Supporting Information

The oxidative degradation of dibenzoazepine derivatives by cerium(IV) complexes in acidic sulfate media.

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Table S1. Rate constants as a function of temperature for the electron-transfer reaction between dibenzoazepine derivatives and cerium(IV) complexes, as well as for the second and third steps of the degradation of TCA (k_{obs}). Experimental conditions: $[Ce^{IV}] = 5 \times 10^{-5}$ M, $[TCA] = 5 \times 10^{-4}$ M, $[H_2SO_4] = 1.0$ M, $[H^+] = 1.2$ M, $I = 1.4$ M (H^+, HSO_4^-, SO_4^{2-}), $T = 278$ K.

		I step	II step	III step
Temp. (K)	[TCA] (M)	k_{obs} (s^{-1})	k_{obs} (s^{-1})	k_{obs} (s^{-1})
283	0.0005	7.09	0.41	0.04
	0.001	13.4	0.54	0.05
	0.002	22.1	0.94	0.13
	0.003	34.2	1.59	0.25
	0.004		2.60	0.44
	0.005		3.64	0.64

288	0.0005	9.46	0.56	0.05
	0.001	18.7	0.86	0.09
	0.002	30.2	1.42	0.18
	0.003	45.7	2.18	0.31
	0.004		3.35	0.54
	0.005		5.02	0.92
293	0.0005	11.9	0.89	0.09
	0.001	21.4	1.38	0.15
	0.002	44.0	2.22	0.29
	0.003	61.4	3.73	0.50
	0.004		5.21	0.83
	0.005		6.97	1.30
298	0.0005	14.16	0.96	0.04
	0.001	24.4	1.27	0.11
	0.002	49.6	2.65	0.29
	0.003		5.21	0.63
	0.004		8.18	1.15
	0.005		10.7	1.62

Table S2. Rate constants as a function of pressure for the electron-transfer reaction between dibenzoazepine derivatives and cerium(IV) complexes, as well as for the second and third steps of the degradation of TCA (k_{obs}). Experimental conditions: $[Ce^{IV}] = 5 \times 10^{-5}$ M, [TCA] $= 5 \times 10^{-4}$ M, $[H_2SO_4] = 1.0$ M, $[H^+] = 1.2$ M, $I = 1.4$ M (H^+, HSO_4^-, SO_4^{2-}), $T = 278$ K.

Pressure (MPa)	I step k_{obs} (s^{-1})	II step k_{obs} (s^{-1}) [a (b)]	III step k_{obs} (s^{-1}) [a (b)]
10	4.45	4.98 (8.76)	0.76 (1.50)
50	5.24	5.43 (10.5)	0.83 (1.91)
90	6.28	6.06 (12.8)	0.92 (2.41)
130	7.53	6.54 (15.2)	1.02 (3.17)

[a] [TCA] = 3×10^{-3} M, $T = 298$ K, [b] [TCA] = 5×10^{-3} M, $T = 298$ K.

