

Supporting Information

Reductions with SmI₂: Mechanistic Probe for Distinguishing Between Two Operational Modes of Proton Transfer

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Table S1: ET30 for THF solutions of MeOH, TFE and i-PrOH.

ROH	[ROH] (M)	λ_{\max}(nm)	ET30 (kcal/mol)
MeOH	1	654	43.7
MeOH	0.5	684	41.8
MeOH	0.25	704	40.6
MeOH	0.0625	748	38.2
MeOH	0	764	37.4
TFE	1	561	51
TFE	0.5	581	49.2
TFE	0.25	607	47.1
TFE	0.0625	659	43.4
TFE	0	765	37.4
i-PrOH	1	689	41.5
i-PrOH	0.5	709	40.3
i-PrOH	0.25	728	39.3
i-PrOH	0.0625	754	37.9

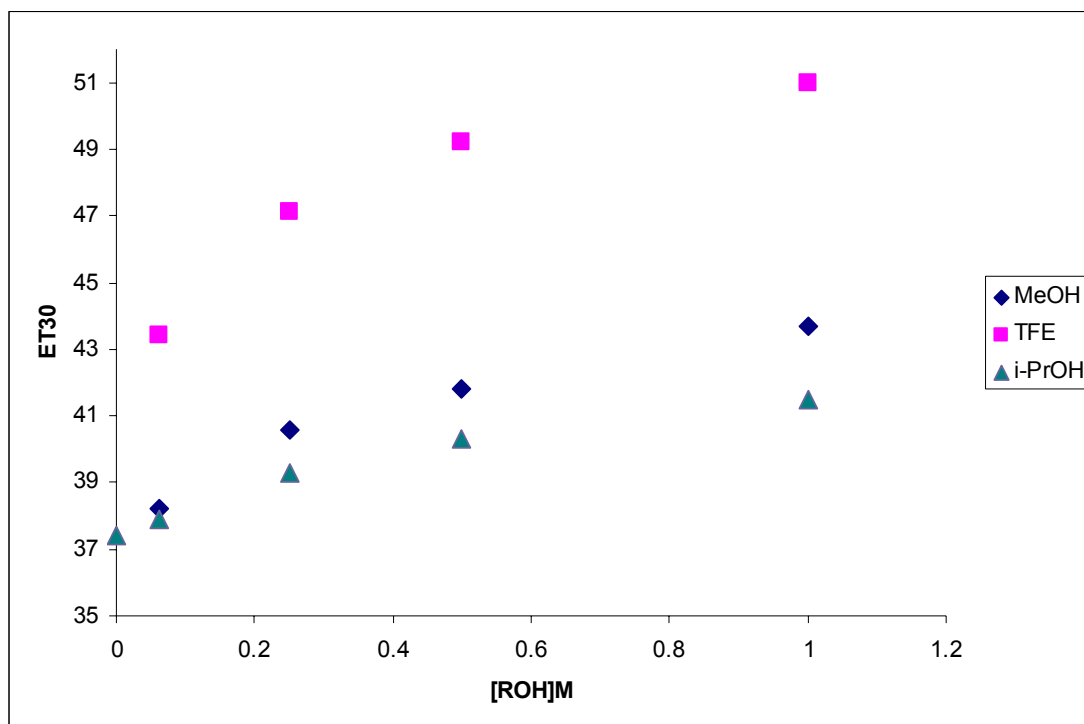


Figure S1: ET30 values as a function of [ROH] concentration.

Table S2: Reaction scheme and Data used for the SPECFIT simulation.

Simulation	kf	kb	[H ₂ O]	k_obs
SmI ₂ + MeOH <====> SmI ₂ (MeOH)	1.00E+07	5.00E+07	1.04	830
SmI ₂ (MeOH) + MeOH <====> SmI ₂ (MeOH) ₂	2.00E+08	5.00E+07	0.52	830
SmI ₂ (MeOH) ₂ + MeOH <====> SmI ₂ (MeOH) ₃	4.00E+09	5.00E+07	0.26	820
SmI ₂ (MeOH) ₃ + MeOH <====> SmI ₂ (MeOH) ₄	8.00E+10	5.00E+07	0.129	780
Substrate + SmI ₂ (MeOH)	7.00E+04		0.0645	390
Substrate + SmI ₂ (MeOH) ₂	1.40E+05		0.03225	72
Substrate + SmI ₂ (MeOH) ₃	2.10E+05		0.016625	6.9
Substrate + SmI ₂ (MeOH) ₄	2.80E+05		0.008813	0.88
			0.004906	0.25
			0.002953	0.13
			0.001	0.039