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Table S1. Rate constants for the growth of the 4-methoxystyrene radical cation by heterolysis of the β-chloro-4-methoxyphenethyl radical **2a** in various acetonitrile-cosolvent mixtures.

	k_{growth}/s^{-1}		
% Co-solvent	Water	HFIP	TFE
16.0	too slow	too slow	too slow
33.3	1.30×10^6	0.36×10^6	0.51×10^6
50.0	1.80×10^6	0.52×10^6	0.64×10^6
66.7	5.76×10^6	1.86×10^6	1.15×10^6
83.3	30.0×10^6	23.5×10^6	2.25×10^6
100.0	too fast	too fast	10.4×10^6

Table S2. Rate constants for the growth of the anethole radical cation by heterolysis of the β-chloro-4-methoxyphenylpropyl radical **2b** in various acetonitrile-cosolvent mixtures.

	k_{growth}/s^{-1}		
% Co-solvent	Water	HFIP	TFE
16.0	4.6×10^6	1.5×10^6	0.79×10^6
33.3	7.3×10^6	2.9×10^6	2.9×10^6
50.0	10.5×10^6	6.6×10^6	6.4×10^6
66.7	17.0×10^6	16.5×10^6	10.6×10^6
83.3	97.0×10^6	35.6×10^6	16.6×10^6
100.0	too fast	too fast	28×10^6

Table S3. Rate constants for the growth of the 4-methoxystyrene radical cation by heterolysis of the β-bromo-4-methoxyphenethyl radical **2c** in various acetonitrile-cosolvent mixtures.

	k_{growth}/s^{-1}		
% Co-solvent	Water	HFIP	TFE
16.0	too slow	too slow	too slow
33.3	4.2×10^6	1.6×10^6	1.1×10^6
50.0	7.0×10^6	2.5×10^6	2.2×10^6
66.7	26.6×10^6	13.3×10^6	6.53×10^6
83.3	82.6×10^6	71.0×10^6	14.0×10^6
100.0	too fast	too fast	45.0×10^6

Table S4. Rate constants for the growth of the anethole radical cation by heterolysis of the β-bromo-4-methoxyphenylpropyl radical **2d** in various acetonitrile-cosolvent mixtures.

	k_{growth}/s^{-1}		
% Co-solvent	Water	HFIP	TFE
6.66	8.6×10^6	--	7.67×10^6
16.6	32.9×10^6	12.0×10^6	12.7×10^6
33.3	43.2×10^6	31.4×10^6	26.1×10^6
50.0	52.0×10^6	46.5×10^6	36.6×10^6
66.7	77.8×10^6	72.3×10^6	47.1×10^6
83.3	too fast	98.2×10^6	63.9×10^6
100.0	too fast	too fast	90.0×10^6

Table S5. Rate constants for the growth of the stilbene radical cation by heterolysis of the β-chloro-1,2-diphenylethyl radical **4a** in various acetonitrile-cosolvent mixtures.

	k_{growth}/s^{-1}	
% Co-solvent	Water	TFE
16.0	6.1×10^6	2.8×10^6
33.3	49.1×10^6	13.3×10^6
50.0	85.2×10^6	39.4×10^6
66.7	too fast	90.1×10^6

Table S6. Observed rate constants for the growth of the radical cations upon ionization of the radicals **2a-d** and **4a** in methanol/water mixtures.

		$k_{growth}/10^7\ s^{-1}$				
% Water	*Y* values[a]	**2a**	**2c**	**2b**	**2d**	**4a**
0	-0.90000	-			2.90	1.50
10	-0.30100	-	0.210		4.40	4.25
20	0.38100	-	0.405	0.795	5.45	7.6
30	0.96000	0.131	1.15	1.08	6.55	
40	1.4900	0.217	1.98	1.33	8.58	
50	1.9700	0.565	3.17	1.50		
60	2.3900	1.17		1.97		
70	2.7900	2.32		2.67		

a-*Y*-values taken from: Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770-2777..