Kinetico-mechanistic study on the oxidation of biologically active [Fe^{II}(thiosemicarbazone)$_2$] complexes by air; importance of NH…O_2 interactions as established by activation volumes

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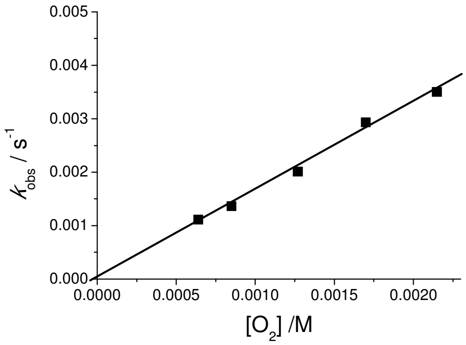
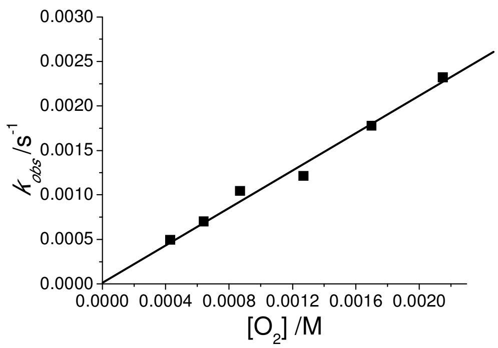
SUPPORTING INFORMATION

a)



b)



c)

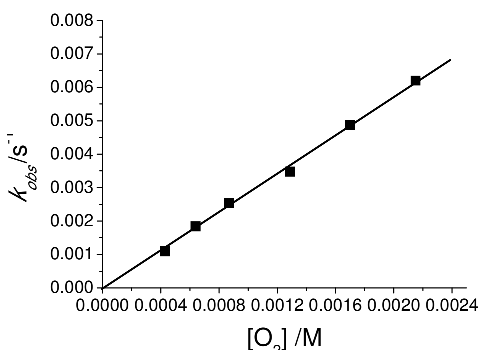


Figure S1.- Plot of the [O_2]-dependence of the values of the observed pseudo-first order rate constant of the single step observed on the oxidation of a) [$Fe^{II}(BpT)_2$], b) [$Fe^{II}(Bp4mT)_2$] and c) [$Fe^{II}(Ap44mT)_2$] complexes in MeOH solution at 25 ºC.

Table S1.- Values obtained for the observed pseudo-first order rate constants as a function of the complexes studied, dioxygen concentration, temperature and pressure.

Fe^{II} complex	T /ºC	P /atm	$10^3\times[O_2]$ /M	$10^3\times k_{obs}$ /s^{-1} [a]
$[Fe^{II}(ApT)_2]$	15	1	2.15 (air sat.)	9.7
	25	1	2.15 (air sat.)	18
	35	1	2.15 (air sat.)	30
$[Fe^{II}(DpT)_2]$	15	1	2.15 (air sat.)	0.77
	24	400	2.15 (air sat.)	0.85
		600	2.15 (air sat.)	0.83
		1000	2.15 (air sat.)	0.78
		1300	2.15 (air sat.)	0.77
		1600	2.15 (air sat.)	0.73
	25	1	2.15 (air sat.)	1.7
	35	1	2.15 (air sat.)	3.7
$[Fe^{II}(BpT)_2]$	15	1	2.15 (air sat.)	1.6
	21	300	2.15 (air sat.)	2.1
		850	2.15 (air sat.)	2.0
		1000	2.15 (air sat.)	1.7
		1300	2.15 (air sat.)	1.6
		1600	2.15 (air sat.)	1.4
	25	1	2.15 (air sat.)	3.4
		1	1.7	2.9
		1	1.3	2.0
		1	0.87	1.4
		1	0.64	1.1
	35	1	2.15 (air sat.)	6.5
$[Fe^{II}(Ap4mT)_2]$	15	1	2.15 (air sat.)	9.0
	25	1	2.15 (air sat.)	16
	35	1	2.15 (air sat.)	26
$[Fe^{II}(Dp4mT)_2]$	15	1	2.15 (air sat.)	0.65
	21	300	2.15 (air sat.)	0.77
		400	2.15 (air sat.)	0.79
		700	2.15 (air sat.)	0.77
		1000	2.15 (air sat.)	0.79
		1300	2.15 (air sat.)	1.0
		1500	2.15 (air sat.)	1.1
		1800	2.15 (air sat.)	1.0
	25	1	2.15 (air sat.)	1.6
	35	1	2.15 (air sat.)	3.0
$[Fe^{II}(Bp4mT)_2]$	15	1	2.15 (air sat.)	1.2
	21	400	2.15 (air sat.)	1.7
		700	2.15 (air sat.)	1.8
		1150	2.15 (air sat.)	1.9
		1300	2.15 (air sat.)	1.9
		1600	2.15 (air sat.)	2.0
	25	1	2.15 (air sat.)	2.5
		1	1.7	1.8
		1	1.3	1.2
		1	0.87	1.0
		1	0.64	0.70
		1	0.43	0.49
	35	1	2.15 (air sat.)	4.8
$[Fe^{II}(Ap44mT)_2]$	15	1	2.15 (air sat.)	3.2
	21	500	2.15 (air sat.)	5.6
		700	2.15 (air sat.)	5.2
		1000	2.15 (air sat.)	5.5

		1300	2.15 (air sat.)	6.6
		1600	2.15 (air sat.)	7.4
		1800	2.15 (air sat.)	7.4
	25	1	2.15 (air sat.)	6.2
		1	1.7	4.9
		1	1.3	3.5
		1	0.87	2.5
		1	0.64	1.8
		1	0.43	1.1
	35	1	2.15 (air sat.)	11
$[Fe^{II}(Dp44mT)_2]$	15	1	0.65	0.19
		1	0.86	0.22
		1	1.3	0.32
		1	1.5	0.37
		1	1.7	0.37
		1	2.15 (air sat.)	0.52
	21	400	2.15 (air sat.)	1.5
		700	2.15 (air sat.)	1.7
		1000	2.15 (air sat.)	2.0
		1100	2.15 (air sat.)	2.2
		1600	2.15 (air sat.)	2.6
		1800	2.15 (air sat.)	3.3
	25	1	0.43	0.28
		1	0.65	0.37
		1	0.86	0.44
		1	1.1	0.67
		1	1.3	0.72
		1	1.7	1.1
		1	2.15 (air sat.)	1.3
	35	1	0.43	0.38
		1	0.65	0.88
		1	0.86	1.0
		1	1.3	1.5
		1	1.5	1.9
		1	2.15 (air sat.)	2.6
$[Fe^{II}(Bp44mT)_2]$	15	1	2.15 (air sat.)	1.0
	21	400	2.15 (air sat.)	1.5
		700	2.15 (air sat.)	1.5
		1000	2.15 (air sat.)	1.9
		1300	2.15 (air sat.)	2.2
		1600	2.15 (air sat.)	2.2
	25	1	2.15 (air sat.)	2.2
	35	1	2.15 (air sat.)	4.3

[a] Average value for all the data collected for the runs under the indicated conditions.