

## **Theoretical Studies of Hydrogen Abstraction from H<sub>2</sub>X and CH<sub>3</sub>XH (X=O, S) by Trichloromethyl Radical**

*Jagannath Pal and Ranga Subramanian\**

Department of Chemistry, Indian Institute of Technology Patna, India 801103

\*Email: ranga@iitp.ac.in; Fax: +91-612-3028123

### **Supplementary data**

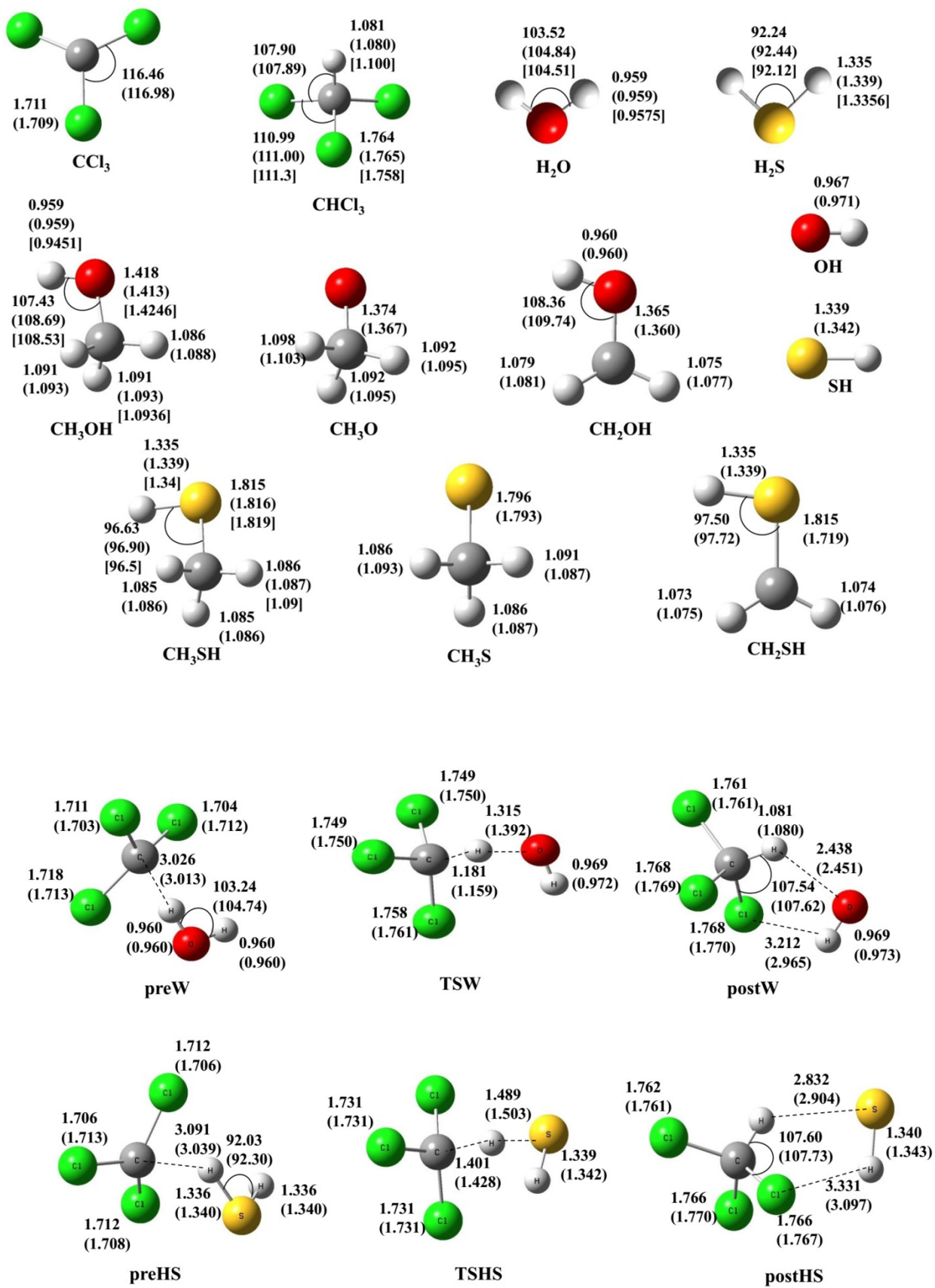
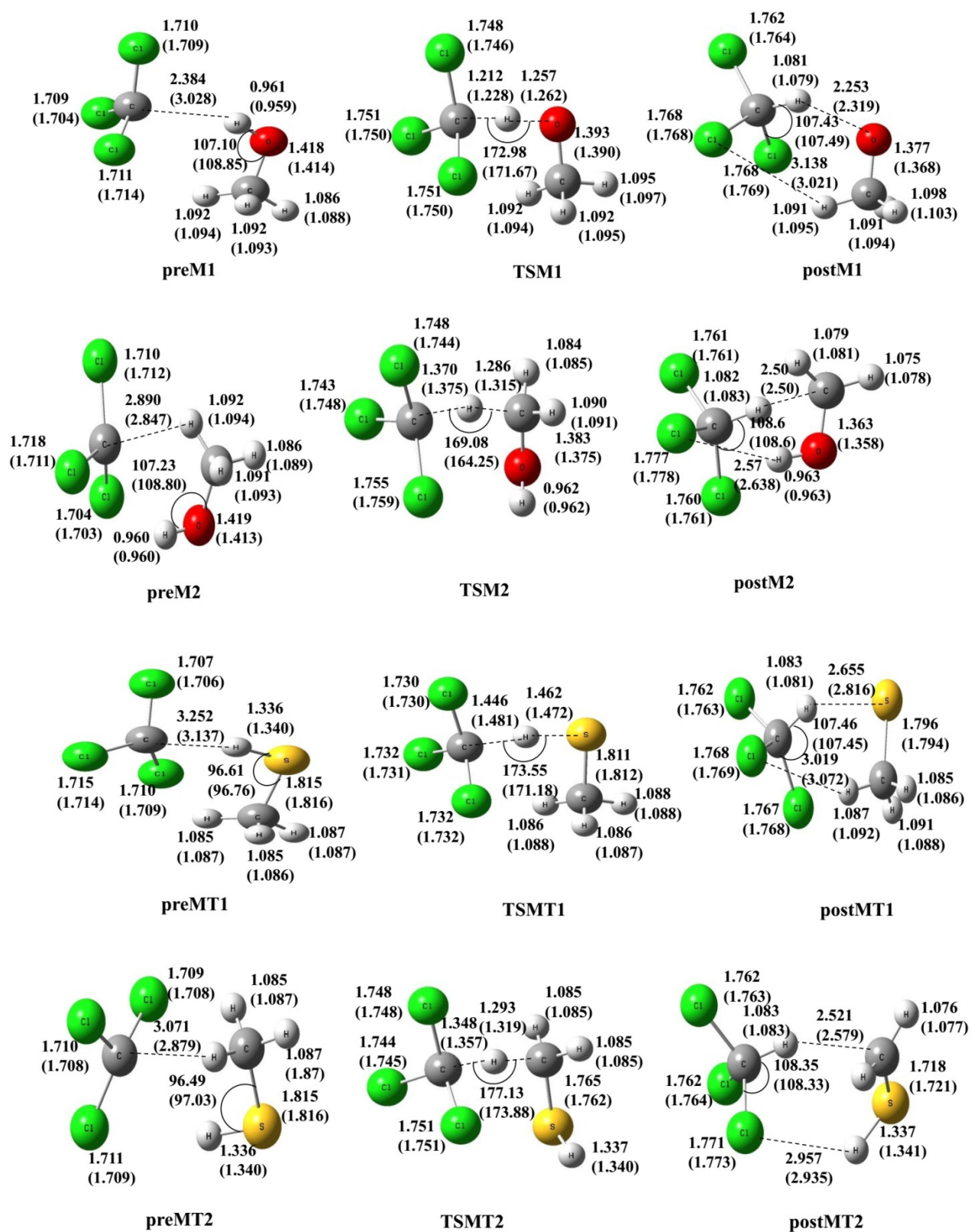


Figure S1. (Continued)



**Figure S1.** Optimized geometries of the reactants, products, transition states, and complexes at the MP2/cc-pVTZ, M06-2X/cc-pVTZ (in parentheses) levels and the limited experimental values (in square brackets). Bond lengths are in angstroms and angles in degree.

**Table S1.** Total Electronic Energy and Zero-point Vibrational Energy for the M06-2X/cc-pVTZ and MP2/cc-pVTZ Geometries (Hartree).

Species	M06-2X/cc-pVTZ		MP2/cc-pVTZ	
	E	ZPE	E	ZPE
CCl <sub>3</sub>	-1418.652018	0.007352	-1417.07847	0.007478
H <sub>2</sub> O	-76.425274	0.021592	-76.318657	0.021604
H <sub>2</sub> S	-399.385798	0.015268	-398.903648	0.015467
CH <sub>3</sub> OH	-115.714121	0.051801	-115.517475	0.052058
CH <sub>3</sub> SH	-438.688801	0.046376	-438.119887	0.046747
CHCl <sub>3</sub>	-1419.308949	0.02024	-1417.7376	0.020296
OH	-75.730487	0.008601	-75.618907	0.008704
HS	-398.737787	0.006177	-398.256334	0.006296
CH <sub>3</sub> O	-115.039487	0.036944	-114.83443	0.037672
CH <sub>2</sub> OH	-115.052655	0.037669	-114.855666	0.038037
CH <sub>3</sub> S	-438.046942	0.035765	-437.477604	0.036262
CH <sub>2</sub> SH	-438.026934	0.031761	-437.457235	0.032063
TSW	-1495.036256	0.026047	-1493.34705	0.025671
TSHS	-1818.027273	0.021358	-1815.97124	0.021571
TSM1	-1534.340195	0.054195	-1532.56029	0.030867
TSM2	-1534.345674	0.055417	-1532.57464	0.05581
TSMT1	-1857.333414	0.051456	-1855.19125	0.052022
TSMT2	-1857.319399	0.049576	-1855.17722	0.050339
preW	-1495.081433	0.030176	-1493.40016	0.030144
preHS	-1818.041192	0.024191	-1815.98485	0.023744
preM1	-1534.371272	0.060323	-1532.5999	0.060224
preM2	-1534.371612	0.060372	-1532.6002	0.060305
preMT1	-1857.345995	0.054765	-1855.2026	0.054829
preMT2	-1857.345383	0.054992	-1855.20245	0.054811
postW	-1495.047365	0.030614	-1493.36218	0.030107
postHS	-1818.052993	0.028002	-1815.99859	0.027365
postM1	-1534.35686	0.058765	-1532.57952	0.05926
postM2	-1534.370626	0.059469	-1532.60083	0.059653
postMT1	-1857.363573	0.057906	-1855.22241	0.057959
postMT2	-1857.343299	0.053644	-1855.2017	0.05396

**Table S2.** Calculated frequencies (Experimental values in parenthesis) (in  $\text{cm}^{-1}$ ) for the reactants, products, transition states, and complexes for the title reactions at the MP2/cc-pVTZ level.

Species	MP2/cc-pVTZ
$\text{CCl}_3$	277, 277, 366, 519, 922, 922
$\text{H}_2\text{O}$	1652 (1595), 3855 (3657), 3976 (3756)
$\text{H}_2\text{S}$	1211 (1183), 2780 (2615), 2799 (2626),
$\text{CH}_3\text{OH}$	309 (295), 1069 (1033), 1104 (1060), 1188 (1165), 1387 (1345), 1497 (1455), 1522 (1477), 1537 (1477), 3053 (2844), 3121 (2960), 3183 (3000), 3882 (3681)
$\text{CH}_3\text{SH}$	243, 737, 810, 986, 1104, 1368, 1493, 1507, 1773, 3098, 3199, 3201
$\text{CHCl}_3$	265 (261), 265 (261), 374 (363), 691 (680), 803 (774), 803 (774), 1252 (1220), 1252 (1220), 3204 (3034)
OH	3821 (3775)
HS	2764
$\text{CH}_3\text{O}$	806, 977, 1136, 1413, 1431, 1541, 3010, 3091, 3131
$\text{CH}_2\text{OH}$	440, 647, 1074, 1225, 1381, 1517, 3192, 3341, 3880
$\text{CH}_3\text{S}$	620, 744, 880, 1346, 1417, 1494, 3070, 3161, 3184
$\text{CH}_2\text{SH}$	131, 361, 796, 866, 1084, 1442, 2780, 3239, 3374
TSW	1979i, 68, 97, 105, 267, 268, 332, 501, 722, 836, 849, 887, 1129, 1409, 3796,
TSHS	1538i, 49, 76, 95, 228, 272, 273, 445, 549, 841, 847, 874, 920, 1237, 2763
TSM1	2493i, 34, 85, 95, 151, 206, 269, 278, 340, 484, 806, 829, 845, 1062, 1139, 1147, 1180, 1399, 1434, 1454, 1532, 3025, 3105, 3130
TSM2	1806i, 33, 59, 84, 168, 264, 271, 319, 361, 448, 565, 787, 832, 846, 1100, 1162, 1214, 1388, 1459, 1473, 1514, 3089, 3215, 3847
TSMT1	1375i, 30, 69, 84, 112, 147, 243, 273, 278, 449, 740, 829, 859, 876, 890, 959, 984, 1226, 1355, 1480, 1497, 3084, 3182, 3190,
TSMT2	1804i, 29, 52, 78, 140, 247, 269, 273, 311, 446, 538, 775, 796, 834, 840, 863, 1061, 1121, 1420, 1429, 1448, 2767, 3129, 3229
preW	18, 42, 57, 78, 106, 183, 276, 277, 369, 519, 912, 931, 1652, 3848, 3964
preHS	14, 31, 48, 53, 101, 119, 276, 277, 365, 515, 917, 929, 1208, 2775, 2793
preM1	20, 26, 39, 67, 77, 87, 277, 277, 328, 377, 525, 920, 924, 1070, 1104, 1189, 1390, 1494, 1520, 1534, 3050, 3119, 3178, 3844
preM2	18, 31, 40, 69, 72, 100, 276, 277, 341, 370, 516, 912, 933, 1069, 1103, 1188, 1389, 1494, 1520, 1534, 3051, 3119, 3181, 3869
preMT1	19, 26, 31, 55, 65, 89, 253, 277, 277, 360, 511, 736, 809, 917, 929, 987, 1102, 1367, 1489, 1505, 2768, 3097, 3197, 3202
preMT2	9, 24, 41, 48, 66, 88, 246, 276, 277, 369, 519, 736, 806, 921, 924, 986, 1100, 1366, 1491, 1504, 2769, 3095, 3196, 3200
postW	26, 38, 69, 103, 238, 265, 272, 374, 689, 793, 810, 1249, 1269, 3221, 3800
postHS	2, 33, 46, 70, 192, 265, 267, 374, 689, 795, 807, 1251, 1265, 2757, 3200
postM1	27, 41, 44, 81, 92, 117, 265, 266, 375, 688, 793, 805, 920, 983, 1129, 1262, 1285, 1409, 1429, 1539, 3009, 3097, 3143, 3215

postM2	17, 47, 65, 87, 109, 187, 265, 267, 374, 518, 678, 687, 789, 812, 1082, 1223, 1259, 1269, 1389, 1514, 3188, 3191, 3339, 3828
postMT1	22, 26, 45, 74, 77, 93, 265, 266, 375, 687, 739, 787, 804, 820, 935, 1265, 1278, 1346, 1440, 1492, 3071, 3161, 3180, 3194
postMT2	19, 36, 56, 69, 90, 152, 265, 266, 351, 375, 474, 688, 792, 801, 806, 865, 1088, 1256, 1268, 1439, 2765, 3185, 3221, 3355

**Table S3.** Cartesian coordinates for the reactants, products, transition states, and complexes for the title reactions at the M06-2X/cc-pVTZ level.

