5	8	14	29
PR Induction Time (s)	-	0	9.7	11.9	43.8
	-	0	10.8	11.9	38.5
	-	0	11.0	12.5	39.8
Average time (s)	-	0	11.0	12.1	40.7
Error (s)	-	0	0.4	0.2	1.6
PR Reaction Time (s)	-	19.4	25.7	24.1	27.0
	-	16.6	22.8	25.3	27.1
	-	18.6	28.7	27.7	23.5
Average time (s)	-	18.2	25.7	25.7	25.9
Error (s)	-	0.9	1.7	1.1	1.2

Table S4 PR induction and reaction times when the $[H_2O]_{RS}$ in a model reagent solution is held constant and the $[H_2O]_{BCF}$ in the catalyst solution (Alfa-Aesar $B(C_6F_5)_3$) varies (Table 2 expanded).

Solution	RS3	BCF3a	BCF3b	BCF 3c	BCF 3d
[H ₂ O] (ppm)	49	209	643	797	855
	65	210	630	780	904
	58	214	676	804	895
Average [H ₂ O] (ppm)	57	211	649	794	885
Error (ppm)	5	2	14	7	15
PR Induction Time (s)	N/A	5.9	17.1	24.7	34.0
	N/A	10.3	10.4	30.0	27.7
	N/A	9.7	16.9	24.3	38.5
Average time (s)	N/A	8.6	14.8	26.4	33.4
Error (s)	N/A	1.4	2.2	1.8	3.1
PR Reaction Time (s)	N/A	20.2	27.2	21.6	23.0
	N/A	23.9	20.9	27.7	25.7
	N/A	23.4	25.7	20.9	27.9
Average time (s)	N/A	22.5	24.6	23.4	25.5
Error (s)	N/A	1.2	1.9	2.2	1.4

Table S5 PR induction and reaction times when $B(C_6F_5)_3$ solution contains tris(trimethylsiloxy)silane in various solvents (Table 3 expanded).

Solution/ BCF Solvent	Reagent	Dry Toluene	Wet Toluene	D₅	PDMS
[H ₂ O] (ppm)	110	29	1252	122	66
	74	26	1185	111	76
	108	57	1194	128	73
Average [H ₂ O] (ppm)	97	47	1210	120	72
Error (ppm)	12	5	21	5	3
PR Induction Time (s)	N/A	0	77.7	0	0
	N/A	0	76.6	0	0
	N/A	0	76.6	0	0
Average PR Induction Time (s)	N/A	0	77.0	0	0
Error (s)	N/A	N/A	0.4	N/A	N/A
PR Reaction Time (s)	N/A	38.8	40.0	46.0	51.3
	N/A	34.4	44.5	51.3	56.8
	N/A	34.0	42.0	51.1	49.7
Average PR Reaction Time (s)	N/A	35.7	42.2	49.5	56.6
Error (s)	N/A	1.5	1.3	1.7	2.1

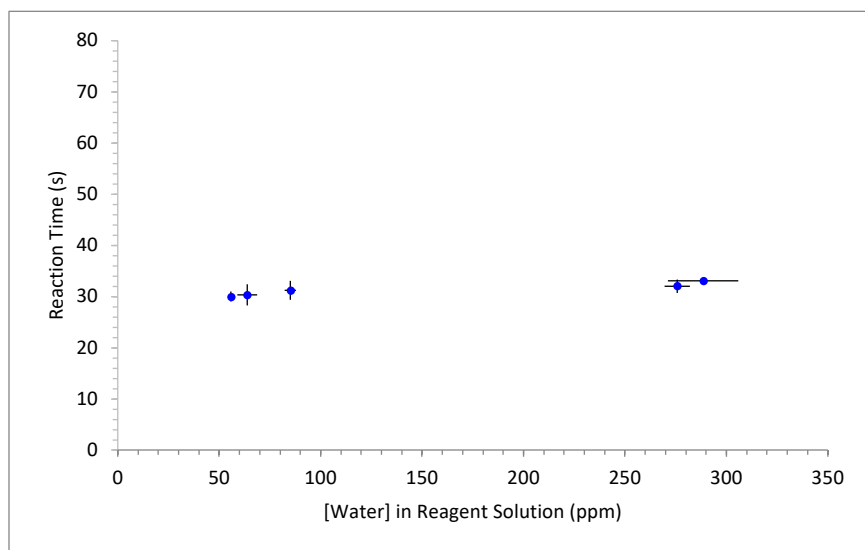


Figure S3 PR overall reaction time as a function of [H₂O] in reagent solution; [H₂O] in BCF solution = 80.59 + 2.64 ppm. Note: no induction time, reactions began immediately following catalyst addition (Table S1).

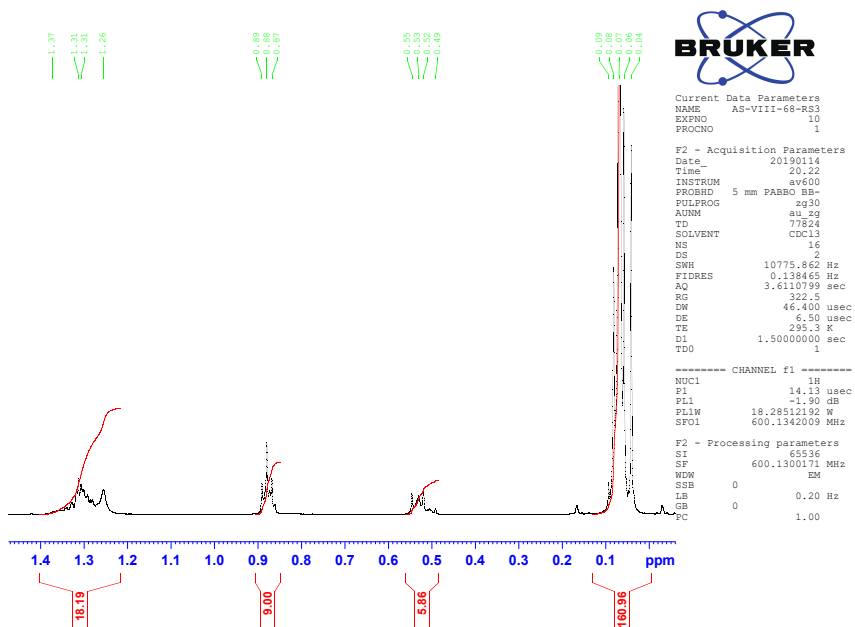


Figure S4 ¹H NMR spectrum of completed model PR reaction.