

## **Biologically Active Thiosemicarbazone Fe Chelators and their Reactions with Ferrioxamine B and Ferric EDTA; a Kinetic Study**

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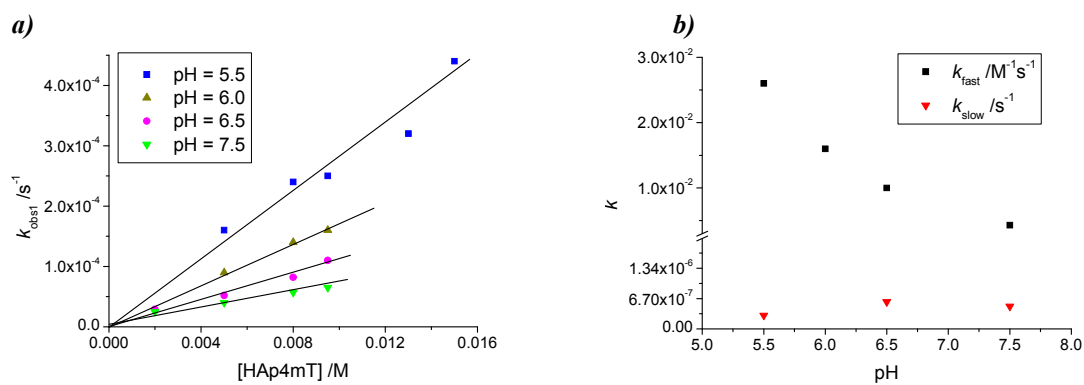
**Supporting Information**

**Table S1.-** Observed rate constants determined for the different systems as a function of the variables used in the study.

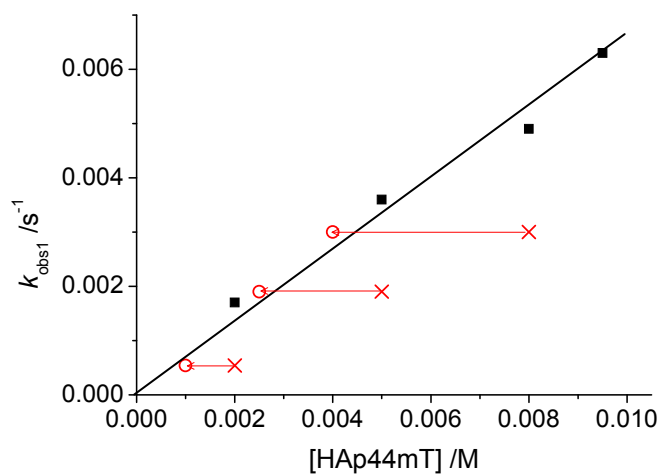
Reaction	pH	$I$ /M	$T$ /°C	$P$ /atm	% DMSO	$10^3 \times [\text{TSC}]$ /M	$10^4 \times k_{\text{obs1}}$ /s <sup>-1</sup>	$10^5 \times k_{\text{obs2}}$ /s <sup>-1</sup>	$10^5 \times k_{\text{obs3}}$ /s <sup>-1</sup>
HAp44mT $E \rightleftharpoons Z$ , 0.08 M PIPPS	4.5	0.27	62	1	23	0.01-0.03 range	19	-	-
	4.8						12	-	-
	5.0						6.5	-	-
HAp44mT $E \rightleftharpoons Z$ , 0.08 M MES	5.1	0.60	60				3.8	-	-
	5.1	0.10	60	1	23		3.3	-	-
		0.60				4.0	-	-	
		1.0				3.8	-	-	
	5.2	0.27	62				5.2	-	-
							5.5	0.12	-
	5.5			41	1	23	0.35	-	-
				51			0.81	-	-
				58			1.9	-	-
							1.9	-	-
							1.9	-	-
5.7			60	300	62	1.9	-	-	
				600		1.9	-	-	
				900		1.9	-	-	
				1200		1.9	-	-	
				1500		1.8	-	-	
6.0			60	1	23	1.6	-	-	
						2.1	-	-	
6.5			62			2.3	-	-	
						2.5	-	-	
5.7						1.4	-	-	
6.0						0.69	-	-	
HAp4mT $E \rightleftharpoons Z$ , 0.08 M MES	5.5	0.27	60		23		0.075	-	-
HAp4pT $E \rightleftharpoons Z$ , 0.08 M MES	5.2		60		62		0.088	-	-