Species	M06-2X/cc-pVTZ			
CCl <sub>3</sub>	C	0.10136200	-0.17536900	0.07160400
	Cl	-0.03728300	0.06446800	1.75792800
	Cl	1.64506800	0.06457800	-0.62110300
	Cl	-0.87947500	-1.39071000	-0.62176200
H <sub>2</sub> O	O	-0.01672900	0.00000000	-0.01182300
	H	0.02223700	0.00000000	0.94628300
	H	0.89942800	0.00000000	-0.29491400
H <sub>2</sub> S	S	-0.09260900	0.00000000	-0.06538700
	H	0.10593500	0.00000000	1.25829600
	H	1.22153500	0.00000000	-0.32019600
CH <sub>3</sub> OH	C	0.00477900	0.00775600	-0.01791700
	H	-0.01719900	-0.02805100	1.06894900
	H	1.04999100	0.01207500	-0.33862100
	H	-0.46586700	0.94100600	-0.33869400
	O	-0.69202000	-1.12932300	-0.48347800
	H	-0.68745900	-1.12129500	-1.44195800
CH <sub>3</sub> SH	C	0.06275000	0.10128200	0.06447800
	H	0.06330800	0.10582400	1.15124800
	H	1.08961400	0.06973000	-0.28716600
	H	-0.43213100	1.00047300	-0.28997800
	H	-0.74343500	-1.20629900	-1.75632100
	S	-0.84787900	-1.38884200	-0.43398000
CHCl <sub>3</sub>	C	0.00000400	0.00000500	-0.02870000
	H	-0.00018700	-0.00000800	1.05171100
	Cl	1.67985400	0.00000000	-0.57112900
	Cl	-0.83983400	-1.45475200	-0.57094200
	Cl	-0.83983700	1.45475400	-0.57094000
OH	O	0.00000000	0.00000000	-0.00571100
	H	0.00000000	0.00000000	0.96571100
HS	S	0.00000000	0.00000000	-0.01616300
	H	0.00000000	0.00000000	1.32616300
CH <sub>3</sub> O	C	-0.00167400	-0.00276400	-0.02304600
	H	-0.00584900	-0.00972000	1.07964100
	H	1.04734800	-0.01565300	-0.33624000
	H	-0.50212000	0.91929100	-0.33625400

	O	-0.68118800	-1.12894500	-0.39449300
CH <sub>2</sub> OH	C	0.05965600	-0.12532900	0.06401000
	H	-0.02254600	0.01734400	1.12873800
	H	0.99894100	0.04185500	-0.44400600
	O	-0.79217200	-1.06481200	-0.42806900
	H	-0.61543700	-1.20576600	-1.36058200
CH <sub>3</sub> S	C	0.00654700	0.01039800	-0.00467800
	H	0.00158600	0.00286800	1.08799000
	H	1.04084700	-0.00898600	-0.33849200
	H	-0.49333900	0.91618800	-0.33841800
	S	-0.88050400	-1.45886200	-0.52433700
CH <sub>2</sub> SH	C	0.15901900	-0.12185500	0.18794700
	H	0.11548600	0.14004000	1.23072000
	H	0.99169900	0.17357800	-0.42479800
	H	-0.62305200	-1.28466600	-1.65671600
	S	-1.01471200	-1.24380700	-0.37706400
TSW	C	-0.00137800	-0.00114800	0.00000600
	H	-0.00447900	-0.00380100	1.15929600
	Cl	1.67759600	0.00321100	-0.49407400
	Cl	-0.84257800	-1.45118300	-0.50314900
	Cl	-0.84173500	1.45845000	-0.51331700
	O	-0.14739400	0.22160600	2.52518000
	H	-0.63983000	1.05871400	2.49505100
TSHS	C	-0.01652600	-0.11528500	-0.01828400
	H	-0.15774200	-0.45148100	1.36188400
	Cl	1.62003100	-0.52471700	-0.40804000
	Cl	-1.20256600	-1.12391700	-0.77538600
	Cl	-0.36351900	1.57843300	-0.10214600
	H	0.72501300	0.05774400	3.09852200
	S	-0.27173300	-0.79615400	2.82017400
TSM1	C	-0.22185300	-0.07710500	-0.18837500
	H	-0.46377400	0.39076600	0.77131300
	H	0.79732600	-0.47556500	-0.11111000
	H	-0.23177600	0.66623900	-0.99063900
	O	-1.03194700	-1.17284000	-0.46281700
	H	-2.22397400	-0.75790500	-0.47730500
	C	-3.31534700	-0.19715700	-0.44140500
	Cl	-3.23379900	1.12144700	-1.58954300
	Cl	-3.52209800	0.36433100	1.20318000
	Cl	-4.48255900	-1.41417000	-0.89230500
	TSM2	C	-0.44584800	-0.29583700
H		-0.87224300	-0.40821400	0.81265100
H		0.63505900	-0.43765000	-0.21479400
H		-0.91307200	-1.30693400	-0.87788700
O		-0.91275500	0.85333400	-0.77241100
H		-0.47276000	0.98007000	-1.61815700
C		-1.42110100	-2.10207800	-1.87860200
Cl		-0.75195100	-1.38337300	-3.33792600
Cl		-3.15804100	-1.96345600	-1.80470800

	Cl	-0.84996000	-3.73295300	-1.61808800
TSMT1	C	0.04782500	0.09028500	-0.02066800
	H	0.21781500	0.10480900	1.05347300
	H	0.99291100	0.03135800	-0.55355100
	H	-0.55227300	-0.78427200	-0.26447700
	C	1.06843300	3.27871000	0.77594800
	Cl	0.66364300	4.91401500	0.38197000
	Cl	0.87047300	2.87581200	2.44839400
	Cl	2.55663100	2.72411400	0.08496900
	H	0.02086600	2.49756600	0.07890400
	S	-0.90932300	1.53882100	-0.53920600
TSMT2	C	-0.26869100	-0.20618700	-0.12809600
	H	-0.66086500	-0.50234900	0.83949100
	H	0.77481500	0.08901600	-0.09601300
	H	-0.27537200	-1.31917800	-0.83668700
	H	-0.54531000	1.27261700	-1.92367900
	C	-0.34150900	-2.38637300	-1.67274200
	Cl	0.22373200	-1.76971800	-3.21142000
	Cl	-2.02473700	-2.84517900	-1.70917200
	Cl	0.69520600	-3.63478200	-1.02265500
	S	-1.35376900	0.94338900	-0.90735800
preW	C	0.21634700	0.00853800	-0.08738700
	H	-0.42947300	1.33922100	2.53712100
	Cl	1.64847300	-0.62217900	-0.75978800
	Cl	-1.15895600	-1.01174600	-0.08009900
	Cl	-0.07552200	1.68280600	-0.30023500
	O	-0.30697700	0.47229200	2.93036400
	H	-1.06609400	-0.03760300	2.63881400
preHS	C	0.08160000	-0.04321700	-0.04471600
	H	-0.20089400	0.25362300	2.96693100
	Cl	1.53355800	-0.04824900	-0.93980500
	Cl	-0.76028500	-1.52245200	0.09316600
	Cl	-0.86425800	1.38347800	-0.10407800
	H	1.18260900	1.48141200	2.40832800
	S	1.11104000	0.39984400	3.19555900
preM1	C	-0.06705800	-0.05411600	-0.05315500
	H	-0.99399100	0.43241000	0.24218600
	H	0.68674700	0.14257700	0.71331900
	H	0.26531300	0.38740500	-0.99781700
	O	-0.34768600	-1.43360100	-0.18067500
	H	0.45005600	-1.88772500	-0.45955300
	C	-0.63775800	-1.11392300	-3.17754200
	Cl	0.36553000	-0.14524700	-4.17337400
	Cl	-2.21002700	-0.53200900	-2.86741500
	Cl	-0.44225900	-2.80730800	-3.30550900
preM2	C	0.06518700	-0.12190800	-0.10436300
	H	0.37406800	-0.58937900	0.82898500
	H	0.96020200	0.18981500	-0.64893000
	H	-0.46912200	-0.86908400	-0.69891700



	O	-0.75711100	0.97615000	0.23606300
	H	-1.12534200	1.34742500	-0.56787500
	C	-2.62952000	-1.24165500	1.11755300
	Cl	-3.56712300	-0.77909700	-0.23749700
	Cl	-2.86292900	-0.37093500	2.56193700
	Cl	-2.25792900	-2.90702500	1.25864000
preMT1	C	-0.04847400	-0.03901200	0.10011500
	H	0.04376000	-0.26973000	1.15822000
	H	0.91640900	0.28519900	-0.27805000
	H	-0.78714100	0.74846000	-0.02384400
	H	-0.71281700	-1.06591800	-1.94158200
	C	-3.45669600	0.04694100	-0.90503300
	Cl	-2.96079300	1.29102400	-1.97477000
	Cl	-3.69504100	0.48601700	0.72937600
	Cl	-4.47881900	-1.15908900	-1.54583900
	S	-0.58611700	-1.57341200	-0.70804500
preMT2	C	-0.01814900	0.05889100	0.30337900
	H	0.54762200	0.60915900	1.05101400
	H	0.62971000	-0.68606500	-0.15138800
	H	-0.86524900	-0.42127500	0.78651800
	H	-1.25875200	0.44553800	-1.69596300
	C	-1.38053000	-2.36881300	-1.34186100
	Cl	-0.57430700	-2.26568900	-2.84427800
	Cl	-3.03374000	-1.93746300	-1.31074900
	Cl	-0.87723700	-3.59986700	-0.27028800
	S	-0.56720200	1.28686100	-0.91608500
postW	C	0.25903600	0.06676300	0.09702300
	H	0.76755700	-0.05720500	1.04192000
	Cl	1.37467800	-0.29950700	-1.21489200
	Cl	-1.12155600	-1.04107800	0.08216600
	Cl	-0.29432000	1.74487100	0.01012200
	O	-0.62919800	0.86912500	2.83033000
	H	-1.51236500	0.65599600	2.48222700
postHS	C	-0.00074500	-0.06659000	0.03017900
	H	-0.00891100	-0.29031800	1.08826500
	Cl	1.68662500	0.05292600	-0.48147700
	Cl	-0.83420800	-1.35704000	-0.83170300
	Cl	-0.83060300	1.48078500	-0.19226200
	H	1.66385400	2.09583800	1.84617700
	S	0.69366000	1.97327800	2.76709100
postM1	C	0.09685900	0.11087300	-0.17807000
	O	0.18550000	0.31519700	1.17201100
	H	1.03600200	-0.39790600	-0.45406300
	H	0.07656000	1.04981900	-0.74077400
	H	-0.72985000	-0.55111000	-0.45071100
	C	1.55917500	2.99979200	1.53620700
	Cl	2.31555800	4.18668300	2.59885900
	Cl	2.71061200	2.41188900	0.32823500
	Cl	0.12561400	3.67481400	0.75300100

	H	1.23963600	2.15007100	2.12023400
postM2	C	0.27391400	0.15985800	-0.04030400
	H	1.23925800	0.08064700	0.43230200
	H	0.15243100	-0.04627800	-1.09417000
	H	-1.44940500	-1.29598600	1.03866500
	O	-0.55076900	1.06416300	0.54832100
	H	-1.35073800	1.16593000	0.02280400
	C	-2.52527400	-1.39269800	0.96383900
	Cl	-2.99143300	-0.78949400	-0.64255800
	Cl	-3.26518100	-0.41708400	2.22951600
	Cl	-2.95430600	-3.09327900	1.12981200
postMT1	C	-0.04235400	-0.08975900	0.04451600
	H	0.06906500	0.13224000	1.10442000
	H	0.94643600	0.00165100	-0.41030700
	H	-0.42272900	-1.09558200	-0.10580500
	C	1.53043700	3.42755700	-0.49024700
	Cl	2.19261300	5.05821500	-0.58987400
	Cl	2.05260000	2.62126200	0.99346800
	Cl	1.98195700	2.47463000	-1.91088700
	H	0.45104200	3.48357700	-0.46603600
	S	-1.09114800	1.14256100	-0.72918400
postMT2	C	0.10722800	0.24556900	-0.05277600
	H	0.22891600	0.55205900	0.97281400
	H	0.96512500	-0.00824600	-0.65236000
	H	-0.83676500	-2.14213700	-0.29211900
	H	-1.14052300	0.13229000	-2.00091900
	C	-0.91493600	-2.90906300	-1.05238100
	Cl	0.18496300	-2.46038300	-2.36812200
	Cl	-2.58242700	-2.95422200	-1.62509500
	Cl	-0.44197000	-4.45273000	-0.34415300
	S	-1.38907000	0.66083600	-0.79361200

**Table S4:** Relative Electronic Energies (in kcal/mol) at different levels of theory for the different species involved in the reaction of  $\text{CCl}_3$  with  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ .

Reaction Pathway	System	M06-2X/cc-pVTZ	M06-2X/CBS <sup>a</sup>	MP2/cc-pVTZ	MP2/CBS <sup>b</sup>	CCSD(T) <sup>c</sup>	W1
X1	$\text{CCl}_3+\text{H}_2\text{O}$	0	0	0	0	0	0
	PreW	-1.83	-1.56	-1.24	-1.29	-1.70	-0.80
	TSW	23.93	27.58	29.28	33.26	25.88	27.60
	PostW	19.83	21.86	22.58	25.45	19.48	24.26
	$\text{CHCl}_3+\text{OH}$	23.69	25.56	25.44	28.24	22.42	25.98
X2	$\text{CCl}_3+\text{H}_2\text{S}$	0	0	0	0	0	0
	PreHS	-1.13	-1.52	-1.21	-1.81	-1.05	-0.14
	TSHS	5.82	7.35	5.97	6.58	8.09	7.84
	PostHS	-6.14	-7.11	-7.56	-8.21	-8.59	-3.62
	$\text{CHCl}_3+\text{SH}$	-3.21	-3.83	-5.12	-5.20	-6.53	-1.58

<sup>a</sup>Including the ZPE correction as estimated at the UM062X/cc-pVTZ level.

