Kinetical and Thermodynamical Analysis of the Reactivity of Thiourea by Association to Ca^{2+}

Supporting Information

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1 Formation rate of products in terms of rates of elementary processes

The rate of formation of the different products can be expressed as:

$$\frac{d}{dt}[a] = k_a[\text{Ca}^{2+}][\textbf{TU}] = k_{6a}[6] \tag{1}$$

$$\frac{d}{dt}[b] = k_b[\text{Ca}^{2+}][\textbf{TU}] = k_{6b}[6] \tag{2}$$

$$\frac{d}{dt}[c] = k_c[\text{Ca}^{2+}][\textbf{TU}] = k_{8bc}[8b] \tag{3}$$

$$\frac{d}{dt}[d] = k_d[\text{Ca}^{2+}][\textbf{TU}] = k_{2d}[2] + k_{3d}[3] \tag{4}$$

$$\frac{d}{dt}[e] = k_e[\text{Ca}^{2+}][\textbf{TU}] = k_{8e}[8] \tag{5}$$

$$\frac{d}{dt}[f] = k_f[\text{Ca}^{2+}][\textbf{TU}] = k_{1f}[1] \tag{6}$$

Within the steady-state approximation, the concetrantion of the reaction intermediates is low and constant, and hence:

$$\begin{aligned}\frac{d}{dt}[1] = {} & k_{capt}[\text{Ca}^{2+}][\textbf{TU}] + k_{-12}[2] + k_{-13}[3] + k_{-18}[8] \\ & - (k_{-capt} + k_{12} + k_{13} + k_{18} + k_{1f})[1] \approx 0\end{aligned} \tag{7}$$

$$\frac{d}{dt}[2] = k_{12}[1] + k_{-23}[3] + k_{-24}[4] - (k_{-12} + k_{23} + k_{24} + k_{2d})[2] \approx 0 \tag{8}$$

$$\frac{d}{dt}[3] = k_{13}[1] + k_{23}[2] + k_{-38b}[8b] - (k_{-13} + k_{-23} + k_{38b} + k_{3d})[3] \approx 0 \tag{9}$$

$$\frac{d}{dt}[4] = k_{24}[2] + k_{-46}[6] + k_{-48b}[8b] - (k_{-24} + k_{46} + k_{48b})[4] \approx 0 \tag{10}$$

$$\frac{d}{dt}[6] = k_{46} - (k_{-46} + k_{6a} + k_{6b})[6] \approx 0 \tag{11}$$

$$\frac{d}{dt}[8] = k_{18}[1] - (k_{-18} + k_{8e})[8] \approx 0 \tag{12}$$

$$\frac{d}{dt}[8b] = k_{38b}[3] + k_{48b}[4] - (k_{-38b} + k_{-48b} + k_{8bc})[8b] \approx 0 \tag{13}$$

By solving this set of linear equations, the concentration of the intermediate species can be expressed in terms of the initial reactants which, when substituted back in eqs. (1) to (6), gives the final rate of formation of each product in term of reaction rates of unimolecular processes.

2 List of Frequencies and Rotational Constants

Table 1: Frequencies (in cm^{-1}) and rotational constants (in GHz) of the transition states located in the $[Ca\mathbf{TU}]^{2+}$ surface

	TS_{12}	TS_{13}	TS_{18}	TS_{1f}	TS_{24}	TS_{38b}
	$110i$	$96i$	$1584i$	$37i$	$1797i$	$1699i$
	84	245	85	30	98	124
	298	268	179	42	167	199
	405	355	251	356	260	302
	451	424	377	413	376	388
	513	461	560	444	415	575
	583	541	589	450	529	614
	650	547	595	474	571	662
	679	724	674	560	676	690
	711	956	788	667	910	696
	805	1109	852	710	997	764
	1053	1117	1003	1060	1053	1023
	1121	1179	1071	1085	1135	1045
	1384	1221	1121	1405	1170	1216
	1533	1269	1300	1523	1322	1373
	1662	1608	1627	1657	1446	1557
	1682	1624	1675	1666	1612	1668
	3479	3394	1720	3546	1993	1752
	3506	3397	3415	3557	3381	3435
	3581	3429	3458	3675	3413	3492
	3615	3430	3484	3686	3462	3596
A	5.08665	9.13475	4.19115	8.78333	4.44507	4.65561
B	1.63459	1.31891	2.11881	0.37506	2.08306	1.97272
C	1.36816	1.16620	1.62428	0.36306	1.51697	1.54066

	TS_{3d}	TS_{46}	TS_{48b}	TS_{6a}	TS_{6b}	TS_{8e}	TS_{8bc}
	$183i$	$120i$	$1543i$	$65i$	$46i$	$225i$	$244i$
	41	45	112	39	9	11	57
	105	89	181	52	73	72	69
	210	117	278	98	79	236	144
	299	223	338	101	180	296	225
	343	365	487	263	319	306	292
	430	444	525	292	325	400	368
	481	459	604	439	337	401	416
	509	519	710	524	448	492	507
	565	590	804	600	473	499	523
	677	913	951	884	725	513	622
	797	937	1000	1477	1459	710	713
	880	1272	1065	1498	1513	780	898
	1108	1340	1150	1501	1518	851	1112
	1565	1668	1328	1727	1734	960	1179
	1592	1669	1573	1731	1735	1563	1589
	1749	1863	1611	1911	2194	2134	2133
	3418	2531	1736	3155	2976	2595	2642
	3472	3427	3403	3400	3410	3422	3427
	3485	3511	3482	3470	3486	3489	3451
	3638	3514	3486	3473	3489	3682	3553
A	4.58379	3.04880	5.31598	2.28209	5.08149	4.82642	4.14041
B	1.07611	1.14079	1.93225	1.39414	0.86442	1.25178	1.49663
C	0.91812	0.83380	1.43950	0.86961	0.74177	0.99917	1.14838