Supplementary Material (ESI) for PCCP

Supplementary Material to

Infrared Matrix Isolation Study of the Oxidation of H_2S by $CrCl_2O_2$

Thompson, Goldberg and Ault

Table S1

HSOH-$CrCl_2O$ Complex, S-Bound

Calculated Freguencies		Calculated Relative Intensity	
$H_2S+CrCl_2O_2$	$D_2S+CrCl_2O_2$	$H_2S+CrCl_2O_2$	$D_2S+CrCl_2O_2$
3574.65	2603	0.87162	0.47305
2588.15	1859.16	0.01323	0.0048
1254.22	923.779	0.52425	0.2908
1137.59	1137.59	1	1
996.114	712.266	0.00079	0.1988
635.379	470.123	0.04181	0.06365
508.834	368.789	0.50694	0.25087
434.75	432.96	0.74	0.726

HSOH-$CrCl_2O$ Complex, O-Bound

Calculated Freguencies		Calculated Relative Intensity	
$H_2S+CrCl_2O_2$	$D_2S+CrCl_2O_2$	$H_2S+CrCl_2O_2$	$D_2S+CrCl_2O_2$
3702.45	2697.4	0.56	0.323
2628.82	1888.7	0.001	0
1191.77	887.6	0.33	0.344
1138.29	1138.7	1	1
1005.47	737.8	0.02	0.022
714.763	693.7	0.2	0.116
551.283	462.9	0.274	0.379
445.116	402.1	0.714	0.412

H_2SO (uncomplexed)

Calculated Frequency	Calculated Rel. Intensity
2346.16	1
2333.98	0.711
1260.08	0.17
1062.71	0.34
1030.48	0.853
963.43	0.003

H_2SO-$CrCl_2O$ Complex (S-bound)

Calculated Frequency	Calculated Rel. Intensity
2463	0.089
2457.5	0.033
1220.4	0.069
1134.3	1
1121.5	0.641
1036.4	0.052
959.1	0.012
479.9	0.0173

H_2SO-$CrCl_2O$ Complex (O-bound)

attempts to optimize the O-bound complex of H_2SO with $CrCl_2O$ were unsuccessful - dissociation to $CrCl_2O_2$ + H_2S occurred from all starting geometries

Table S2

Band positions (cm^{-1}), assignments and comparison to literature values for the products of the merged-jet reaction of CrO_2Cl_2 with H_2S or D_2S

Exp. freq.		**Lit. freq.**		**Assignment**
H_2S	**D_2S**	**H_2S**	**D_2S**	
2884	2074	2888	2089	H(D)Cl[a]
2845	1942	2856	2040	$(H(D)Cl)_2$[a]
2678	1875	2678	*	H(D)Cl-$H(D)_2S$[b]
1351	1351	1352	1352	SO_2 asym str[c]
1342	1342	*	*	H(D)Cl-SO_2
1153	1153	1157	1157	SO_2 sym str[c]
522	523	523	523	SO_2 bend[c]

* no literature value available

[a] reference 31

[b] reference 32

[c] reference 18