<sup>b</sup>Including the zero-point energy (ZPE) correction as estimated at the UMP2/cc-pVTZ level.

<sup>c</sup>CalculationsUCCSD(T)/cc-pVTZ//UM062X/cc-pVTZ.

**Table S5:** Relative Electronic Energies (in kcal/mol) at different levels of theory for the different species involved in the reaction of  $\text{CCl}_3$  with  $\text{CH}_3\text{OH}$ .

Reaction Pathway	System	M06-2X/cc-pVTZ	M06-2X/CBS <sup>a</sup>	MP2/cc-pVTZ	MP2/CBS <sup>b</sup>	CCSD(T) <sup>c</sup>	W1
X3	$\text{CCl}_3 + \text{CH}_3\text{OH}$	0	0	0	0	0	0
	PreM1	-2.49	-2.28	-2.05	-2.18	-2.27	-1.26
	TSM1	13.17	17.28	19.37	23.19	17.46	16.76
	PostM1	5.58	8.04	10.13	12.72	6.52	8.82
	$\text{CHCl}_3 + \text{CH}_3\text{O}$	9.87	12.14	14.02	16.75	10.81	11.91
Y1	$\text{CCl}_3 + \text{CH}_3\text{OH}$	0	0	0	0	0	0
	PreM2	-2.67	-2.54	-2.19	-2.25	-2.48	-1.32
	TSM2	10.50	13.55	11.03	13.18	14.26	13.04
	PostM2	-2.62	-1.42	-2.99	-2.43	-1.79	-0.46
	$\text{CHCl}_3 + \text{CH}_2\text{OH}$	2.07	3.34	0.93	1.91	2.50	2.87

<sup>a</sup>Including the ZPE correction as estimated at the UM062X/cc-pVTZ level.

<sup>b</sup>Including the zero-point energy (ZPE) correction as estimated at the UMP2/cc-pVTZ level.

<sup>c</sup>Calculations UCCSD(T)/cc-pVTZ//UM062X/cc-pVTZ.

**Table S6:** Relative Electronic Energies (in kcal/mol) at different levels of theory for the different species involved in the reaction of CCl<sub>3</sub> with CH<sub>3</sub>SH.

Reaction Pathway	System	M06-2X/cc-pVTZ	M06-2X/CBS <sup>a</sup>	MP2/cc-pVTZ	MP2/CBS <sup>b</sup>	CCSD(T) <sup>c</sup>	W1
X4	CCl <sub>3</sub> +CH <sub>3</sub> SH	0	0	0	0	0	0
	PreMT1	-2.60	-2.72	-2.28	-2.90	-1.91	-1.61
	TSMT1	3.22	5.13	3.08	4.00	5.89	5.19
	PostMT1	-11.66	-12.05	-12.75	-13.25	-13.15	-9.09
	CHCl <sub>3</sub> +CH <sub>3</sub> S	-8.03	-7.99	-9.11	-4.42	-9.80	-6.21
Y2	CCl <sub>3</sub> +CH <sub>3</sub> SH	0	0	0	0	0	0
	PreMT2	-2.07	-2.39	-2.20	-2.70	-1.80	-0.23
	TSMT2	10.84	13.60	10.83	12.43	14.62	12.66
	PostMT2	-1.61	-1.05	-2.26	-2.69	-1.12	-0.81
	CHCl <sub>3</sub> +CH <sub>2</sub> SH	2.01	2.92	1.04	1.52	2.45	1.39

<sup>a</sup>Including the ZPE correction as estimated at the UM062X/cc-pVTZ level.  
<sup>b</sup>Including the zero-point energy (ZPE) correction as estimated at the UMP2/cc-pVTZ level.  
<sup>c</sup>Calculations UCCSD(T)/cc-pVTZ//UM062X/cc-pVTZ.

**Table S7.** Reaction Gibbs Free energy ( $\Delta G_{r,298.15}^{\theta}$ ) and Reaction enthalpy ( $\Delta H_{r,298.15}^{\theta}$ ) for all reaction channels at the W1 levels (kcal/mol) with the ZPE corrections.

Reaction Channel	Reaction System	$\Delta G_{r,298.15}^{\theta}$	$\Delta H_{r,298.15}^{\theta}$	
			Calculated value (in this work)	Literature value [1-8]
X1	H <sub>2</sub> O + CCl <sub>3</sub> → CHCl <sub>3</sub> + OH	27.24	25.68	25.18
X2	H <sub>2</sub> S + CCl <sub>3</sub> → CHCl <sub>3</sub> + SH	-0.11	-1.90	-3.05
X3	CH <sub>3</sub> OH + CCl <sub>3</sub> → CHCl <sub>3</sub> + CH <sub>3</sub> O	12.20	11.71	11.52
Y1	CH <sub>3</sub> OH + CCl <sub>3</sub> → CHCl <sub>3</sub> + CH <sub>2</sub> OH	13.13	2.87	2.44
X4	CH <sub>3</sub> SH + CCl <sub>3</sub> → CHCl <sub>3</sub> + CH <sub>3</sub> S	-5.83	-6.48	-5.04
Y2	CH <sub>3</sub> SH + CCl <sub>3</sub> → CHCl <sub>3</sub> + CH <sub>2</sub> SH	1.11	1.71	1.47

**Table S8:** Reaction Energies (Electronic) ( $\Delta E$ ) and Forward ( $\Delta E_{\text{fwd}}$ ) and Reverse ( $\Delta E_{\text{rev}}$ ) Barriers (kcal/mol) for the Reaction  $\text{H}_2\text{O} + \text{CCl}_3 \rightarrow \text{CHCl}_3 + \text{OH}$ .

Level of theory	$\Delta E_{\text{fwd}}$	$\Delta E$	$\Delta E_{\text{rev}}$
M06-2X/cc-pVTZ	23.93	23.69	0.24
M06-2X/CBS <sup>b</sup>	27.58	25.56	2.02
MP2/cc-pVTZ	29.28	25.44	3.84
MP2/CBS <sup>a</sup>	33.26	28.24	5.02
CCSD(T) <sup>c</sup>	25.88	22.42	3.46
W1	27.60	25.98	1.62

<sup>a</sup>Including the zero-point energy (ZPE) correction as estimated at the UMP2/cc-pVTZ level.

<sup>b</sup>Including the ZPE correction as estimated at the UM062X/cc-pVTZ level.

<sup>c</sup>Calculations UCCSD(T)/cc-pVTZ//UM062X/cc-pVTZ.

**Table S9:** Reaction Energies (Electronic) ( $\Delta E$ ) and Forward ( $\Delta E_{\text{fwd}}$ ) and Reverse ( $\Delta E_{\text{rev}}$ ) Barriers (kcal/mol) for the Reaction  $\text{H}_2\text{S} + \text{CCl}_3 \rightarrow \text{CHCl}_3 + \text{SH}$ .

Level of theory	$\Delta E_{\text{fwd}}$	$\Delta E$	$\Delta E_{\text{rev}}$
M06-2X/cc-pVTZ	5.82	-3.21	9.03
M06-2X/CBS <sup>b</sup>	7.35	-3.83	11.18
MP2/cc-pVTZ	5.97	-5.12	11.09
MP2/CBS <sup>a</sup>	6.58	-5.20	11.78
CCSD(T) <sup>c</sup>	8.09	-6.53	14.62
W1	7.84	-1.58	9.42

**Table S10:** Reaction Energies (Electronic) ( $\Delta E$ ) and Forward ( $\Delta E_{\text{fwd}}$ ) and Reverse ( $\Delta E_{\text{rev}}$ ) Barriers (kcal/mol) for the Reaction  $\text{CH}_3\text{OH} + \text{CCl}_3 \rightarrow \text{CHCl}_3 + \text{CH}_3\text{O}$ .

Level of theory	$\Delta E_{\text{fwd}}$	$\Delta E$	$\Delta E_{\text{rev}}$
M06-2X/cc-pVTZ	13.17	9.87	3.3
M06-2X/CBS <sup>b</sup>	17.28	12.14	5.14
MP2/cc-pVTZ	19.37	14.02	5.35
MP2/CBS <sup>a</sup>	23.19	16.75	6.44
CCSD(T) <sup>c</sup>	17.46	10.81	6.65
W1	16.76	11.91	4.85

**Table S11:** Reaction Energies (Electronic) ( $\Delta E$ ) and Forward ( $\Delta E_{\text{fwd}}$ ) and Reverse ( $\Delta E_{\text{rev}}$ ) Barriers (kcal/mol) for the Reaction  $\text{CH}_3\text{OH} + \text{CCl}_3 \rightarrow \text{CHCl}_3 + \text{CH}_2\text{OH}$ .

Level of theory	$\Delta E_{\text{fwd}}$	$\Delta E$	$\Delta E_{\text{rev}}$
M06-2X/cc-pVTZ	10.50	2.07	8.43
M06-2X/CBS <sup>b</sup>	13.55	3.34	10.21
MP2/cc-pVTZ	11.03	0.93	10.10
MP2/CBS <sup>a</sup>	13.18	1.91	11.27
CCSD(T) <sup>c</sup>	14.26	2.50	11.76
W1	13.04	2.87	10.17

**Table S12:** Reaction Energies (Electronic) ( $\Delta E$ ) and Forward ( $\Delta E_{\text{fwd}}$ ) and Reverse ( $\Delta E_{\text{rev}}$ ) Barriers (kcal/mol) for the Reaction  $\text{CH}_3\text{SH} + \text{CCl}_3 \rightarrow \text{CHCl}_3 + \text{CH}_3\text{S}$ .

Level of theory	$\Delta E_{\text{fwd}}$	$\Delta E$	$\Delta E_{\text{rev}}$
M06-2X/cc-pVTZ	3.22	-8.03	11.25
M06-2X/CBS <sup>b</sup>	5.13	-7.99	13.12
MP2/cc-pVTZ	3.08	-9.11	12.19
MP2/CBS <sup>a</sup>	4.00	-4.42	8.42
CCSD(T) <sup>c</sup>	5.89	-9.80	15.69
W1	5.19	-6.21	11.40

**Table S13:** Reaction Energies (Electronic) ( $\Delta E$ ) and Forward ( $\Delta E_{\text{fwd}}$ ) and Reverse ( $\Delta E_{\text{rev}}$ ) Barriers (kcal/mol) for the Reaction  $\text{CH}_3\text{SH} + \text{CCl}_3 \rightarrow \text{CHCl}_3 + \text{CH}_2\text{SH}$ .

Level of theory	$\Delta E_{\text{fwd}}$	$\Delta E$	$\Delta E_{\text{rev}}$
M06-2X/cc-pVTZ	10.84	2.01	8.83
M06-2X/CBS <sup>b</sup>	13.60	2.92	10.68
MP2/cc-pVTZ	10.83	1.04	9.79
MP2/CBS <sup>a</sup>	12.43	1.52	10.91
CCSD(T) <sup>c</sup>	14.62	2.45	12.17
W1	12.66	1.39	11.27

**Table S14:** Calculated Rate Coefficients (TST/ZCT) ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ ) at W1 and CCSD(T) method for the  $\text{CCl}_3+\text{H}_2\text{X}$  Reaction at 1atm Pressure.

	Rate Coefficient, k ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ )		Rate Coefficient, k ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ )	
	W1		CCSD(T)	
T(K)	$k_{x1}$ (HO-H)	$k_{x2}$ (HS-H)	$k_{x1}$ (HO-H)	$k_{x2}$ (HS-H)
200	9.71E-43	5.78E-20	7.21E-41	5.97E-20
225	1.88E-39	1.98E-19	8.60E-38	1.71E-19
250	8.10E-37	5.96E-19	2.52E-35	4.65E-19
275	1.18E-34	1.59E-18	2.67E-33	1.17E-18
298	5.53E-33	3.59E-18	9.84E-32	2.57E-18
300	7.52E-33	3.83E-18	1.31E-31	2.74E-18
325	2.57E-31	8.41E-18	3.58E-30	5.91E-18
350	5.34E-30	1.70E-17	6.16E-29	1.19E-17
375	7.48E-29	3.22E-17	7.31E-28	2.24E-17
400	7.60E-28	5.74E-17	6.43E-27	4.01E-17
450	3.70E-26	1.58E-16	2.46E-25	1.11E-16
500	8.50E-25	3.73E-16	4.66E-24	2.65E-16
550	1.13E-23	7.83E-16	5.29E-23	5.62E-16
600	9.96E-23	1.50E-15	4.09E-22	1.09E-15
650	6.39E-22	2.67E-15	2.35E-21	1.95E-15
700	3.20E-21	4.47E-15	1.07E-20	3.30E-15
750	1.31E-20	7.11E-15	4.02E-20	5.30E-15
800	4.55E-20	1.09E-14	1.30E-19	8.15E-15
850	1.38E-19	1.60E-14	3.71E-19	1.21E-14
900	3.75E-19	2.29E-14	9.50E-19	1.74E-14
950	9.23E-19	3.18E-14	2.23E-18	2.43E-14
1000	2.10E-18	4.33E-14	4.83E-18	3.32E-14
1050	4.44E-18	5.77E-14	9.82E-18	4.45E-14



1100	8.85E-18	7.54E-14	1.88E-17	5.84E-14
1150	1.67E-17	9.71E-14	3.44E-17	7.55E-14
1200	3.01E-17	1.23E-13	6.01E-17	9.61E-14
1250	5.21E-17	1.54E-13	1.01E-16	1.21E-13
1300	8.68E-17	1.91E-13	1.64E-16	1.50E-13
1350	1.40E-16	2.33E-13	2.58E-16	1.84E-13
1400	2.19E-16	2.83E-13	3.94E-16	2.24E-13
1450	3.34E-16	3.40E-13	5.88E-16	2.69E-13
1500	4.97E-16	4.05E-13	8.57E-16	3.21E-13
1550	7.23E-16	4.78E-13	1.22E-15	3.81E-13
1600	1.03E-15	5.61E-13	1.72E-15	4.48E-13
1650	1.44E-15	6.55E-13	2.36E-15	5.24E-13
1700	1.99E-15	7.59E-13	3.21E-15	6.08E-13
1750	2.69E-15	8.75E-13	4.28E-15	7.02E-13
1800	3.60E-15	1.00E-12	5.65E-15	8.07E-13
1850	4.75E-15	1.14E-12	7.35E-15	9.22E-13
1900	6.19E-15	1.30E-12	9.47E-15	1.05E-12
1950	7.98E-15	1.47E-12	1.21E-14	1.19E-12
2000	1.02E-14	1.66E-12	1.52E-14	1.34E-12

**Table S15:** Calculated Rate Coefficients (TST/ZCT) ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) at a W1 method for the  $\text{CCl}_3+\text{CH}_3\text{OH}$  Reaction at 1atm Pressure.

