Supplementary Material (ESI) for *PCCP*

Experimental and Theoretical Characterization of Molecular Complexes Formed between OCS and XY Molecules (X, Y = F, Cl and Br) and their Role in Photochemical Matrix Reactions

Supplementary Information

A. Lorena Picone, Carlos O. Della Védova, Helge Willner, Anthony J. Downs, and Rosana M. Romano *

Table S1. Geometric parameters for the different complexes formed between OCS and ClF, Cl_2, Br_2, or BrCl, (distances in Å, angles in degrees) calculated using the B3LYP method and the aug-cc-pVDZ for all the atoms with the exception of Br atoms in the Br_2 complexes for which the LANL2DZ basis set was used (S=C=O···Br_2 (II) were optimized with the B3LYP/6-31+G* approximation)

	r_{CO}	Δr_{CO} [a]	r_{CS}	Δr_{CS} [b]	r_{XY}	Δr_{XY} [c]	α [d]	r [e]	d_p [f]
OCS···FCl (I)	1.163	$-2.\times 10^{-5}$	1.579	-1×10^{-4}	1.675	+0.001	76.6	3.548	–0.25
OCS···FCl (II)	1.164	+0.001	1.579	-4×10^{-4}	1.674	$+5. 10^{-4}$	180.0	3.425	–0.12
OCS···ClF	1.159	–0.004	1.587	+0.008	1.698	+0.024	93.8	2.943	0.62
SCO···FCl	1.163	-3×10^{-4}	1.579	$+2 \times 10^{-4}$	1.674	-7×10^{-5}	90.1	3.327	–0.31
SCO···ClF (I)	1.166	+0.003	1.575	–0.004	1.678	+0.004	142.7	2.819	0.46
SCO···ClF (II)	1.165	+0.002	1.575	–0.004	1.677	+0.003	180.0	2.863	0.42
OCS···Cl_2	1.162	–0.001	1.582	+0.003	2.056	+0.010	98.0	3.354	0.21
SCO···Cl_2 (I)	1.164	+0.001	1.577	–0.002	2.048	+0.002	180.0	3.119	0.16
SCO···Cl_2 (II)	1.165	+0.002	1.577	–0.002	2.048	+0.002	147.1	3.110	0.17
OCS···Br_2	1.159	–0.004	1.587	+0.008	2.540	+0.030	93.8	3.138	0.51
SCO···Br_2 (I)	1.165	+0.002	1.576	–0.003	2.513	+0.003	136.0	3.120	0.25
SCO···Br_2 (II)	1.168	+0.002	1.568	–0.004	2.327	+0.003	177.8	2.895	0.47
OCS···ClBr	1.162	–0.001	1.582	+0.003	2.199	+0.009	93.0	3.373	0.19
OCS···BrCl	1.160	–0.003	1.585	+0.006	2.209	+0.019	96.9	3.210	0.44
SCO···ClBr	1.164	+0.001	1.578	–0.001	2.192	+0.002	180.0	3.263	0.02
SCO···BrCl	1.165	+0.002	1.576	–0.003	2.193	+0.003	180.0	3.075	0.29

[a] $\Delta r_{CO} = r_{CO\ complex} - r_{CO\ free\ OCS}$

[b] $\Delta r_{CS} = r_{CS\ complex} - r_{CS\ free\ OCS}$

[c] $\Delta r_{XY} = r_{XY} - r_{XY\ free\ XY}$

[d] Intermolecular angle CE···X (E = O, S and X = halogen)

[e] Intermolecular distance E···X (E = O, S, or X = halogen)

[f] van der Waals penetration distance, d_p

Table S2. Theoretical IR spectra (wavenumbers in cm^{-1}) of the different complexes formed between OCS and ClF calculated using the B3LYP/aug-cc-pVDZ approximation. Predicted IR intensities are given in parentheses

