DATA FOR **SUPPLEMENTARY MATERIAL**

Table S1.
Ab initio rotational constants B and vibrational frequencies ν for reactants, transition states, intermediate and products in $CH_3S + CO \rightarrow CH_3 + OCS$. ν calculated at the HF/6-31G(d) level and scaled by 0.8929. B calculated at the MP2=full/6-31G(d) level.

	CH_3S	CO	TS1	Adduct	TS2	CH_3	OCS
B, GHz	159.2	56.0	16.7	20.1	17.4	287.5	5.99
	13.4	56.2	3.10	3.61	3.19	287.5	5.99
	13.3		2.66	3.12	2.74	143.8	
ν, cm^{-1}	565	2178	352 i	98 [a]	529 i	275	506
	689		93 [a]	199	41 [b]	1375	506
	884		149	208	121	1375	794
	1346		179	391	386	2932	2059
	1398		403	558	439	3090	
	1453		695	696	617	3090	
	2874		962	971	663		
	2945		968	985	697		
	2955		1355	1359	1046		
			1442	1444	1399		
			1454	1452	1405		
			1952	1877	1925		
			2894	2898	2918		
			2970	2977	3043		
			2981	2986	3059		

[a] Replaced by 3-fold hindered rotor with a barrier of 0.5 kcal mol^{-1}.

[b] Replaced by 3-fold free rotor.

Tables S2a – S2g. Cartesian coordinates for for reactants, transition states, intermediate and products in $CH_3S + CO \rightarrow CH_3 + OCS$, calculated at the MP2=full/6-31G(d) level of theory, in 10^{-10} m.

Table S2a. CH_3S.

S	0.0107	0.0000	-0.6926
C	-0.0269	0.0000	1.1062
H	1.0125	0.0000	1.4497
H	-0.5113	0.8947	1.4974
H	-0.5113	-0.8947	1.4974

Table S2b. CO.

C	0.0000	0.0000	0.0000
O	0.0000	0.0000	1.1503

Table S2c. TS1

O	0.0000	0.0000	0.0000
C	0.0000	0.0000	1.1583
S	1.7612	0.0000	2.4473
C	0.8045	0.0000	3.9796
H	1.5278	0.0000	4.7983
H	0.1853	0.8928	4.0637
H	0.1853	-0.8928	4.0637

Table S2d. Adduct

O	-0.6974	0.0000	-2.0312
C	-0.6756	0.0000	-0.8386
S	0.7271	0.0000	0.2455
C	-0.1697	0.0000	1.8195
H	0.5876	0.0000	2.6051
H	-0.7852	0.8933	1.9180
H	-0.7852	-0.8933	1.9180

Table S2e. TS2.

O	2.1344	0.5831	0.0000
C	1.1668	-0.0990	0.0000
S	-0.3289	-0.6557	0.0000
C	-2.0149	0.6614	0.0000
H	-2.8454	-0.0419	0.0000
H	-1.9393	1.2474	0.9112
H	-1.9393	1.2474	-0.9112

Table S2f. CH_3.

H	0.0000	1.0783	0.0000
C	0.0000	0.0000	0.0000
H	0.9338	-0.5391	0.0000
H	-0.9338	-0.5391	0.0000

Table S2g. OCS

O	0.0000	0.0000	-1.6993
C	0.0000	0.0000	-0.5207
S	0.0000	0.0000	1.0449

Table S3.
Gaussian-3 energies, thermal corrections and enthalpies relative to reactants at 0 and 298 K for reactants, transition states, intermediate and products in $CH_3S + CO \rightarrow CH_3 + OCS$.

Species	G3 energy, au	H_{298}-H_0, kcal mol^{-1} [a]	$H_{rel,\ 0}$, kcal mol^{-1}	$H_{rel,\ 298}$, kcal mol^{-1}
CH_3S	-437.86577 b	2.8	0	0
CO	-113.26736	2.1		
TS1	-551.12674	3.8	4.0	2.9
Adduct	-551.13508	3.9	-1.2	-2.2
TS2	-551.117701	3.8	9.7	8.6
CH_3	-39.79330	2.5	-4.3	-4.3
OCS	-511.34664	2.4		

[a] Includes hindered internal rotor and electronic contributions.
[b] Includes a spin-orbit correction of –0.00058 au.