T(K)	Rate Coefficient, k ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )			Branching ratio, $\phi$ (%)	
	$k_{X3}$ (O-H)	$k_{Y1}$ (C-H)	$k_{OV1}(=k_{X3}+k_{Y1})$	X3 ( $\text{CH}_3\text{O} + \text{P}$ ) P= $\text{CHCl}_3$	Y1 ( $\text{CH}_2\text{OH} + \text{P}$ )
200	4.61E-28	2.46E-23	2.46E-23	0.00	100.00
225	1.38E-26	1.20E-22	1.20E-22	0.01	99.99
250	2.23E-25	5.16E-22	5.16E-22	0.04	99.96

275	2.29E-24	1.97E-21	1.97E-21	0.12	99.88
298	1.43E-23	6.09E-21	6.10E-21	0.23	99.77
300	1.66E-23	6.69E-21	6.71E-21	0.25	99.75
325	9.18E-23	2.04E-20	2.05E-20	0.45	99.55
350	4.08E-22	5.62E-20	5.66E-20	0.72	99.28
375	1.52E-21	1.41E-19	1.43E-19	1.07	98.93
400	4.90E-21	3.28E-19	3.33E-19	1.47	98.53
450	3.61E-20	1.44E-18	1.48E-18	2.45	97.55
500	1.87E-19	5.03E-18	5.22E-18	3.58	96.42
550	7.48E-19	1.48E-17	1.55E-17	4.81	95.19
600	2.45E-18	3.78E-17	4.03E-17	6.09	93.91
650	6.86E-18	8.63E-17	9.32E-17	7.36	92.64
700	1.70E-17	1.80E-16	1.97E-16	8.63	91.37
750	3.79E-17	3.48E-16	3.86E-16	9.82	90.18
800	7.80E-17	6.30E-16	7.08E-16	11.02	88.98
850	1.50E-16	1.08E-15	1.23E-15	12.20	87.80
900	2.70E-16	1.77E-15	2.04E-15	13.24	86.76
950	4.64E-16	2.80E-15	3.26E-15	14.22	85.78
1000	7.63E-16	4.26E-15	5.02E-15	15.19	84.81
1050	1.21E-15	6.29E-15	7.50E-15	16.13	83.87
1100	1.85E-15	9.04E-15	1.09E-14	16.99	83.01
1150	2.75E-15	1.27E-14	1.55E-14	17.80	82.20
1200	3.98E-15	1.74E-14	2.14E-14	18.62	81.38
1250	5.63E-15	2.35E-14	2.91E-14	19.33	80.67
1300	7.81E-15	3.12E-14	3.90E-14	20.02	79.98
1350	1.06E-14	4.07E-14	5.13E-14	20.66	79.34
1400	1.42E-14	5.23E-14	6.65E-14	21.35	78.65

1450	1.87E-14	6.65E-14	8.52E-14	21.95	78.05
1500	2.43E-14	8.34E-14	1.08E-13	22.56	77.44
1550	3.11E-14	1.04E-13	1.35E-13	23.02	76.98
1600	3.94E-14	1.27E-13	1.66E-13	23.68	76.32
1650	4.94E-14	1.55E-13	2.04E-13	24.17	75.83
1700	6.12E-14	1.87E-13	2.48E-13	24.66	75.34
1750	7.53E-14	2.25E-13	3.00E-13	25.07	74.93
1800	9.17E-14	2.67E-13	3.59E-13	25.56	74.44
1850	1.11E-13	3.16E-13	4.27E-13	26.00	74.00
1900	1.33E-13	3.71E-13	5.04E-13	26.39	73.61
1950	1.58E-13	4.33E-13	5.91E-13	26.73	73.27
2000	1.87E-13	5.03E-13	6.90E-13	27.10	72.90

**Table S16:** Calculated Rate Coefficients (TST/ZCT) ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) at a W1 method for the  $\text{CCl}_3+\text{CH}_3\text{SH}$  Reaction at 1atm Pressure.

T(K)	Rate Coefficient, k ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )			Branching ratio, $\phi$ (%)	
	$k_{\text{X4}}(\text{S-H})$	$k_{\text{Y2}}(\text{C-H})$	$k_{\text{OV2}}(= k_{\text{X4}} + k_{\text{Y2}})$	X3 ( $\text{CH}_3\text{S} + \text{P}$ ) P= $\text{CHCl}_3$	Y1 ( $\text{CH}_2\text{SH} + \text{P}$ )
200	1.71E-17	1.44E-22	1.71E-17	100.00	0.00
225	3.47E-17	5.05E-22	3.47E-17	100.00	0.00
250	6.61E-17	1.70E-21	6.61E-17	100.00	0.00
275	1.19E-16	5.38E-21	1.19E-16	100.00	0.00
298	1.94E-16	1.46E-20	1.94E-16	99.99	0.01
300	2.02E-16	1.59E-20	2.02E-16	99.99	0.01
325	3.27E-16	4.35E-20	3.27E-16	99.99	0.01
350	5.08E-16	1.10E-19	5.08E-16	99.98	0.02
375	7.61E-16	2.58E-19	7.61E-16	99.97	0.03

400	1.10E-15	5.66E-19	1.10E-15	99.95	0.05
450	2.15E-15	2.27E-18	2.15E-15	99.89	0.11
500	3.83E-15	7.43E-18	3.84E-15	99.81	0.19
550	6.38E-15	2.07E-17	6.40E-15	99.68	0.32
600	1.01E-14	5.07E-17	1.02E-14	99.50	0.50
650	1.52E-14	1.12E-16	1.53E-14	99.27	0.73
700	2.20E-14	2.26E-16	2.22E-14	98.98	1.02
750	3.10E-14	4.26E-16	3.14E-14	98.64	1.36
800	4.26E-14	7.55E-16	4.34E-14	98.26	1.74
850	5.70E-14	1.27E-15	5.83E-14	97.82	2.18
900	7.48E-14	2.05E-15	7.69E-14	97.33	2.67
950	9.65E-14	3.18E-15	9.97E-14	96.81	3.19
1000	1.22E-13	4.78E-15	1.27E-13	96.23	3.77
1050	1.53E-13	6.98E-15	1.60E-13	95.64	4.36
1100	1.89E-13	9.92E-15	1.99E-13	95.01	4.99
1150	2.31E-13	1.38E-14	2.45E-13	94.36	5.64
1200	2.80E-13	1.88E-14	2.99E-13	93.71	6.29
1250	3.36E-13	2.51E-14	3.61E-13	93.05	6.95
1300	3.99E-13	3.30E-14	4.32E-13	92.36	7.64
1350	4.70E-13	4.28E-14	5.13E-13	91.65	8.35
1400	5.50E-13	5.47E-14	6.05E-13	90.95	9.05
1450	6.40E-13	6.90E-14	7.09E-13	90.27	9.73
1500	7.39E-13	8.62E-14	8.25E-13	89.55	10.45
1550	8.49E-13	1.06E-13	9.55E-13	88.90	11.10
1600	9.71E-13	1.30E-13	1.10E-12	88.19	11.81
1650	1.10E-12	1.58E-13	1.26E-12	87.44	12.56
1700	1.25E-12	1.90E-13	1.44E-12	86.81	13.19

1750	1.41E-12	2.27E-13	1.64E-12	86.13	13.87
1800	1.58E-12	2.69E-13	1.85E-12	85.45	14.55
1850	1.77E-12	3.17E-13	2.09E-12	84.81	15.19
1900	1.97E-12	3.71E-13	2.34E-12	84.15	15.85
1950	2.19E-12	4.31E-13	2.62E-12	83.56	16.44
2000	2.43E-12	4.99E-13	2.93E-12	82.96	17.04

**Table S17:** Calculated Rate Coefficients (TST/ZCT) ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) at CCSD(T) method for the  $\text{CCl}_3+\text{CH}_3\text{OH}$  Reaction at 1atm Pressure.

T(K)	Rate Coefficient, k ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )			Branching ratio, $\phi$ (%)	
	$k_{X3}(\text{O-H})$	$k_{Y1}(\text{C-H})$	$k_{\text{OV1}} (= k_{X3} + k_{Y1})$	X3 ( $\text{CH}_3\text{O} + \text{P}$ ) P= $\text{CHCl}_3$	Y1 ( $\text{CH}_2\text{OH} + \text{P}$ )
200	2.62E-28	2.55E-24	2.55E-24	0.01	99.99
225	6.91E-27	1.32E-23	1.32E-23	0.05	99.95
250	1.05E-25	6.21E-23	6.22E-23	0.17	99.83
275	1.05E-24	2.62E-22	2.63E-22	0.40	99.60
298	6.53E-24	8.97E-22	9.04E-22	0.72	99.28
300	7.57E-24	9.94E-22	1.00E-21	0.76	99.24
325	4.22E-23	3.37E-21	3.41E-21	1.24	98.76
350	1.91E-22	1.03E-20	1.05E-20	1.82	98.18
375	7.28E-22	2.83E-20	2.90E-20	2.51	97.49
400	2.40E-21	7.16E-20	7.40E-20	3.24	96.76
450	1.86E-20	3.64E-19	3.83E-19	4.86	95.14
500	1.01E-19	1.44E-18	1.54E-18	6.55	93.45
550	4.20E-19	4.70E-18	5.12E-18	8.20	91.80
600	1.43E-18	1.31E-17	1.45E-17	9.84	90.16
650	4.13E-18	3.22E-17	3.63E-17	11.37	88.63

700	1.05E-17	7.17E-17	8.22E-17	12.77	87.23
750	2.41E-17	1.46E-16	1.70E-16	14.17	85.83
800	5.07E-17	2.79E-16	3.30E-16	15.38	84.62
850	9.93E-17	5.00E-16	5.99E-16	16.57	83.43
900	1.83E-16	8.53E-16	1.04E-15	17.66	82.34
950	3.20E-16	1.39E-15	1.71E-15	18.71	81.29
1000	5.34E-16	2.19E-15	2.72E-15	19.60	80.40
1050	8.57E-16	3.32E-15	4.18E-15	20.52	79.48
1100	1.33E-15	4.91E-15	6.24E-15	21.31	78.69
1150	2.00E-15	7.05E-15	9.05E-15	22.10	77.90
1200	2.93E-15	9.90E-15	1.28E-14	22.84	77.16
1250	4.19E-15	1.36E-14	1.78E-14	23.55	76.45
1300	5.87E-15	1.84E-14	2.43E-14	24.19	75.81
1350	8.05E-15	2.44E-14	3.25E-14	24.81	75.19
1400	1.09E-14	3.19E-14	4.28E-14	25.47	74.53
1450	1.44E-14	4.12E-14	5.56E-14	25.90	74.10
1500	1.88E-14	5.24E-14	7.12E-14	26.40	73.60
1550	2.43E-14	6.59E-14	9.02E-14	26.94	73.06
1600	3.10E-14	8.20E-14	1.13E-13	27.43	72.57
1650	3.91E-14	1.01E-13	1.40E-13	27.91	72.09
1700	4.87E-14	1.23E-13	1.72E-13	28.36	71.64
1750	6.02E-14	1.49E-13	2.09E-13	28.78	71.22
1800	7.38E-14	1.80E-13	2.54E-13	29.08	70.92
1850	8.96E-14	2.14E-13	3.04E-13	29.51	70.49
1900	1.08E-13	2.54E-13	3.62E-13	29.83	70.17
1950	1.29E-13	2.99E-13	4.28E-13	30.14	69.86
2000	1.54E-13	3.49E-13	5.03E-13	30.62	69.38

**Table S18:** Calculated Rate Coefficients (TST/ZCT) ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) at CCSD(T) method for the  $\text{CCl}_3+\text{CH}_3\text{SH}$  Reaction at 1atm Pressure.

T(K)	Rate Coefficient, k ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )			Branching ratio, $\phi$ (%)	
	$k_{X4}$ (S-H)	$k_{Y2}$ (C-H)	$k_{Ov2}(= k_{X4} + k_{Y2})$	X3 ( $\text{CH}_3\text{S} + \text{P}$ ) P= $\text{CHCl}_3$	Y1 ( $\text{CH}_2\text{SH} + \text{P}$ )
200	3.96E-18	2.23E-24	3.96E-18	100.00	0.00
225	8.84E-18	1.05E-23	8.84E-18	100.00	0.00
250	1.85E-17	4.59E-23	1.85E-17	100.00	0.00
275	3.60E-17	1.85E-22	3.60E-17	100.00	0.00
298	6.31E-17	6.16E-22	6.31E-17	100.00	0.00
300	6.60E-17	6.82E-22	6.60E-17	100.00	0.00
325	1.15E-16	2.28E-21	1.15E-16	100.00	0.00
350	1.89E-16	6.91E-21	1.89E-16	100.00	0.00
375	2.99E-16	1.91E-20	2.99E-16	99.99	0.01
400	4.56E-16	4.85E-20	4.56E-16	99.99	0.01
450	9.64E-16	2.50E-19	9.64E-16	99.97	0.03
500	1.84E-15	1.00E-18	1.84E-15	99.95	0.05
550	3.25E-15	3.32E-18	3.25E-15	99.90	0.10
600	5.38E-15	9.39E-18	5.39E-15	99.83	0.17
650	8.46E-15	2.34E-17	8.48E-15	99.72	0.28
700	1.27E-14	5.26E-17	1.28E-14	99.59	0.41
750	1.85E-14	1.09E-16	1.86E-14	99.41	0.59
800	2.61E-14	2.09E-16	2.63E-14	99.21	0.79
850	3.58E-14	3.77E-16	3.62E-14	98.96	1.04
900	4.80E-14	6.48E-16	4.86E-14	98.67	1.33
950	6.31E-14	1.06E-15	6.42E-14	98.35	1.65