OCS···FCl (I)	OCS···FCl (II)	OCS···ClF	SCO···FCl	SCO···ClF(I)	SCO···ClF(II)	assignment [a]
2095.9 (100.0)	2093.6 (100.0)	2108.8 (100.0)	2096.9 (100.0)	2085.4 (100.0)	2092.2 (100.0)	ν_{CO}
868.1 (1.1)	868.5 (0.8)	853.0 (1.4)	867.6 (1.14)	876.8 (0.4)	876.4 (0.5)	ν_{CS}
774.7 (2.6)	781.2 (3.9)	705.4 (24.6)	779.5 (3.7)	767.8 (6.6)	775.1(5.6)	ν_{ClF}
509.8 (0.3)		503.2 (0.3)	509.8 (0.3)	506.5 (0.2)		$\delta_{oop\ OCS}$
508.0 (0.4)	510.9 (0.3) [b]	508.0 (0.2)	508.6 (0.5)	509.4 (0.2)	505.9 (0.2) [b]	δ_{OCS}
35.1 (0.1)	30.1 (0.1) [b]	133.2 (<0.1)	35.7 (0.1)	90.7 (0.1)	81.5 (0.1) [b]	δ_{EXY}
29.6 (0.2)		117.0 (<0.1)	21.2 (0.1)	88.0 (0.1)		$\delta_{oop\ EXY}$
20.0 (<0.1)	24.9 (<0.1)	93.1 (1.0)	18.8 (<0.1)	69.8 (0.3)	57.9 (0.1)	ν_{EX}
4.3 (<0.1)	8.3 (<0.1) [b]	37.3 (<0.1)	11.9 (<0.1)	13.4 (<0.1)	7.4 (<0.1) [b]	δ_{CEX}

[a] E = O, S, or X, Y = F or Cl.

[b] Doubly degenerate.

Table S3. Theoretical IR spectra (wavenumbers in cm^{-1}) of the different complexes formed between OCS and Cl_2 calculated using the B3LYP/aug-cc-pVDZ approximation. Predicted IR intensities are given in parentheses

OCS···Cl_2	SCO···Cl_2 (I)	SCO···Cl_2 (II)	assignment [a]
2099.9 (100.0)	2094.0 (100.0)	2091.8 (100.0)	ν_{CO}
862.1 (1.5)	872.3 (0.8)	872.1 (0.8)	ν_{CS}
509.4 (0.4)	508.2 (0.2) [b]	508.0 (0.2)	δ_{OCS}
507.2 (0.3)		508.0 (0.2)	$\delta_{oop\ OCS}$
502.2 (1.6)	523.8 (0.1)	523.9 (0.1)	ν_{ClCl}
66.1 (<0.1)	49.0 (<0.1) [b]	54.0 (<0.1)	δ_{EClCl}
47.3 (<0.1)		42.9 (<0.1)	$\delta_{oop\ EClCl}$
44.0 (0.2)	33.0 (<0.1)	36.9 (<0.1)	ν_{ECl}
18.5 (<0.1)	14.9 (<0.1)	12.0 (<0.1)	δ_{CECl}

[a] E = O or S.

[b] Doubly degenerate.

Table S4. Theoretical IR spectra (wavenumbers in cm^{-1}) of the different complexes formed between OCS and Br_2 calculated using the B3LYP method and the aug-cc-pVDZ for all the atoms with the exception of Br atoms for which the LANL2DZ basis set was used (S=C=O···Br_2 (II) were optimized with the B3LYP/6-31+G* approximation). Predicted IR intensities are given in parentheses

OCS···Br_2	SCO···Br_2 (I)	SCO···Br_2 (II)	assignment [a]
2103.9 (100.0)	2088.6 (100)	2102.9 (100.0)	ν_{CO}
853.0 (2.3)	873.5 (0.6)	881.3 (0.6)	ν_{CS}
504.0 (0.3)	508.8 (0.2)	509.4 (0.3)	$\delta_{oop\ OCS}$
504.0 (0.1)	510.6 (0.2)	509.2 (0.3)	δ_{OCS}
249.6 (2.1)	268.8 (0.1)	323.9 (0.2)	ν_{BrBr}
84.0 (1.0)	59.1 (0.2)	77.5 (<0.1)	δ_{EBrBr}
56.5 (0.2)	37.8 (<0.1)	75.0 (<0.1)	$\delta_{oop\ EbrBr}$
42.9 (<0.1)	32.4 (<0.1)	56.4(0.1)	ν_{Ebr}
25.2 (<0.1)	11.1 (<0.1)	28.2 (<0.1)	δ_{CEBr}

[a] E = O or S.

