

Supplemental Information

Functional group	Hammett's constant, σ_p
Bis <i>o</i> -trifluoromethyl phenyl	0.15 ^c
Bis 2-tolyl ^a	-0.03
Bis <i>t</i> -butyl	-0.20
Bis 2-norbonyl ^b	-0.15
<i>o</i> -trifluoromethyl phenyl, <i>m</i> -trifluoromethyl phenyl	0.15 ^c
Bis 2,4,4' trimethylpentyl (Cyanex 301) ^c	-0.12
Bis <i>m</i> -trifluoromethyl phenyl	0.15 ^d
Dicyclohexyl	-0.15
Diphenyl	-0.01
Bis 3,5 bis(<i>m</i> -trifluoromethyl) phenyl	0.20 ^d

Table 1: Hammett's constants for the DPAH functional groups.

^a value for *para*- tolyl

^b value for cyclohexyl

^cvalue for CH₂CH(Me)₂

^dvalues interpolated from the tabulated values for -C₆H₄-3Cl and -C₆H₄-3NO₂. The trifluoromethyl group appears to have a σ_p of 0.54, between-Cl (0.23) and -NO₂ (0.78)

Bisortho DPAH, 6	1 h	1 week	2 weeks	1 month	2 months
1 mM HNO ₃	ND	ND	ND	ND	PD (<5%)
+ 10 mM La(NO ₃) ₃	ND	ND	ND	ND	PD (<10%)
+ 10 mM La(NO ₃) ₃ & 1 mM urea	ND	ND	ND	PD (<5%)	-
+ 10 mM La (NO ₃) ₃ & 1 mM hydrazine	ND	ND	ND	PD (<5%)	PD (<10%)
+ 1 mM urea	ND	ND	ND	PD (<5%)	-
+ 1 mM hydrazine	ND	ND	ND	ND	PD (<5%)
0.1 M HNO ₃	ND	PD (<5%)	PD (<10%)	PD (<25%)	-
+ 10 mM La(NO ₃) ₃ & 1 mM urea	ND	PD (<2%)	PD (<10%)	PD (<25%)	
+ 10 mM La (NO ₃) ₃ & 1 mM hydrazine	ND	PD(<2%)	PD (<5%)	-	-
+ 1 mM urea	ND	PD (<2%)	PD (<5%)	PD (<33%)	-
+ 1 mM hydrazine	ND	PD (<2%)	PD (<10%)	PD (<20%)	-
0.5 M HNO ₃	PD (<20%)	CD	-	-	-
+ 10 mM La(NO ₃) ₃ & 1 mM urea	PD (<10%)	CD	-	-	-
+ 10 mM La (NO ₃) ₃ & 1 mM hydrazine	ND	ND	PD (<3%)	PD (<10%)	-
+ 1 mM urea	PD (<10%)	CD	-	-	-
+ 1 mM hydrazine	ND	ND	PD (<3%)	PD (<10%)	-
2 M HNO ₃	CD	-	-	-	-
+ 10 mM La(NO ₃) ₃	CD	-	-	-	-
+ 10 mM La(NO ₃) ₃ & 1 mM urea	CD	-	-	-	-
+ 10 mM La(NO ₃) ₃ & 1 mM hydrazine	CD	-	-	-	-
+ 1 mM urea	ND	CD	-	-	-
+ 1 mM hydrazine	ND	CD	-	-	-

Table 2: The stability of 0.01 M Bisortho DPAH in toluene (ND – no degradation, PD – partially degraded, CD – complete degradation, as determined by ³¹P NMR)