1000	8.15E-14	1.68E-15	8.32E-14	97.98	2.02
1050	1.04E-13	2.57E-15	1.07E-13	97.59	2.41
1100	1.30E-13	3.81E-15	1.34E-13	97.15	2.85
1150	1.61E-13	5.51E-15	1.67E-13	96.69	3.31
1200	1.97E-13	7.77E-15	2.05E-13	96.21	3.79
1250	2.39E-13	1.07E-14	2.50E-13	95.71	4.29
1300	2.87E-13	1.45E-14	3.02E-13	95.19	4.81
1350	3.42E-13	1.94E-14	3.61E-13	94.63	5.37
1400	4.03E-13	2.54E-14	4.28E-13	94.07	5.93
1450	4.73E-13	3.29E-14	5.06E-13	93.50	6.50
1500	5.51E-13	4.20E-14	5.93E-13	92.92	7.08
1550	6.38E-13	5.29E-14	6.91E-13	92.34	7.66
1600	7.34E-13	6.61E-14	8.00E-13	91.74	8.26
1650	8.41E-13	8.16E-14	9.23E-13	91.16	8.84
1700	9.57E-13	9.99E-14	1.06E-12	90.55	9.45
1750	1.09E-12	1.21E-13	1.21E-12	90.01	9.99
1800	1.23E-12	1.46E-13	1.38E-12	89.39	10.61
1850	1.38E-12	1.74E-13	1.55E-12	88.80	11.20
1900	1.54E-12	2.07E-13	1.75E-12	88.15	11.85
1950	1.72E-12	2.44E-13	1.96E-12	87.58	12.42
2000	1.92E-12	2.86E-13	2.21E-12	87.04	12.96



**Table S19.** The contribution ratio at a W1 method for all six reaction channels in the temperature range 200-2000 K.

Contribution ratios						
T(K)	X1	X2	X3	Y1	X4	Y2
	OH + CHCl <sub>3</sub>	SH + CHCl <sub>3</sub>	CH <sub>3</sub> O + CHCl <sub>3</sub>	CH <sub>2</sub> OH + CHCl <sub>3</sub>	CH <sub>3</sub> S + CHCl <sub>3</sub>	CH <sub>2</sub> SH + CHCl <sub>3</sub>
200	0.00	0.34	0.00	0.00	99.66	0.00
225	0.00	0.57	0.00	0.00	99.43	0.00
250	0.00	0.89	0.00	0.00	99.10	0.00
275	0.00	1.32	0.00	0.00	98.68	0.00
298	0.00	1.82	0.00	0.00	98.17	0.01
300	0.00	1.86	0.00	0.00	98.13	0.01
325	0.00	2.51	0.00	0.01	97.47	0.01
350	0.00	3.24	0.00	0.01	96.73	0.02
375	0.00	4.06	0.00	0.02	95.89	0.03
400	0.00	4.96	0.00	0.03	94.97	0.05
450	0.00	0.07	0.00	0.00	0.93	0.00
500	0.00	0.09	0.00	0.00	0.91	0.00
550	0.00	0.11	0.00	0.00	0.89	0.00
600	0.00	0.13	0.00	0.00	0.86	0.00
650	0.00	0.15	0.00	0.00	0.84	0.01
700	0.00	0.17	0.00	0.01	0.82	0.01
750	0.00	0.18	0.00	0.01	0.80	0.01
800	0.00	0.20	0.00	0.01	0.78	0.01
850	0.00	0.21	0.00	0.01	0.75	0.02

900	0.00	0.22	0.00	0.02	0.73	0.02
950	0.00	0.24	0.00	0.02	0.72	0.02
1000	0.00	0.25	0.00	0.02	0.70	0.03
1050	0.00	0.26	0.01	0.03	0.68	0.03
1100	0.00	0.26	0.01	0.03	0.66	0.03
1150	0.00	0.27	0.01	0.04	0.65	0.04
1200	0.00	0.28	0.01	0.04	0.63	0.04
1250	0.00	0.28	0.01	0.04	0.62	0.05
1300	0.00	0.29	0.01	0.05	0.60	0.05
1350	0.00	0.29	0.01	0.05	0.59	0.05
1400	0.00	0.30	0.01	0.05	0.58	0.06
1450	0.00	0.30	0.02	0.06	0.56	0.06
1500	0.00	0.30	0.02	0.06	0.55	0.06
1550	0.00	0.30	0.02	0.07	0.54	0.07
1600	0.00	0.31	0.02	0.07	0.53	0.07
1650	0.00	0.31	0.02	0.07	0.52	0.07
1700	0.00	0.31	0.02	0.08	0.51	0.08
1750	0.00	0.31	0.03	0.08	0.50	0.08
1800	0.00	0.31	0.03	0.08	0.49	0.08
1850	0.00	0.31	0.03	0.09	0.48	0.09
1900	0.00	0.31	0.03	0.09	0.47	0.09
1950	0.00	0.31	0.03	0.09	0.47	0.09
2000	0.00	0.31	0.04	0.10	0.46	0.09

**Table S20:** Calculated TST, TST/W, and TST/ZCT rate coefficient ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ ) for reaction  $\text{CCl}_3+\text{H}_2\text{O}$  at W1 method along with CVT and CVT/SCT in the temperature range of 200–2000 K at 1atm Pressure.

T(K)	Rate coefficient, k ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ )					Ratios	
	$k_{x1}(\text{HO-H})$					B/A	C/A
	A=TST	B=TST/W	C=TST/ZCT	D=CVT	E=CVT/SCT		
200	9.34E-43	9.87E-43	9.71E-43	6.31E-41	7.32E-38	1.06	1.04
225	1.82E-39	1.90E-39	1.88E-39	7.14E-38	3.40E-35	1.04	1.03
250	7.91E-37	8.19E-37	8.10E-37	2.01E-35	4.69E-33	1.04	1.02
275	1.15E-34	1.19E-34	1.18E-34	2.05E-33	2.68E-31	1.03	1.03
298	5.44E-33	5.58E-33	5.53E-33	7.35E-32	6.15E-30	1.03	1.02
300	7.40E-33	7.58E-33	7.52E-33	9.78E-32	7.90E-30	1.02	1.02
325	2.53E-31	2.58E-31	2.57E-31	2.60E-30	1.40E-28	1.02	1.02
350	5.27E-30	5.37E-30	5.34E-30	4.37E-29	1.66E-27	1.02	1.01
375	7.40E-29	7.52E-29	7.48E-29	5.09E-28	1.43E-26	1.02	1.01
400	7.53E-28	7.63E-28	7.60E-28	4.40E-27	9.52E-26	1.01	1.01
450	3.67E-26	3.71E-26	3.70E-26	1.63E-25	2.29E-24	1.01	1.01
500	8.45E-25	8.53E-25	8.50E-25	3.02E-24	3.00E-23	1.01	1.01
550	1.12E-23	1.13E-23	1.13E-23	3.37E-23	2.52E-22	1.01	1.01
600	9.92E-23	9.98E-23	9.96E-23	2.56E-22	1.52E-21	1.01	1.00
650	6.37E-22	6.41E-22	6.39E-22	1.45E-21	7.09E-21	1.01	1.00
700	3.19E-21	3.20E-21	3.20E-21	6.49E-21	2.70E-20	1.00	1.00
750	1.30E-20	1.31E-20	1.31E-20	2.42E-20	8.75E-20	1.01	1.01
800	4.54E-20	4.55E-20	4.55E-20	7.74E-20	2.48E-19	1.00	1.00
850	1.38E-19	1.38E-19	1.38E-19	2.19E-19	6.32E-19	1.00	1.00
900	3.74E-19	3.75E-19	3.75E-19	5.56E-19	1.47E-18	1.00	1.00

950	9.22E-19	9.24E-19	9.23E-19	1.29E-18	3.15E-18	1.00	1.00
1000	2.09E-18	2.10E-18	2.10E-18	2.79E-18	6.32E-18	1.00	1.00
1050	4.44E-18	4.44E-18	4.44E-18	5.64E-18	1.20E-17	1.00	1.00
1100	8.84E-18	8.86E-18	8.85E-18	1.08E-17	2.17E-17	1.00	1.00
1150	1.67E-17	1.67E-17	1.67E-17	1.96E-17	3.74E-17	1.00	1.00
1200	3.01E-17	3.01E-17	3.01E-17	3.41E-17	6.22E-17	1.00	1.00
1250	5.20E-17	5.21E-17	5.21E-17	5.70E-17	1.00E-16	1.00	1.00
1300	8.67E-17	8.69E-17	8.68E-17	9.23E-17	1.56E-16	1.00	1.00
1350	1.40E-16	1.40E-16	1.40E-16	1.45E-16	2.37E-16	1.00	1.00
1400	2.19E-16	2.19E-16	2.19E-16	2.21E-16	3.51E-16	1.00	1.00
1450	3.34E-16	3.34E-16	3.34E-16	3.29E-16	5.08E-16	1.00	1.00
1500	4.96E-16	4.97E-16	4.97E-16	4.79E-16	7.21E-16	1.00	1.00
1550	7.22E-16	7.23E-16	7.23E-16	6.84E-16	1.00E-15	1.00	1.00
1600	1.03E-15	1.03E-15	1.03E-15	9.58E-16	1.38E-15	1.00	1.00
1650	1.44E-15	1.44E-15	1.44E-15	1.32E-15	1.86E-15	1.00	1.00
1700	1.99E-15	1.99E-15	1.99E-15	1.79E-15	2.47E-15	1.00	1.00
1750	2.69E-15	2.70E-15	2.69E-15	2.39E-15	3.25E-15	1.00	1.00
1800	3.60E-15	3.60E-15	3.60E-15	3.15E-15	4.22E-15	1.00	1.00
1850	4.75E-15	4.75E-15	4.75E-15	4.10E-15	5.41E-15	1.00	1.00
1900	6.19E-15	6.19E-15	6.19E-15	5.28E-15	6.88E-15	1.00	1.00
1950	7.98E-15	7.98E-15	7.98E-15	6.72E-15	8.65E-15	1.00	1.00
2000	1.02E-14	1.02E-14	1.02E-14	8.48E-15	1.08E-14	1.00	1.00

**Table S21:** Calculated TST, TST/W, and TST/ZCT rate coefficients ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ ) for reaction  $\text{CCl}_3+\text{H}_2\text{S}$  at W1 method along with CVT and CVT/SCT in the temperature range of 200–2000 K at 1atm Pressure.

T(K)	Rate coefficient, k ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ )					Ratios	
	$k_{x2}$ (HS-H)					B/A	C/A
	A=TST	B=TST/W	C=TST/ZCT	D=CVT	E=CVT/SCT		
200	2.11E-21	1.02E-20	5.78E-20	7.65E-20	8.50E-19	4.83	27.39
225	1.61E-20	6.52E-20	1.98E-19	3.72E-19	2.71E-18	4.05	12.30
250	8.40E-20	2.91E-19	5.96E-19	1.35E-18	7.08E-18	3.46	7.10
275	3.30E-19	1.00E-18	1.59E-18	3.97E-18	1.60E-17	3.03	4.82
298	9.65E-19	2.64E-18	3.59E-18	9.28E-18	3.06E-17	2.74	3.72
300	1.05E-18	2.85E-18	3.83E-18	9.94E-18	3.23E-17	2.71	3.65
325	2.85E-18	6.99E-18	8.41E-18	2.20E-17	5.98E-17	2.45	2.95
350	6.78E-18	1.53E-17	1.70E-17	4.40E-17	1.03E-16	2.26	2.51
375	1.46E-17	3.05E-17	3.22E-17	8.15E-17	1.68E-16	2.09	2.21
400	2.88E-17	5.64E-17	5.74E-17	1.42E-16	2.62E-16	1.96	1.99
450	9.22E-17	1.62E-16	1.58E-16	3.67E-16	5.68E-16	1.76	1.71
500	2.42E-16	3.91E-16	3.73E-16	8.15E-16	1.10E-15	1.62	1.54
550	5.50E-16	8.29E-16	7.83E-16	1.61E-15	1.96E-15	1.51	1.42
600	1.12E-15	1.59E-15	1.50E-15	2.93E-15	3.25E-15	1.42	1.34
650	2.08E-15	2.83E-15	2.67E-15	4.97E-15	5.14E-15	1.36	1.28
700	3.60E-15	4.73E-15	4.47E-15	7.96E-15	7.77E-15	1.31	1.24
750	5.90E-15	7.51E-15	7.11E-15	1.22E-14	1.13E-14	1.27	1.21
800	9.22E-15	1.14E-14	1.09E-14	1.80E-14	1.61E-14	1.24	1.18
850	1.38E-14	1.68E-14	1.60E-14	2.57E-14	2.22E-14	1.22	1.16

900	2.01E-14	2.39E-14	2.29E-14	3.58E-14	3.00E-14	1.19	1.14
950	2.84E-14	3.32E-14	3.18E-14	4.86E-14	3.98E-14	1.17	1.12
1000	3.90E-14	4.50E-14	4.33E-14	6.46E-14	5.18E-14	1.15	1.11
1050	5.25E-14	5.98E-14	5.77E-14	8.44E-14	6.66E-14	1.14	1.10
1100	6.92E-14	7.80E-14	7.54E-14	1.08E-13	8.44E-14	1.13	1.09
1150	8.97E-14	1.00E-13	9.71E-14	1.37E-13	1.06E-13	1.11	1.08
1200	1.15E-13	1.27E-13	1.23E-13	1.72E-13	1.31E-13	1.10	1.07
1250	1.44E-13	1.58E-13	1.54E-13	2.13E-13	1.60E-13	1.10	1.07
1300	1.79E-13	1.96E-13	1.91E-13	2.60E-13	1.95E-13	1.09	1.07
1350	2.20E-13	2.39E-13	2.33E-13	3.15E-13	2.35E-13	1.09	1.06
1400	2.68E-13	2.89E-13	2.83E-13	3.78E-13	2.81E-13	1.08	1.06
1450	3.23E-13	3.47E-13	3.40E-13	4.51E-13	3.34E-13	1.07	1.05
1500	3.86E-13	4.13E-13	4.05E-13	5.33E-13	3.94E-13	1.07	1.05
1550	4.58E-13	4.87E-13	4.78E-13	6.26E-13	4.61E-13	1.06	1.04
1600	5.39E-13	5.72E-13	5.61E-13	7.31E-13	5.38E-13	1.06	1.04
1650	6.30E-13	6.66E-13	6.55E-13	8.48E-13	6.23E-13	1.06	1.04
1700	7.32E-13	7.71E-13	7.59E-13	9.78E-13	7.19E-13	1.05	1.04
1750	8.46E-13	8.88E-13	8.75E-13	1.12E-12	8.25E-13	1.05	1.03
1800	9.71E-13	1.02E-12	1.00E-12	1.28E-12	9.42E-13	1.05	1.03
1850	1.11E-12	1.16E-12	1.14E-12	1.46E-12	1.07E-12	1.05	1.03
1900	1.26E-12	1.32E-12	1.30E-12	1.65E-12	1.22E-12	1.05	1.03
1950	1.43E-12	1.49E-12	1.47E-12	1.86E-12	1.37E-12	1.04	1.03
2000	1.61E-12	1.68E-12	1.66E-12	2.09E-12	1.54E-12	1.04	1.03

**Table S22:** Calculated TST, TST/W, and TST/ZCT rate coefficient ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ) for reaction  $\text{CCl}_3 + \text{CH}_3\text{O-H}$  (X3) at W1 method along with CVT and CVT/SCT in the temperature range of 200–2000 K at 1atm Pressure.

