Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

State-to-State Chemiluminescence in Reactions of Mn Atoms with S_2Cl_2

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Electronic Supplementary Information

Tables ES1-ES4

Table ES1 Parameters of the MLC analysis (σ_k/arbitrary units; E_k/kJ mol^{-1})

Data		k	0	1	2	3	4	5	6
UV	'hot'	σ_k	5.0[a]	-7.57[a]	2.92 ± 0.11	0.60 ± 0.04	0.69 ± 0.09		
		E_k	0.2[a]	40[a]	106 ± 4	604 ± 27	1475 ± 50		
blue:	'hot'	σ_k	0.92 ± 0.03	-0.88 ± 0.03	-0.58 ± 0.22	0.43 ± 0.22	0.13 ± 0.03	0.054 ± 0.014	0.140± 0.014
		E_k	0 ± 2	120 ± 3	231 ± 13	286 ± 20	455 ± 29	755 ± 65	1334 ± 32
	'cold'	σ_k	0.662 ± 0.002	-0.575 ± 0.006	-0.153 ± 0.011				
		E_k	43.7 ± 0.2	206.9 ± 0.7	353 ± 6				
green:	'hot'	σ_k	1.14 ± 0.09	-0.74 ± 0.09	-0.87 ± 0.05	0.41 ± 0.05	0.069 ± 0.007	0.025 ± 0.004	
		E_k	23 ± 4	96 ± 4	202 ± 4	307 ± 9	738 ± 40	2073 ± 150	
	'cold'	σ_k	0.53 ± 0.02	0.83 ± 0.03	-0.75 ± 0.04	-0.71 ± 0.04	0.28 ± 0.02		
		E_k	67.6 ± 0.9	122 ± 2	180 ± 3	242 ± 3	357 ± 7		
red:	'hot'	σ_k	0.400[a]	-0.625[a]	0.225[a]	0.0403 ± 0.0003	-0.0278 ± 0.0032	-0.0220 ± 0.0034	-0.0092 ± 0.0016
		E_k	0.2[a]	90[a]	249.6[a]	96.3[b]	535 ± 14	779 ± 23	1234 ± 51
	'cold	σ_k	0.0576 ± 0.0004	0.0424 ± 0.0004	0.0416 ± 0.0016				
		E_k	45.2 ± 0.7	165.7 ± 1.1	361 ± 3				
IR:	'hot'	σ_k	0.548 ± 0.004	-0.272 ± 0.009	-0.188 ± 0.009				
		E_k	-21 ± 2	487 ± 8	897 ± 14				
	'cold'	σ_k	0.262 ± 0.004	0.352 ± 0.009	0.639 ± 0.013				
		E_k	33.4 ± 0.9	185 ± 2	320 ± 2				

[a] parameters fixed [b] weighted average from k = 0, 1 processes of corresponding 'cold' data

NB Optimised parameters correspond to r^2 values ranging between 0.88 ('hot' green) and 0.999 ('cold' green). With the exception of the UV and red cases, discussed in the main text, all parameters were allowed to vary freely. The only strong correlations between parameters were found for σ_0 and E_0 in the 'cold' green and 'hot' blue and green cases, and for σ_k,E_k (k = 2,3) in the 'hot' blue case; however, with the latter exception, the parameters are themselves quite well determined.

Table ES2 Tentative deconvolutions (σ_k/(arbitrary units); E_k/kJ mol^{-1}), transition state shifts and reagent state assignments

Data		Process	k	0	1	2	R_s/R_0 or R_d/R_0	E_s	Reagent State
$A^7\Pi$	'hot'	**1**	σ_k	~1.22	-1.49	0.296 ± 0.006	~1.10		z^8P_J
(UV)			E_k	~0.1	40	148 ± 4		~29	
$e^5\Sigma^+$	'hot'	**1h**	σ_k	0.60±0.09	-0.88	0.28-/+0.09	1.21 -0.08/+0.10		z^8P_J
(blue)			E_k	~0.0	122	297 +11/-7		95±27	
		2h	σ_k	0.30-/+0.09	-0.435-/+0.075	0.135 ± 0.015	1.20+0.11/-0.06		z^8P_J
			E_k	~0.0	225.5-/+6.5	439 ± 11		136+42/-27	
	'cold'		σ_k	0.662 ± 0.002	-0.575 ± 0.006	-0.153 ± 0.011	1.05		a^6D_J
			E_k	43.7 ± 0.2	206.9 ± 0.7	353 ± 6		≤206.9	
$d^5\Pi$	'hot'	**1h**	σ_k	0.80	-1.20	0.40	1.225		z^8P_J
(green)			E_k	0.2	103	307		103	
		2h	σ_k	0.874	-0.933	0.068	1.04		z^8P_J
			E_k	103	196	743		149	
	'cold'	**1c**	σ_k	0.53	-0.65		1.11		a^6D_J
			E_k	67.6	247			≤247	
		2c	σ_k	0.83	-0.83				a^6D_J
			E_k	122	183				
		3c	σ_k	0.29					a^6S
			E_k	352					
$e'^5\Delta$	'hot'	**1**	σ_k	0.400	-0.625	0.225	≤1.25		z^8P_J
(red)			E_k	0.2	90	249.6		90	
	'hot'/	**2**	σ_k	0.0228	-0.0278-/+0.0050	0.0050+/-0.0050	1.10±0.10		a^6D_J
	'cold'[b]		E_k	45.2	554+/-20	1284		268+160/-223[a]	
		3	σ_k	0.0168	-0.0220+/-0.0052	0.0052-/+0.0052	1.14-/+0.14		a^6D_J
			E_k	165.7	786	1284		430 -264[a]/+163	
	'cold'	**4**	σ_k	0.0416 ± 0.0016					a^6S
			E_k	361 ± 3					
$c^5\Sigma^+$	'hot'		σ_k	0.548 ± 0.004	-0.272 ± 0.009	-0.188 ± 0.009			z^8P_J
(IR)			E_k	-21 ± 2	487 ± 8	897 ± 14			
	'cold'	**1c**	σ_k	0.262 ± 0.004	0.352 ± 0.009	0.639 ± 0.013			a^6D_J
			E_k	33.4 ± 0.9	185 ± 2	320 ± 2			
		2c	σ_k	0.352 ± 0.009					a^6D_J or a^6S
			E_k	185 ± 2					
		3c	σ_k	0.639 ± 0.013					a^6S
			E_k	320 ± 2					