Cyanex 301	1 h	1 week	2 weeks	1 month	2 months
1 mM HNO ₃	ND	ND	ND	ND	PD (<2%)
+ 10 mM La(NO ₃) ₃	ND	ND	ND	ND	PD (<5%)
+ 10 mM La(NO ₃) ₃ + 1 mM urea	ND	ND	ND	PD (<5%)	PD (<5%)
+ 10 mM La(NO ₃) ₃ + 1 mM hydrazine	ND	ND	ND	PD (<5%)	PD (<5%)
+ 1 mM urea	ND	ND	ND	PD (<5%)	PD (<5%)
+ 1 mM hydrazine	ND	ND	ND	ND	PD (<10%)
0.1 M HNO ₃	ND	ND	ND	ND	ND
+ 1 mM urea	ND	ND	ND	ND	ND
+ 1 mM hydrazine	ND	ND	ND	ND	PD (<5%)
+ 10 mM La(NO ₃) ₃ + 1 mM urea	ND	ND	ND	ND	PD (<5%)
+ 10 mM La(NO ₃) ₃ + 1 mM hydrazine	ND	ND	ND	ND	PD (<5%)
0.5 M HNO ₃	PD (50%)	CD	-	-	-
+ 1 mM urea	ND	CD	-	-	-
+ 1 mM hydrazine	ND	ND	ND	ND	PD
+ 10 mM La(NO ₃) ₃ + 1 mM urea	PD (5%)	CD	-	-	-
+ 10 mM La(NO ₃) ₃ + 1 mM hydrazine	ND	ND	ND	ND	PD
2 M HNO ₃	CD	-	-	-	-
+ 10 mM La(NO ₃) ₃	CD	-	-	-	-
+ 10 mM La(NO ₃) ₃ + 1 mM urea	CD	-	-	-	-
+ 10 mM La(NO ₃) ₃ + 1 mM hydrazine	CD	-	-	-	-
+ 1 mM urea	CD	-	-	-	-
+ 1 mM hydrazine	CD	-	-	-	-

Table 3: The stability of 0.01 M Cyanex 301 in toluene (ND – no degradation, PD – partially degraded, CD – complete degradation, as determined by ³¹P NMR)

Diphenyl DPAH, 4	1 h	1 week	2 weeks	1 month
2 M HNO ₃	CD	-	-	-
+ 10 mM La(NO ₃) ₃	CD	-	-	-
+ 1 mM hydrazine	ND	ND	ND	PD (<3%)
+ 1 mM urea	CD	-	-	-
+ 10 mM La(NO ₃) ₃ + 1 mM hydrazine	ND	ND	ND	PD (~3%)
+ 10 mM La(NO ₃) ₃ + 1 mM urea	CD	-	-	-
Dicyclohexyl DPAH, 3				
2 M HNO ₃	CD	-	-	-
+ 10 mM La(NO ₃) ₃	CD	-	-	-
+ 1 mM hydrazine	ND	ND	ND	PD (~5%)
+ 1 mM urea	ND	CD	-	-
+ 10 mM La(NO ₃) ₃ + 1 mM hydrazine	ND	ND	ND	PD (~5%)
+ 10 mM La(NO ₃) ₃ + 1 mM urea	ND	CD	-	-

Table 4: Stability of 0.01 M Diphenyl and Dicyclohexyl DPAH in toluene contacted with various aqueous phases (ND – no degradation, PD – partially degraded, CD – complete degradation, as determined by ³¹P NMR)

DPAH	1 h	1 week	2 weeks	1 month	2 months
1	CD	-	-	-	-
2	CD	-	-	-	-
3	ND	ND	ND	ND	PD (<10%)
4	ND	ND	ND	ND	PD (<10%)
5	ND	ND	ND	ND	PD (<10%)
6	ND	ND	ND	ND	PD (<10%)
7	ND	ND	ND	ND	PD (<10%)
8	PD (<5%)	-	-	-	-
9	PD (<5%)	-	-	-	-
10	CD	-	-	-	-

Table 5: 0.01 M DPAH in toluene contacted with 2 M HNO₃ with 10 mM hydrazine (ND – no degradation, PD – partially degraded, CD – complete degradation, as determined by ³¹P NMR)