	Rate coefficient, k (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )					Ratios	
	k <sub>x3</sub> (O-H)						
T(K)	A=TST	B=TST/W	C=TST/ZCT	D=CVT	E=CVT/SCT	B/A	C/A
200	2.68E-29	1.68E-28	4.61E-28	9.11E-28	3.42E-30	6.27	17.20
225	1.42E-27	7.34E-27	1.38E-26	3.12E-26	2.17E-28	5.17	9.72
250	3.51E-26	1.53E-25	2.23E-25	5.42E-25	6.21E-27	4.36	6.35
275	4.94E-25	1.87E-24	2.29E-24	5.75E-24	9.89E-26	3.79	4.64
298	3.87E-24	1.31E-23	1.43E-23	3.63E-23	8.54E-25	3.39	3.70
300	4.57E-24	1.52E-23	1.66E-23	4.21E-23	1.02E-24	3.33	3.63
325	3.05E-23	9.13E-23	9.18E-23	2.31E-22	7.42E-24	2.99	3.01
350	1.58E-22	4.29E-22	4.08E-22	1.01E-21	4.16E-23	2.72	2.58
375	6.65E-22	1.66E-21	1.52E-21	3.69E-21	1.88E-22	2.50	2.29
400	2.37E-21	5.49E-21	4.90E-21	1.16E-20	7.12E-22	2.32	2.07
450	2.03E-20	4.14E-20	3.61E-20	8.13E-20	6.79E-21	2.04	1.78
500	1.18E-19	2.17E-19	1.87E-19	4.00E-19	4.29E-20	1.84	1.58
550	5.09E-19	8.64E-19	7.48E-19	1.52E-18	2.00E-19	1.70	1.47
600	1.77E-18	2.81E-18	2.45E-18	4.77E-18	7.41E-19	1.59	1.38
650	5.21E-18	7.81E-18	6.86E-18	1.28E-17	2.30E-18	1.50	1.32
700	1.34E-17	1.91E-17	1.70E-17	3.05E-17	6.19E-18	1.43	1.27
750	3.09E-17	4.24E-17	3.79E-17	6.60E-17	1.49E-17	1.37	1.23
800	6.51E-17	8.65E-17	7.80E-17	1.31E-16	3.25E-17	1.33	1.20
850	1.27E-16	1.64E-16	1.50E-16	2.45E-16	6.58E-17	1.29	1.18

900	2.34E-16	2.95E-16	2.70E-16	4.31E-16	1.25E-16	1.26	1.15
950	4.08E-16	5.03E-16	4.64E-16	7.23E-16	2.23E-16	1.23	1.14
1000	6.79E-16	8.22E-16	7.63E-16	1.16E-15	3.80E-16	1.21	1.12
1050	1.09E-15	1.29E-15	1.21E-15	1.80E-15	6.22E-16	1.18	1.11
1100	1.68E-15	1.97E-15	1.85E-15	9.52E-18	1.06E-17	1.17	1.10
1150	2.52E-15	2.92E-15	2.75E-15	1.13E-17	1.25E-17	1.16	1.09
1200	3.67E-15	4.21E-15	3.98E-15	1.31E-17	1.44E-17	1.15	1.08
1250	5.23E-15	5.93E-15	5.63E-15	1.50E-17	1.64E-17	1.13	1.08
1300	7.29E-15	8.20E-15	7.81E-15	1.68E-17	1.84E-17	1.12	1.07
1350	9.96E-15	1.11E-14	1.06E-14	1.87E-17	2.03E-17	1.11	1.06
1400	1.34E-14	1.48E-14	1.42E-14	2.05E-17	2.23E-17	1.10	1.06
1450	1.77E-14	1.95E-14	1.87E-14	2.22E-17	2.41E-17	1.10	1.06
1500	2.31E-14	2.52E-14	2.43E-14	2.39E-17	2.59E-17	1.09	1.05
1550	2.96E-14	3.22E-14	3.11E-14	2.55E-17	2.75E-17	1.09	1.05
1600	3.77E-14	4.08E-14	3.94E-14	2.71E-17	2.91E-17	1.08	1.05
1650	4.73E-14	5.10E-14	4.94E-14	2.85E-17	3.06E-17	1.08	1.04
1700	5.88E-14	6.31E-14	6.12E-14	2.99E-17	3.20E-17	1.07	1.04
1750	7.25E-14	7.74E-14	7.53E-14	3.11E-17	3.32E-17	1.07	1.04
1800	8.85E-14	9.42E-14	9.17E-14	3.22E-17	3.44E-17	1.06	1.04
1850	1.07E-13	1.14E-13	1.11E-13	3.33E-17	3.55E-17	1.07	1.04
1900	1.29E-13	1.36E-13	1.33E-13	3.43E-17	3.64E-17	1.05	1.03



1950	1.54E-13	1.62E-13	1.58E-13	3.51E-17	3.73E-17	1.05	1.03
2000	1.82E-13	1.92E-13	1.87E-13	3.59E-17	3.81E-17	1.05	1.03

**Table S23:** Calculated TST, TST/W, and TST/ZCT rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for reaction  $\text{CCl}_3 + \text{H-CH}_2\text{OH}$  (Y1) at W1 method along with CVT and CVT/SCT in the temperature range of 200–2000 K at 1atm Pressure.

T(K)	Rate coefficient, k ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )					Ratios	
	$k_{Y1}(\text{C-H})$					B/A	C/A
	A=TST	B=TST/W	C=TST/ZCT	D=CVT	E=CVT/SCT		
200	4.50E-26	3.00E-25	2.46E-23	2.88E-30	1.04E-28	6.67	546.67
225	1.04E-24	5.71E-24	1.20E-22	1.92E-28	4.07E-27	5.49	115.38
250	1.32E-23	6.13E-23	5.16E-22	5.72E-27	7.98E-26	4.64	39.09
275	1.09E-22	4.35E-22	1.97E-21	9.46E-26	9.44E-25	3.99	18.07
298	5.63E-22	2.00E-21	6.09E-21	8.44E-25	6.53E-24	3.55	10.82
300	6.43E-22	2.26E-21	6.69E-21	1.01E-24	7.63E-24	3.51	10.40
325	2.95E-21	9.28E-21	2.04E-20	7.60E-24	4.59E-23	3.15	6.92
350	1.11E-20	3.16E-20	5.62E-20	4.38E-23	2.19E-22	2.85	5.06
375	3.54E-20	9.25E-20	1.41E-19	2.04E-22	8.66E-22	2.61	3.98
400	9.93E-20	2.40E-19	3.28E-19	7.94E-22	2.93E-21	2.42	3.30
450	5.73E-19	1.22E-18	1.44E-18	7.95E-21	2.35E-20	2.13	2.51
500	2.42E-18	4.63E-18	5.03E-18	5.23E-20	1.30E-19	1.91	2.08
550	8.15E-18	1.43E-17	1.48E-17	2.53E-19	5.48E-19	1.75	1.82
600	2.30E-17	3.76E-17	3.78E-17	9.65E-19	1.88E-18	1.63	1.64
650	5.68E-17	8.73E-17	8.63E-17	3.07E-18	5.48E-18	1.54	1.52
700	1.26E-16	1.84E-16	1.80E-16	8.43E-18	1.40E-17	1.46	1.43
750	2.55E-16	3.58E-16	3.48E-16	2.06E-17	3.22E-17	1.40	1.36

800	4.80E-16	6.50E-16	6.30E-16	4.56E-17	6.79E-17	1.35	1.31
850	8.51E-16	1.12E-15	1.08E-15	9.30E-17	1.33E-16	1.32	1.27
900	1.43E-15	1.84E-15	1.77E-15	1.77E-16	2.45E-16	1.29	1.24
950	2.31E-15	2.89E-15	2.80E-15	3.19E-16	4.27E-16	1.25	1.21
1000	3.59E-15	4.40E-15	4.26E-15	5.46E-16	7.11E-16	1.23	1.19
1050	5.38E-15	6.49E-15	6.29E-15	8.95E-16	1.14E-15	1.21	1.17
1100	7.85E-15	9.32E-15	9.04E-15	1.41E-15	1.76E-15	1.19	1.15
1150	1.11E-14	1.31E-14	1.27E-14	2.15E-15	2.64E-15	1.18	1.14
1200	1.55E-14	1.79E-14	1.74E-14	3.19E-15	3.84E-15	1.15	1.12
1250	2.11E-14	2.41E-14	2.35E-14	4.60E-15	5.47E-15	1.14	1.11
1300	2.82E-14	3.20E-14	3.12E-14	6.48E-15	7.61E-15	1.13	1.11
1350	3.70E-14	4.16E-14	4.07E-14	8.95E-15	1.04E-14	1.12	1.10
1400	4.80E-14	5.35E-14	5.23E-14	1.21E-14	1.39E-14	1.11	1.09
1450	6.13E-14	6.79E-14	6.65E-14	1.61E-14	1.84E-14	1.11	1.08
1500	7.74E-14	8.52E-14	8.34E-14	2.11E-14	2.39E-14	1.10	1.08
1550	9.65E-14	1.06E-13	1.04E-13	2.73E-14	3.06E-14	1.10	1.08
1600	1.19E-13	1.30E-13	1.27E-13	3.48E-14	3.88E-14	1.09	1.07
1650	1.46E-13	1.58E-13	1.55E-13	9.25E-17	3.32E-17	1.08	1.06
1700	1.77E-13	1.91E-13	1.87E-13	9.33E-17	3.44E-17	1.08	1.06
1750	2.13E-13	2.28E-13	2.25E-13	9.39E-17	3.55E-17	1.07	1.06
1800	2.54E-13	2.71E-13	2.67E-13	9.42E-17	3.65E-17	1.07	1.05
1850	3.01E-13	3.21E-13	3.16E-13	9.42E-17	3.74E-17	1.07	1.05
1900	3.54E-13	3.76E-13	3.71E-13	9.39E-17	3.81E-17	1.06	1.05
1950	4.14E-13	4.39E-13	4.33E-13	9.35E-17	3.88E-17	1.06	1.05
2000	4.82E-13	5.09E-13	5.03E-13	9.29E-17	3.93E-17	1.06	1.04

**Table S24:** Calculated TST, TST/W, and TST/ZCT rate coefficients ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ) for reaction  $\text{CCl}_3 + \text{CH}_3\text{S-H}$  (X4) at W1 method along with CVT and CVT/SCT in the temperature range of 200–2000 K at 1atm Pressure.

	Rate coefficient, k ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )					Ratios	
	$k_{X4}$ (S-H)						
T(K)	A=TST	B=TST/W	C=TST/ZCT	D=CVT	E=CVT/SCT	B/A	C/A
200	1.61E-18	7.20E-18	1.71E-17	5.05E-21	1.80E-19	4.47	10.62
225	5.53E-18	2.07E-17	3.47E-17	3.14E-20	6.59E-19	3.74	6.27
250	1.52E-17	4.90E-17	6.61E-17	1.40E-19	1.93E-18	3.22	4.35
275	3.58E-17	1.01E-16	1.19E-16	4.87E-19	4.82E-18	2.82	3.32
298	7.04E-17	1.80E-16	1.94E-16	1.30E-18	1.00E-17	2.56	2.76
300	7.43E-17	1.89E-16	2.02E-16	1.41E-18	1.06E-17	2.54	2.72
325	1.40E-16	3.25E-16	3.27E-16	3.53E-18	2.12E-17	2.32	2.34
350	2.46E-16	5.25E-16	5.08E-16	7.89E-18	3.91E-17	2.13	2.07
375	4.06E-16	8.06E-16	7.61E-16	1.61E-17	6.78E-17	1.99	1.87
400	6.38E-16	1.19E-15	1.10E-15	3.04E-17	1.12E-16	1.87	1.72
450	1.40E-15	2.35E-15	2.15E-15	9.11E-17	2.67E-16	1.68	1.54
500	2.71E-15	4.20E-15	3.83E-15	2.28E-16	5.62E-16	1.55	1.41

550	4.79E-15	6.99E-15	6.38E-15	4.97E-16	1.07E-15	1.46	1.33
600	7.92E-15	1.10E-14	1.01E-14	9.79E-16	1.90E-15	1.39	1.28
650	1.24E-14	1.64E-14	1.52E-14	1.78E-15	3.16E-15	1.32	1.23
700	1.85E-14	2.37E-14	2.20E-14	3.02E-15	5.00E-15	1.28	1.19
750	2.67E-14	3.32E-14	3.10E-14	4.88E-15	7.61E-15	1.24	1.16
800	3.72E-14	4.53E-14	4.26E-14	7.52E-15	1.12E-14	1.22	1.15
850	5.06E-14	6.03E-14	5.70E-14	1.12E-14	1.59E-14	1.19	1.13
900	6.73E-14	7.88E-14	7.48E-14	1.61E-14	2.21E-14	1.17	1.11
950	8.78E-14	1.01E-13	9.65E-14	2.25E-14	2.99E-14	1.15	1.10
1000	1.12E-13	1.28E-13	1.22E-13	3.07E-14	3.98E-14	1.14	1.09
1050	1.42E-13	1.60E-13	1.53E-13	4.10E-14	5.20E-14	1.13	1.08
1100	1.77E-13	1.97E-13	1.89E-13	5.37E-14	6.68E-14	1.11	1.07
1150	2.17E-13	2.40E-13	2.31E-13	6.93E-14	8.47E-14	1.11	1.06
1200	2.64E-13	2.89E-13	2.80E-13	8.81E-14	1.06E-13	1.09	1.06
1250	3.18E-13	3.46E-13	3.36E-13	1.11E-13	1.31E-13	1.09	1.06
1300	3.79E-13	4.10E-13	3.99E-13	1.37E-13	1.60E-13	1.08	1.05
1350	4.49E-13	4.83E-13	4.70E-13	1.68E-13	1.94E-13	1.08	1.05
1400	5.27E-13	5.64E-13	5.50E-13	2.04E-13	2.34E-13	1.07	1.04
1450	6.14E-13	6.55E-13	6.40E-13	1.10E-14	1.13E-15	1.07	1.04
1500	7.12E-13	7.56E-13	7.39E-13	9.65E-15	1.07E-15	1.06	1.04
1550	8.20E-13	8.67E-13	8.49E-13	8.53E-15	1.01E-15	1.06	1.04

1600	9.39E-13	9.90E-13	9.71E-13	7.57E-15	9.58E-16	1.05	1.03
1650	1.07E-12	1.12E-12	1.10E-12	6.74E-15	9.06E-16	1.05	1.03
1700	1.21E-12	1.27E-12	1.25E-12	6.03E-15	8.57E-16	1.05	1.03
1750	1.37E-12	1.43E-12	1.41E-12	5.41E-15	8.11E-16	1.04	1.03
1800	1.54E-12	1.61E-12	1.58E-12	4.87E-15	7.68E-16	1.05	1.03
1850	1.73E-12	1.80E-12	1.77E-12	4.39E-15	7.27E-16	1.04	1.02
1900	1.93E-12	2.00E-12	1.97E-12	3.98E-15	6.89E-16	1.04	1.02
1950	2.14E-12	2.22E-12	2.19E-12	3.61E-15	6.54E-16	1.04	1.02
2000	2.38E-12	2.46E-12	2.43E-12	3.29E-15	6.20E-16	1.03	1.02

**Table S25:** Calculated TST, TST/W, and TST/ZCT rate coefficients ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ) for reaction  $\text{CCl}_3 + \text{H-CH}_2\text{SH}$  (Y2) at W1 method along with CVT and CVT/SCT in the temperature range of 200–2000 K at 1atm Pressure.