[a] *ie*, at lower limit, no shift (E_s just coincident with E_0). [b] Scale up σ_k values by factor of 2.525 for 'cold' data in Fig.4(d).

Table ES3 DFT calculation summary

	Bond Length / Å				Bond or Dihedral Angle / °			E / hartree
	Mn-Cl	S-S	S-Cl	S-S-Cl	Mn-Cl-S	Cl-Mn-Cl	Cl-S-S-Cl	
$Cl(^2P_J)$								-460.16688
$Mn(a^6S)$	-	-	-	-	-	-	-	-1150.96768
$Mn^*(z^8P_J)$	-	-	-	-	-	-	-	-1150.87604
$MnCl(X^7\Sigma^+)$	2.2656 (2.2351[a])	-	-	-	-	-	-	-1611.25853
$MnCl(a^5\Sigma^+)$	2.1899	-	-	-	-	-	-	-1611.24729
$^6MnCl_2$	2.1981 (2.184[b])	-	-	-	-	179.9 (180.0[b])	-	-2071.58927
$^8MnCl_2$	2.6682	-	-	-	-	179.9	-	-2071.41014
$S_2(X^3\Sigma_g^-)$	-	1.9273 (1.889[c])	-	-	-	-	-	-796.41604
S_2Cl	-	1.9336	2.1654	111.4	-	-	-	-1256.64012
$^1S_2Cl_2$	-	1.9786 (1.97[d],1.93[e])	2.1390 (2.07[d],2.06[e])	109.2 (108[d],107[e])	-	-	87.3 (82.5[d],85[e])	-1716.87203
$^1S_2Cl_2$	-	1.9336[f]	2.1390[f]; 2.1654[f]	109.2[f]; 111.4[f]			87.3[f]	-1716.87124
$^1S_2Cl_2$ (planar C_{2v})	-	2.2374	2.0586	105.91	-	-	0.0	-1716.83947
$^3S_2Cl_2$	-	1.9336[f]	2.1390[f]; 2.1654[f]	109.2[f]; 111.4[f]	-	-	87.3[f]	-1716.77044
$^3S_2Cl_2$	-	1.9680	2.5136; 2.1335	113.0; 110.4	-	-	0.0	-1716.82403
$^6MnCl_2S_2$ (planar C_{2v})	2.2040	1.9348	3.9162	108.2	77.4	168.8	0.0	-2867.99769
$^8MnCl_2S_2$ (planar C_{2v})	2.2053	1.9352	3.8617	108.3	78.0	167.4	0.0	-2868.00607
$^6MnClS_2Cl$ (nonplanar)	2.2388	1.9461	3.0090; 2.1835	109.6; 111.1	176.2	n/a	87.4	-2867.87214

Experimental values in parentheses. [a] Ref. 48. [b] Ref. 49 [c] Ref. 20 [d] Ref. 50 [e] Ref. 51 [f] fixed in calculation..

Table ES4 Energies and geometries of optimised Mn insertion species

	Bond Length / Å						Bond or Dihedral Angle / °				E / hartree
	Cl^1-Mn	Mn-S^1	Mn-S^2	S-S	S^2-Cl^2	S-S-Cl	Mn-S^1-S^2	Cl^1-Mn-S^1	Cl^1-Mn-S^2	Mn-S^1-S^2-Cl	
$^6ClMnS_2Cl$	2.2053	2.3357	2.6014	2.0854	2.1475	108.2	71.8	170.0	-139.8	87.3	-2867.99273
$^8ClMnS_2Cl$	2.1941	2.4734	2.4753	2.0686	2.5290	138.0	65.3	152.1	-158.4	180.	-2867.94609