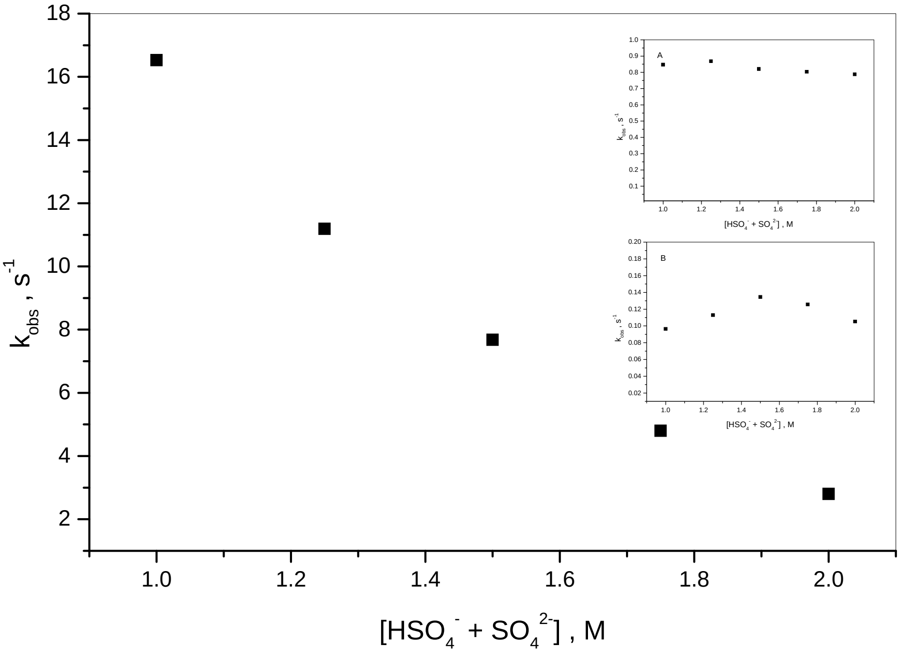


Figure S1. Plot of k_{obs} *versus* $[HSO_4^- + SO_4^{2-}]$ for the electron-transfer reaction between imipramine and cerium(IV). Inset: (A): the second reaction step, (B): the third reaction step. Experimental conditions: $[Ce^{IV}] = 5 \times 10^{-5}$ M, [TCA] = 1×10^{-3} M, $[H_2SO_4] = 1.0$ M, $[Na_2SO_4] = 0 – 1.0$ M, $I \neq$ const, $T = 288$ K.

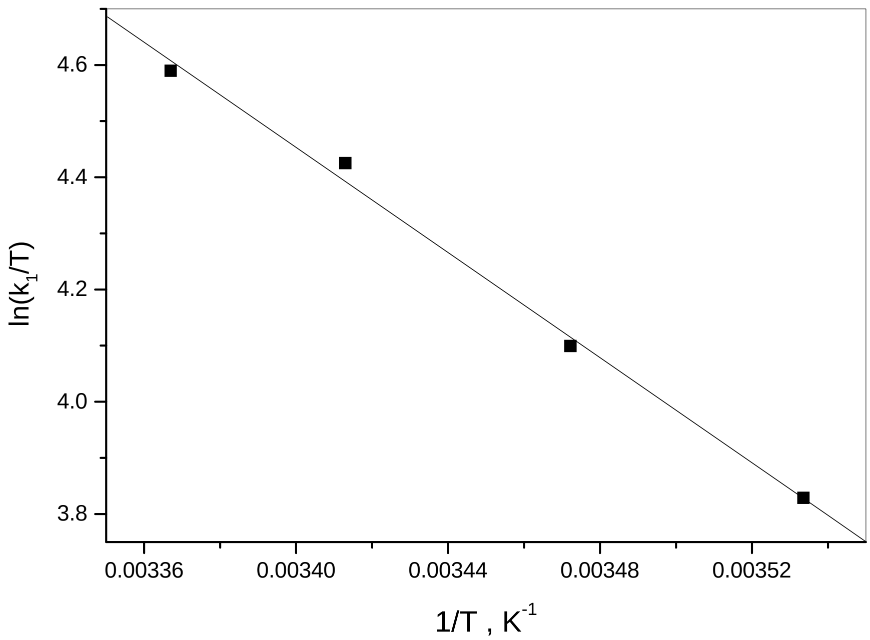
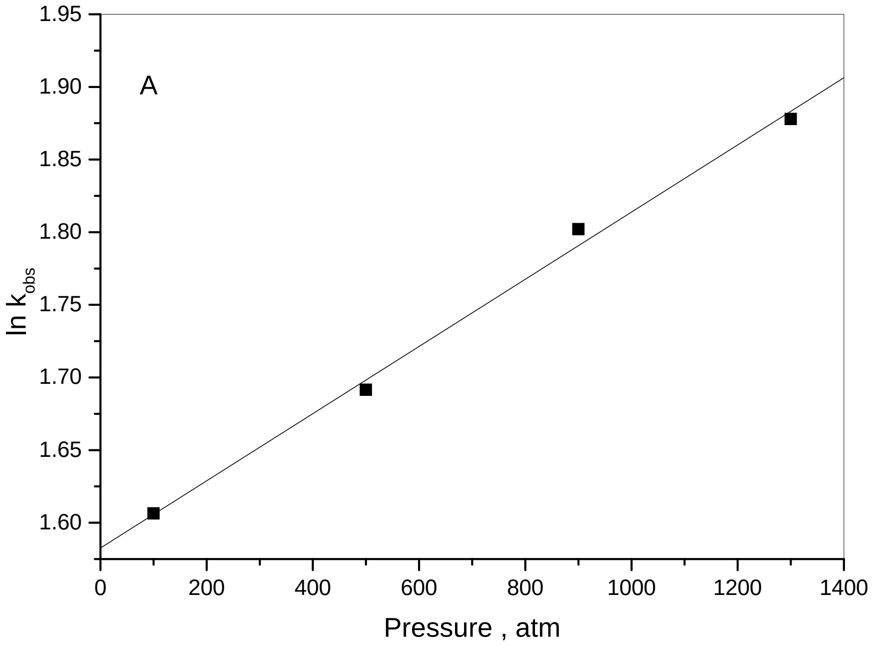