T(K)	Rate coefficient, $k$ ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )					Ratios	
	$k_{\text{V2}} \text{ (C-H)}$					B/A	C/A
A=TST	B=TST/W	C=TST/ZCT	D=CVT	E=CVT/SCT			
200	1.16E-25	8.11E-25	1.44E-22	2.07E-28	7.01E-27	6.99	1241.38
225	2.39E-24	1.37E-23	5.05E-22	8.05E-27	1.61E-25	5.73	211.30
250	2.77E-23	1.34E-22	1.70E-21	1.55E-25	2.06E-24	4.84	61.37
275	2.11E-22	8.80E-22	5.38E-21	1.80E-24	1.72E-23	4.17	25.50
298	1.03E-21	3.82E-21	1.46E-20	1.21E-23	9.04E-23	3.71	14.17
300	1.17E-21	4.29E-21	1.59E-20	1.41E-23	1.03E-22	3.67	13.59

325	5.09E-21	1.67E-20	4.35E-20	8.28E-23	4.83E-22	3.28	8.55
350	1.83E-20	5.41E-20	1.10E-19	3.83E-22	1.85E-21	2.96	6.01
375	5.61E-20	1.52E-19	2.58E-19	1.47E-21	6.06E-21	2.71	4.60
400	1.52E-19	3.80E-19	5.66E-19	4.83E-21	1.74E-20	2.50	3.72
450	8.28E-19	1.81E-18	2.27E-18	3.64E-20	1.05E-19	2.19	2.74
500	3.34E-18	6.55E-18	7.43E-18	1.90E-19	4.62E-19	1.96	2.22
550	1.08E-17	1.94E-17	2.07E-17	7.60E-19	1.62E-18	1.80	1.92
600	2.96E-17	4.93E-17	5.07E-17	2.48E-18	4.75E-18	1.67	1.71
650	7.09E-17	1.11E-16	1.12E-16	6.90E-18	1.21E-17	1.57	1.58
700	1.53E-16	2.28E-16	2.26E-16	1.69E-17	2.78E-17	1.49	1.48
750	3.04E-16	4.34E-16	4.26E-16	3.75E-17	5.81E-17	1.43	1.40
800	5.62E-16	7.73E-16	7.55E-16	7.64E-17	1.13E-16	1.38	1.34
850	9.80E-16	1.31E-15	1.27E-15	1.45E-16	2.05E-16	1.34	1.30
900	1.63E-15	2.11E-15	2.05E-15	2.60E-16	3.55E-16	1.29	1.26
950	2.59E-15	3.28E-15	3.18E-15	5.69E-16	5.86E-16	1.27	1.23
1000	3.97E-15	4.92E-15	4.78E-15	9.06E-16	9.30E-16	1.24	1.20
1050	5.89E-15	7.18E-15	6.98E-15	1.39E-15	1.43E-15	1.22	1.19
1100	8.51E-15	1.02E-14	9.92E-15	2.08E-15	2.12E-15	1.20	1.17
1150	1.20E-14	1.42E-14	1.38E-14	3.01E-15	3.08E-15	1.18	1.15
1200	1.65E-14	1.93E-14	1.88E-14	4.27E-15	4.35E-15	1.17	1.14
1250	2.23E-14	2.57E-14	2.51E-14	5.92E-15	6.03E-15	1.15	1.13
1300	2.96E-14	3.38E-14	3.30E-14	8.06E-15	8.19E-15	1.14	1.11
1350	3.87E-14	4.37E-14	4.28E-14	1.08E-14	1.09E-14	1.13	1.11
1400	4.98E-14	5.59E-14	5.47E-14	1.42E-14	1.44E-14	1.12	1.10

1450	6.32E-14	7.05E-14	6.90E-14	1.84E-14	1.87E-14	1.12	1.09
1500	7.94E-14	8.79E-14	8.62E-14	2.36E-14	2.39E-14	1.11	1.09
1550	9.86E-14	1.08E-13	1.06E-13	2.98E-14	3.02E-14	1.10	1.08
1600	1.21E-13	1.33E-13	1.30E-13	3.73E-14	3.77E-14	1.10	1.07
1650	1.48E-13	1.61E-13	1.58E-13	4.62E-14	4.67E-14	1.09	1.07
1700	1.78E-13	1.93E-13	1.90E-13	5.67E-14	5.73E-14	1.08	1.07
1750	2.14E-13	2.30E-13	2.27E-13	6.90E-14	6.97E-14	1.07	1.06
1800	2.54E-13	2.73E-13	2.69E-13	8.33E-14	8.41E-14	1.07	1.06
1850	3.00E-13	3.21E-13	3.17E-13	9.98E-14	1.01E-13	1.07	1.06
1900	3.52E-13	3.76E-13	3.71E-13	1.19E-13	1.20E-13	1.07	1.05
1950	4.11E-13	4.37E-13	4.31E-13	1.40E-13	1.41E-13	1.06	1.05
2000	4.77E-13	5.05E-13	4.99E-13	1.33E-15	1.34E-15	1.06	1.05

**Table S26:** Calculated Rate Coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) at W1 and CCSD(T) method for the  $\text{CCl}_3 + \text{H}_2\text{O}$  Reaction at 1atm Pressure.

T(K)	Rate Coefficient, k ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )			Rate Coefficient, k ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )		
	W1- $k_{x1}$ (HO-H)			CCSD(T)- $k_{x1}$ (HO-H)		
	A=TST/W	B=TST/ZCT	Ratios =A/B	C=TST/W	D=TST/ZCT	Ratios =C/D
200	9.87E-43	9.71E-43	1.02	7.25E-41	7.21E-41	1.01
225	1.90E-39	1.88E-39	1.01	8.64E-38	8.60E-38	1.00
250	8.19E-37	8.10E-37	1.01	2.53E-35	2.52E-35	1.00
275	1.19E-34	1.18E-34	1.01	2.68E-33	2.67E-33	1.00
298	5.58E-33	5.53E-33	1.01	9.87E-32	9.84E-32	1.00
300	7.58E-33	7.52E-33	1.01	1.32E-31	1.31E-31	1.01
325	2.58E-31	2.57E-31	1.00	3.59E-30	3.58E-30	1.00

350	5.37E-30	5.34E-30	1.01	6.18E-29	6.16E-29	1.00
375	7.52E-29	7.48E-29	1.01	7.33E-28	7.31E-28	1.00
400	7.63E-28	7.60E-28	1.00	6.44E-27	6.43E-27	1.00
450	3.71E-26	3.70E-26	1.00	2.46E-25	2.46E-25	1.00
500	8.53E-25	8.50E-25	1.00	4.67E-24	4.66E-24	1.00
550	1.13E-23	1.13E-23	1.00	5.30E-23	5.29E-23	1.00
600	9.98E-23	9.96E-23	1.00	4.09E-22	4.09E-22	1.00
650	6.41E-22	6.39E-22	1.00	2.35E-21	2.35E-21	1.00
700	3.20E-21	3.20E-21	1.00	1.07E-20	1.07E-20	1.00
750	1.31E-20	1.31E-20	1.00	4.03E-20	4.02E-20	1.00
800	4.55E-20	4.55E-20	1.00	1.30E-19	1.30E-19	1.00
850	1.38E-19	1.38E-19	1.00	3.71E-19	3.71E-19	1.00
900	3.75E-19	3.75E-19	1.00	9.51E-19	9.50E-19	1.00
950	9.24E-19	9.23E-19	1.00	2.23E-18	2.23E-18	1.00
1000	2.10E-18	2.10E-18	1.00	4.84E-18	4.83E-18	1.00
1050	4.44E-18	4.44E-18	1.00	9.83E-18	9.82E-18	1.00
1100	8.86E-18	8.85E-18	1.00	1.89E-17	1.88E-17	1.01
1150	1.67E-17	1.67E-17	1.00	3.44E-17	3.44E-17	1.00
1200	3.01E-17	3.01E-17	1.00	6.01E-17	6.01E-17	1.00
1250	5.21E-17	5.21E-17	1.00	1.01E-16	1.01E-16	1.00
1300	8.69E-17	8.68E-17	1.00	1.64E-16	1.64E-16	1.00
1350	1.40E-16	1.40E-16	1.00	2.58E-16	2.58E-16	1.00
1400	2.19E-16	2.19E-16	1.00	3.94E-16	3.94E-16	1.00
1450	3.34E-16	3.34E-16	1.00	5.88E-16	5.88E-16	1.00
1500	4.97E-16	4.97E-16	1.00	8.58E-16	8.57E-16	1.00
1550	7.23E-16	7.23E-16	1.00	1.22E-15	1.22E-15	1.00
1600	1.03E-15	1.03E-15	1.00	1.72E-15	1.72E-15	1.00



1650	1.44E-15	1.44E-15	1.00	2.36E-15	2.36E-15	1.00
1700	1.99E-15	1.99E-15	1.00	3.21E-15	3.21E-15	1.00
1750	2.70E-15	2.69E-15	1.00	4.28E-15	4.28E-15	1.00
1800	3.60E-15	3.60E-15	1.00	5.65E-15	5.65E-15	1.00
1850	4.75E-15	4.75E-15	1.00	7.36E-15	7.35E-15	1.00
1900	6.19E-15	6.19E-15	1.00	9.47E-15	9.47E-15	1.00
1950	7.98E-15	7.98E-15	1.00	1.21E-14	1.21E-14	1.00
2000	1.02E-14	1.02E-14	1.00	1.52E-14	1.52E-14	1.00

**Table S27:** Calculated Rate Coefficients ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ ) at W1 and CCSD(T) method for the  $\text{CCl}_3+\text{H}_2\text{S}$  Reaction at 1atm Pressure.

T(K)	Rate Coefficient, k ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ )			Rate Coefficient, k ( $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ )		
	W1- $k_{X2}$ (HS-H)			CCSD(T)- $k_{X2}$ (HS-H)		
	A=TST/W	B=TST/ZCT	Ratios= A/B	C=TST/W	D=TST/ZCT	Ratios= C/D
200	1.02E-20	5.78E-20	0.18	4.68E-21	5.97E-20	0.08
225	6.52E-20	1.98E-19	0.33	3.20E-20	1.71E-19	0.19
250	2.91E-19	5.96E-19	0.49	1.51E-19	4.65E-19	0.32
275	1.00E-18	1.59E-18	0.63	5.45E-19	1.17E-18	0.47
298	2.64E-18	3.59E-18	0.74	1.48E-18	2.57E-18	0.58
300	2.85E-18	3.83E-18	0.74	1.61E-18	2.74E-18	0.59
325	6.99E-18	8.41E-18	0.83	4.08E-18	5.91E-18	0.69
350	1.53E-17	1.70E-17	0.90	9.17E-18	1.19E-17	0.77
375	3.05E-17	3.22E-17	0.95	1.87E-17	2.24E-17	0.83
400	5.64E-17	5.74E-17	0.98	3.54E-17	4.01E-17	0.88
450	1.62E-16	1.58E-16	1.03	1.05E-16	1.11E-16	0.95
500	3.91E-16	3.73E-16	1.05	2.61E-16	2.65E-16	0.98
550	8.29E-16	7.83E-16	1.06	5.67E-16	5.62E-16	1.01
600	1.59E-15	1.50E-15	1.06	1.11E-15	1.09E-15	1.02

650	2.83E-15	2.67E-15	1.06	2.00E-15	1.95E-15	1.03
700	4.73E-15	4.47E-15	1.06	3.39E-15	3.30E-15	1.03
750	7.51E-15	7.11E-15	1.06	5.46E-15	5.30E-15	1.03
800	1.14E-14	1.09E-14	1.05	8.39E-15	8.15E-15	1.03
850	1.68E-14	1.60E-14	1.05	1.24E-14	1.21E-14	1.02
900	2.39E-14	2.29E-14	1.04	1.79E-14	1.74E-14	1.03
950	3.32E-14	3.18E-14	1.04	2.50E-14	2.43E-14	1.03
1000	4.50E-14	4.33E-14	1.04	3.41E-14	3.32E-14	1.03
1050	5.98E-14	5.77E-14	1.04	4.55E-14	4.45E-14	1.02
1100	7.80E-14	7.54E-14	1.03	5.97E-14	5.84E-14	1.02
1150	1.00E-13	9.71E-14	1.03	7.71E-14	7.55E-14	1.02
1200	1.27E-13	1.23E-13	1.03	9.80E-14	9.61E-14	1.02
1250	1.58E-13	1.54E-13	1.03	1.23E-13	1.21E-13	1.02
1300	1.96E-13	1.91E-13	1.03	1.53E-13	1.50E-13	1.02
1350	2.39E-13	2.33E-13	1.03	1.87E-13	1.84E-13	1.02
1400	2.89E-13	2.83E-13	1.02	2.27E-13	2.24E-13	1.01
1450	3.47E-13	3.40E-13	1.02	2.73E-13	2.69E-13	1.01
1500	4.13E-13	4.05E-13	1.02	3.26E-13	3.21E-13	1.02
1550	4.87E-13	4.78E-13	1.02	3.86E-13	3.81E-13	1.01
1600	5.72E-13	5.61E-13	1.02	4.54E-13	4.48E-13	1.01
1650	6.66E-13	6.55E-13	1.02	5.30E-13	5.24E-13	1.01
1700	7.71E-13	7.59E-13	1.02	6.15E-13	6.08E-13	1.01
1750	8.88E-13	8.75E-13	1.01	7.10E-13	7.02E-13	1.01
1800	1.02E-12	1.00E-12	1.02	8.15E-13	8.07E-13	1.01
1850	1.16E-12	1.14E-12	1.02	9.31E-13	9.22E-13	1.01
1900	1.32E-12	1.30E-12	1.02	1.06E-12	1.05E-12	1.01
1950	1.49E-12	1.47E-12	1.01	1.20E-12	1.19E-12	1.01

2000	1.68E-12	1.66E-12	1.01	1.35E-12	1.34E-12	1.01
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**Table S28:** Calculated Rate Coefficients ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) at a W1 method for the  $\text{CCl}_3+\text{CH}_3\text{OH}$  Reaction at 1atm Pressure.