Table S5. Theoretical IR spectra (wavenumbers in cm^{-1}) of the different complexes formed between OCS and Cl_2 calculated using the B3LYP/aug-cc-pVDZ approximation. Predicted IR intensities are given in parentheses

OCS···ClBr	OCS···BrCl	SCO···ClBr	SCO···BrCl	assignment
2098.6 (100.0)	2104.0 (100.0)	2094.8 (100.0)	2091.9 (100.0)	ν_{CO}
862.8 (1.5)	855.7 (1.9)	870.8 (1.0)	875.4 (0.6)	ν_{CS}
508.8 (0.2)	508.0 (0.1)	508.8 (0.2) [b]	507.0 deg.(0.2)	δ_{OCS}
507.7(0.3)	504.7(0.3)			$\delta_{oop\ OCS}$
405.4 (0.6)	395.5 (3.6)	421.3 (<0.1)	419.9 (0.5)	ν_{BrCl}
58.0 (<0.1)	76.8 (0.3)	47.6 (<0.1) [b]	49.2 deg.(<0.1)	δ_{EXY}
44.1 (0.1)	61.3 (0.3)	25.3 (<0.1)	43.7 (<0.1)	ν_{EX}
38.5 (<0.1)	55.7 (<0.1)			$\delta_{oop\ EXY}$
19.4 (<0.1)	27.5 (<0.1)	16.4 (<0.1)	9.6 deg.(<0.1)	δ_{CEX}

[a] E = O or S.

[b] Doubly degenerate.

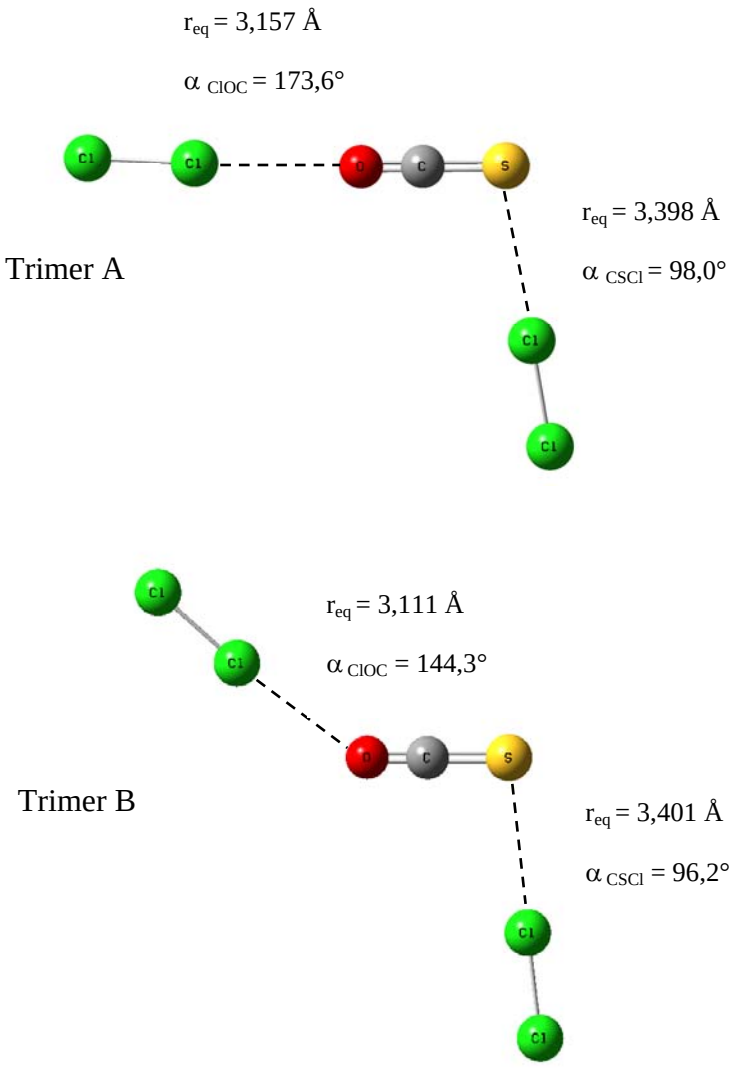

Figure S1. Molecular models of the trimers formed between OCS and Cl_2 calculated with the B3LYP/6-31+G* approximation.