Figure S2. Eyring plot of ln(k_1/T) *versus* 1/T for the electron-transfer reaction between desipramine and cerium(IV). Experimental conditions: [Ce^{IV}] = 5 × 10^{-5} M, [TCA] = (0.5 – 3) × 10^{-3} M, [H_2SO_4] = 1.0 M, [H^+] = 1.2 M, I = 1.4 M (H^+, HSO_4^-, SO_4^{2-}), T = 283 – 298 K, λ = 630 nm.



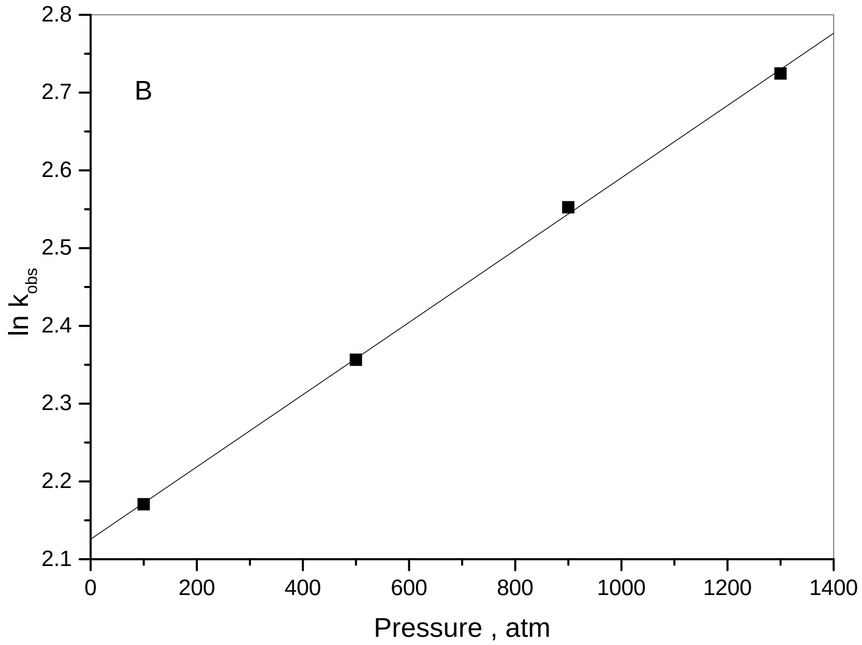
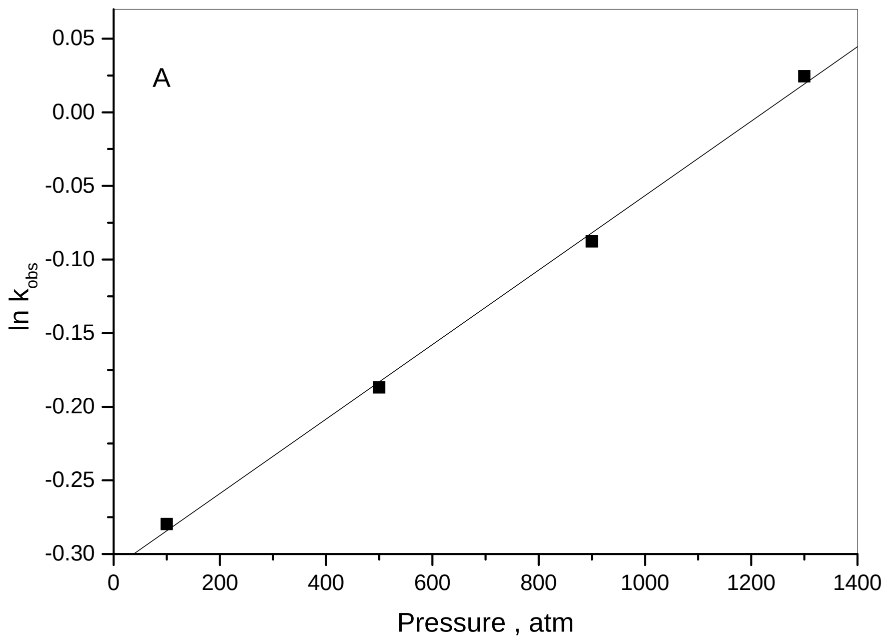