	5.5		55				0.034	-	-
			62				0.093	-	-
			69				0.25	-	-
			76				0.51	-	-
HAp4pT $E \rightleftharpoons Z$ , 0.08 M PIPPS	6.0		60				0.049	-	-
	4.5		60				0.29	-	-
	4.8						0.22	-	-
HAp4mT + (1-5)×10 <sup>-5</sup> M range [Fe(HDFO)] <sup>+</sup>	5.5	0.27	70	1	23	5.0	1.6		-
						8.0	2.4	Average	-
						9.5	2.5	0.030	-
						13	3.2		-
						15	4.4		-
	6.0	0.27	70		23	5.0	0.90	not determined	-
						8.0	1.4	not determined	-
						9.5	1.6	not determined	-
	6.5	0.27	70		23	2.0	0.29		-
						5.0	0.52	Average	-
						8.0	0.82	0.060	-
						9.5	1.1		-
	7.5	0.27	70		23	2.0	0.25		-
						5.0	0.40	Average	-
						8.0	0.57	0.050	-
						9.5	0.65		-
HAp44mT + (1-5)×10 <sup>-5</sup> M range [Fe(HDFO)] <sup>+</sup>	5.5	0.27	55		23	2.0	5.0	4.0	-
						5.0	13	4.5	-
						8.0	20	-	-
						9.5	23	3.0	-
			60		23	2.0	18	6.0	-
						2.0 (equilibrated)	5.4	5.5	-
						5.0	36	-	-

HAp44mT + $(1-5) \times 10^{-5}$ M range [Fe(EDTA)(H <sub>2</sub> O)] <sup>-</sup>	6.5	0.27	55	40	5.0 (equilibrated)	19	6.0	-
					8.0	49	-	-
	7.4	0.27	55		8.0 (equilibrated)	30	5.5	-
					9.5	63	5.0	-
					2.0	1.8	3.0	-
					5.0	4.2	4.5	-
					8.0	6.2	4.0	-
	7.5	0.27	55		9.5	7.3	3.0	-
					2.0	1.4	2.3	-
					5.0	2.4	2.3	-
					8.0	4.0	2.4	-
					9.5	4.6	2.5	-
	5.5	0.27	50		2.0	1.4	2.3	-
					5.0	2.0	2.3	-
					8.0	3.3	2.4	-
					9.5	4.2	2.5	-
					2.0-9.0 range	Average	Average	Average
	6.5		60			0.92	10	0.68
						Average	Average	Average
						2.1	16	1.7
				Average	Average	Average		
				3.3	40	4.0		
6.5		60		Average	Average	Average		
				0.18	12	1.2		
				Average	Average	Average		
		70		0.58	30	3.0		



**Figure S1.-** *a)* Dependence on the concentration of HAp4mT for the faster process observed on its addition to a  $\text{Fe}^{\text{III}}$ /DFO solution at 70 °C; *b)* pH profile of the values derived from  $k_{\text{fast}}$  and  $k_{\text{slow}}$  for the same reaction.



**Figure S2.-** Dependence on the concentration of the ligand for the reaction of freshly recrystallized HAp44mT with the  $\text{Fe}^{\text{III}}$ /DFO system at 60 °C and pH = 5.5. Crosses indicate the data obtained after isomeric equilibration and the empty circles its position once the *EZ thiolate* relative proportion is considered.