Figure S3. Plot of ln(k_{obs}) *versus* pressure for the second degradation step of imipramine. Experimental conditions: [Ce^{IV}] = 5×10^{-5} M, [H_2SO_4] = 1.0 M, [H^+] = 1.2 M, T = 298 K, λ = 630 nm, (A): [TCA] = 3×10^{-3} M, (B): [TCA] = 5×10^{-3} M.



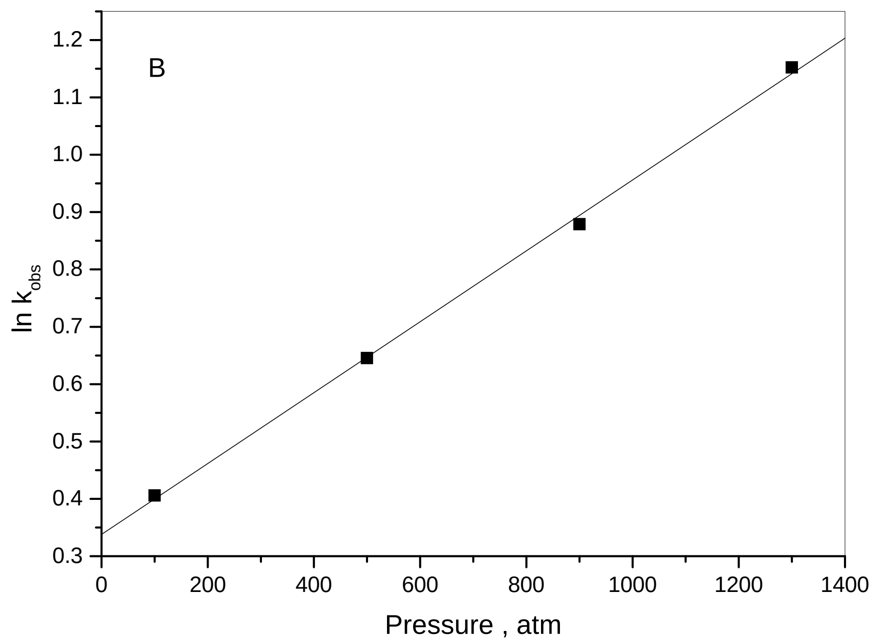


Figure S4. Plot of ln(k_{obs}) *versus* pressure for the third degradation step of imipramine. Experimental conditions: $[Ce^{IV}] = 5 \times 10^{-5}$ M, $[H_2SO_4] = 1.0$ M, $[H^+] = 1.2$ M, $T = 298$ K, $\lambda =$ 630 nm, (A): [TCA] = 3×10^{-3} M, (B): [TCA] = 5×10^{-3} M.