T(K)	Rate Coefficient, k ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )			Rate Coefficient, k ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )		
	$k_{X3}$ (O-H)			$k_{Y1}$ (C-H)		
	A=TST/W	B=TST/ZCT	Ratios =A/B	C=TST/W	D=TST/ZCT	Ratios =C/D
200	1.68E-28	4.61E-28	0.36	3.00E-25	2.46E-23	0.01
225	7.34E-27	1.38E-26	0.53	5.71E-24	1.20E-22	0.05
250	1.53E-25	2.23E-25	0.69	6.13E-23	5.16E-22	0.12
275	1.87E-24	2.29E-24	0.82	4.35E-22	1.97E-21	0.22
298	1.31E-23	1.43E-23	0.92	2.00E-21	6.09E-21	0.33
300	1.52E-23	1.66E-23	0.92	2.26E-21	6.69E-21	0.34
325	9.13E-23	9.18E-23	0.99	9.28E-21	2.04E-20	0.45
350	4.29E-22	4.08E-22	1.05	3.16E-20	5.62E-20	0.56
375	1.66E-21	1.52E-21	1.09	9.25E-20	1.41E-19	0.66
400	5.49E-21	4.90E-21	1.12	2.40E-19	3.28E-19	0.73
450	4.14E-20	3.61E-20	1.15	1.22E-18	1.44E-18	0.85
500	2.17E-19	1.87E-19	1.16	4.63E-18	5.03E-18	0.92
550	8.64E-19	7.48E-19	1.16	1.43E-17	1.48E-17	0.97
600	2.81E-18	2.45E-18	1.15	3.76E-17	3.78E-17	0.99
650	7.81E-18	6.86E-18	1.14	8.73E-17	8.63E-17	1.01

700	1.91E-17	1.70E-17	1.12	1.84E-16	1.80E-16	1.02
750	4.24E-17	3.79E-17	1.12	3.58E-16	3.48E-16	1.03
800	8.65E-17	7.80E-17	1.11	6.50E-16	6.30E-16	1.03
850	1.64E-16	1.50E-16	1.09	1.12E-15	1.08E-15	1.04
900	2.95E-16	2.70E-16	1.09	1.84E-15	1.77E-15	1.04
950	5.03E-16	4.64E-16	1.08	2.89E-15	2.80E-15	1.03
1000	8.22E-16	7.63E-16	1.08	4.40E-15	4.26E-15	1.03
1050	1.29E-15	1.21E-15	1.07	6.49E-15	6.29E-15	1.03
1100	1.97E-15	1.85E-15	1.06	9.32E-15	9.04E-15	1.03
1150	2.92E-15	2.75E-15	1.06	1.31E-14	1.27E-14	1.03
1200	4.21E-15	3.98E-15	1.06	1.79E-14	1.74E-14	1.03
1250	5.93E-15	5.63E-15	1.05	2.41E-14	2.35E-14	1.03
1300	8.20E-15	7.81E-15	1.05	3.20E-14	3.12E-14	1.03
1350	1.11E-14	1.06E-14	1.05	4.16E-14	4.07E-14	1.02
1400	1.48E-14	1.42E-14	1.04	5.35E-14	5.23E-14	1.02
1450	1.95E-14	1.87E-14	1.04	6.79E-14	6.65E-14	1.02
1500	2.52E-14	2.43E-14	1.04	8.52E-14	8.34E-14	1.02
1550	3.22E-14	3.11E-14	1.04	1.06E-13	1.04E-13	1.02
1600	4.08E-14	3.94E-14	1.04	1.30E-13	1.27E-13	1.02
1650	5.10E-14	4.94E-14	1.03	1.58E-13	1.55E-13	1.02
1700	6.31E-14	6.12E-14	1.03	1.91E-13	1.87E-13	1.02
1750	7.74E-14	7.53E-14	1.03	2.28E-13	2.25E-13	1.01
1800	9.42E-14	9.17E-14	1.03	2.71E-13	2.67E-13	1.01
1850	1.14E-13	1.11E-13	1.03	3.21E-13	3.16E-13	1.02
1900	1.36E-13	1.33E-13	1.02	3.76E-13	3.71E-13	1.01
1950	1.62E-13	1.58E-13	1.03	4.39E-13	4.33E-13	1.01
2000	1.92E-13	1.87E-13	1.03	5.09E-13	5.03E-13	1.01

<b>Table S29:</b> Calculated Rate Coefficients ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) at a CCSD(T) method for the $\text{CCl}_3+\text{CH}_3\text{OH}$ Reaction at 1atm Pressure.						
	Rate Coefficient, $k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )			Rate Coefficient, $k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )		
	$k_{X3}$ (O-H)			$k_{Y1}$ (C-H)		
T(K)	A=TST/W	B=TST/ZCT	Ratios =A/B	C=TST/W	D=TST/ZCT	Ratios =C/D
200	2.80E-29	2.62E-28	0.11	1.31E-26	2.55E-24	0.01
225	1.49E-27	6.91E-27	0.22	3.52E-25	1.32E-23	0.03
250	3.64E-26	1.05E-25	0.35	4.96E-24	6.21E-23	0.08
275	5.04E-25	1.05E-24	0.48	4.40E-23	2.62E-22	0.17
298	3.89E-24	6.53E-24	0.60	2.41E-22	8.97E-22	0.27
300	4.58E-24	7.57E-24	0.61	2.76E-22	9.94E-22	0.28
325	3.00E-23	4.22E-23	0.71	1.32E-21	3.37E-21	0.39
350	1.52E-22	1.91E-22	0.80	5.15E-21	1.03E-20	0.50
375	6.30E-22	7.28E-22	0.87	1.70E-20	2.83E-20	0.60
400	2.21E-21	2.40E-21	0.92	4.88E-20	7.16E-20	0.68
450	1.84E-20	1.86E-20	0.99	2.93E-19	3.64E-19	0.80
500	1.04E-19	1.01E-19	1.03	1.28E-18	1.44E-18	0.89
550	4.42E-19	4.20E-19	1.05	4.41E-18	4.70E-18	0.94
600	1.52E-18	1.43E-18	1.06	1.27E-17	1.31E-17	0.97
650	4.41E-18	4.13E-18	1.07	3.20E-17	3.22E-17	0.99
700	1.12E-17	1.05E-17	1.07	7.22E-17	7.17E-17	1.01
750	2.58E-17	2.41E-17	1.07	1.49E-16	1.46E-16	1.02
800	5.41E-17	5.07E-17	1.07	2.85E-16	2.79E-16	1.02
850	1.06E-16	9.93E-17	1.07	5.12E-16	5.00E-16	1.02
900	1.94E-16	1.83E-16	1.06	8.75E-16	8.53E-16	1.03

950	3.37E-16	3.20E-16	1.05	1.43E-15	1.39E-15	1.03
1000	5.61E-16	5.34E-16	1.05	2.24E-15	2.19E-15	1.02
1050	8.99E-16	8.57E-16	1.05	3.41E-15	3.32E-15	1.03
1100	1.39E-15	1.33E-15	1.05	5.03E-15	4.91E-15	1.02
1150	2.09E-15	2.00E-15	1.05	7.22E-15	7.05E-15	1.02
1200	3.05E-15	2.93E-15	1.04	1.01E-14	9.90E-15	1.02
1250	4.35E-15	4.19E-15	1.04	1.39E-14	1.36E-14	1.02
1300	6.07E-15	5.87E-15	1.03	1.88E-14	1.84E-14	1.02
1350	8.32E-15	8.05E-15	1.03	2.49E-14	2.44E-14	1.02
1400	1.12E-14	1.09E-14	1.03	3.26E-14	3.19E-14	1.02
1450	1.48E-14	1.44E-14	1.03	4.19E-14	4.12E-14	1.02
1500	1.94E-14	1.88E-14	1.03	5.33E-14	5.24E-14	1.02
1550	2.49E-14	2.43E-14	1.02	6.70E-14	6.59E-14	1.02
1600	3.18E-14	3.10E-14	1.03	8.34E-14	8.20E-14	1.02
1650	4.00E-14	3.91E-14	1.02	1.03E-13	1.01E-13	1.02
1700	4.98E-14	4.87E-14	1.02	1.25E-13	1.23E-13	1.02
1750	6.15E-14	6.02E-14	1.02	1.52E-13	1.49E-13	1.02
1800	7.52E-14	7.38E-14	1.02	1.82E-13	1.80E-13	1.01
1850	9.13E-14	8.96E-14	1.02	2.17E-13	2.14E-13	1.01
1900	1.10E-13	1.08E-13	1.02	2.57E-13	2.54E-13	1.01
1950	1.31E-13	1.29E-13	1.02	3.02E-13	2.99E-13	1.01
2000	1.56E-13	1.54E-13	1.01	3.53E-13	3.49E-13	1.01

**Table S30:** Calculated Rate Coefficients ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) at a W1 method for the  $\text{CCl}_3+\text{CH}_3\text{SH}$  Reaction at 1atm Pressure.

	Rate Coefficient, k (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )			Rate Coefficient, k (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )		
	<b>k<sub>X4</sub> (S-H)</b>			<b>k<sub>V2</sub> (C-H)</b>		
<b>T(K)</b>	<b>A=TST/W</b>	<b>B=TST/ZCT</b>	<b>Ratios =A/B</b>	<b>C=TST/W</b>	<b>D=TST/ZCT</b>	<b>Ratios =C/D</b>
200	7.20E-18	1.71E-17	0.42	8.11E-25	1.44E-22	0.01
225	2.07E-17	3.47E-17	0.60	1.37E-23	5.05E-22	0.03
250	4.90E-17	6.61E-17	0.74	1.34E-22	1.70E-21	0.08
275	1.01E-16	1.19E-16	0.85	8.80E-22	5.38E-21	0.16
298	1.80E-16	1.94E-16	0.93	3.82E-21	1.46E-20	0.26
300	1.89E-16	2.02E-16	0.94	4.29E-21	1.59E-20	0.27
325	3.25E-16	3.27E-16	0.99	1.67E-20	4.35E-20	0.38
350	5.25E-16	5.08E-16	1.03	5.41E-20	1.10E-19	0.49
375	8.06E-16	7.61E-16	1.06	1.52E-19	2.58E-19	0.59
400	1.19E-15	1.10E-15	1.08	3.80E-19	5.66E-19	0.67
450	2.35E-15	2.15E-15	1.09	1.81E-18	2.27E-18	0.80
500	4.20E-15	3.83E-15	1.10	6.55E-18	7.43E-18	0.88
550	6.99E-15	6.38E-15	1.10	1.94E-17	2.07E-17	0.94
600	1.10E-14	1.01E-14	1.09	4.93E-17	5.07E-17	0.97
650	1.64E-14	1.52E-14	1.08	1.11E-16	1.12E-16	0.99
700	2.37E-14	2.20E-14	1.08	2.28E-16	2.26E-16	1.01
750	3.32E-14	3.10E-14	1.07	4.34E-16	4.26E-16	1.02
800	4.53E-14	4.26E-14	1.06	7.73E-16	7.55E-16	1.02
850	6.03E-14	5.70E-14	1.06	1.31E-15	1.27E-15	1.03
900	7.88E-14	7.48E-14	1.05	2.11E-15	2.05E-15	1.03
950	1.01E-13	9.65E-14	1.05	3.28E-15	3.18E-15	1.03
1000	1.28E-13	1.22E-13	1.05	4.92E-15	4.78E-15	1.03
1050	1.60E-13	1.53E-13	1.05	7.18E-15	6.98E-15	1.03
1100	1.97E-13	1.89E-13	1.04	1.02E-14	9.92E-15	1.03
1150	2.40E-13	2.31E-13	1.04	1.42E-14	1.38E-14	1.03

1200	2.89E-13	2.80E-13	1.03	1.93E-14	1.88E-14	1.03
1250	3.46E-13	3.36E-13	1.03	2.57E-14	2.51E-14	1.02
1300	4.10E-13	3.99E-13	1.03	3.38E-14	3.30E-14	1.02
1350	4.83E-13	4.70E-13	1.03	4.37E-14	4.28E-14	1.02
1400	5.64E-13	5.50E-13	1.03	5.59E-14	5.47E-14	1.02
1450	6.55E-13	6.40E-13	1.02	7.05E-14	6.90E-14	1.02
1500	7.56E-13	7.39E-13	1.02	8.79E-14	8.62E-14	1.02
1550	8.67E-13	8.49E-13	1.02	1.08E-13	1.06E-13	1.02
1600	9.90E-13	9.71E-13	1.02	1.33E-13	1.30E-13	1.02
1650	1.12E-12	1.10E-12	1.02	1.61E-13	1.58E-13	1.02
1700	1.27E-12	1.25E-12	1.02	1.93E-13	1.90E-13	1.02
1750	1.43E-12	1.41E-12	1.01	2.30E-13	2.27E-13	1.01
1800	1.61E-12	1.58E-12	1.02	2.73E-13	2.69E-13	1.01
1850	1.80E-12	1.77E-12	1.02	3.21E-13	3.17E-13	1.01
1900	2.00E-12	1.97E-12	1.02	3.76E-13	3.71E-13	1.01
1950	2.22E-12	2.19E-12	1.01	4.37E-13	4.31E-13	1.01
2000	2.46E-12	2.43E-12	1.01	5.05E-13	4.99E-13	1.01

**Table S31:** Calculated Rate Coefficients ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) at a CCSD(T) method for the  $\text{CCl}_3+\text{CH}_3\text{SH}$  Reaction at 1atm Pressure.

	Rate Coefficient, k ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )			Rate Coefficient, k ( $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ )		
	$k_{\text{X4}}(\text{S-H})$			$k_{\text{Y2}}(\text{C-H})$		
T(K)	A=TST/W	B=TST/ZCT	Ratios =A/B	C=TST/W	D=TST/ZCT	Ratios =C/D
200	1.16E-18	3.96E-18	0.29	5.48E-27	2.23E-24	0.00
225	4.06E-18	8.84E-18	0.46	1.60E-25	1.05E-23	0.02



250	1.13E-17	1.85E-17	0.61	2.43E-24	4.59E-23	0.05
275	2.64E-17	3.60E-17	0.73	2.28E-23	1.85E-22	0.12
298	5.19E-17	6.31E-17	0.82	1.31E-22	6.16E-22	0.21
300	5.48E-17	6.60E-17	0.83	1.50E-22	6.82E-22	0.22
325	1.03E-16	1.15E-16	0.90	7.51E-22	2.28E-21	0.33
350	1.80E-16	1.89E-16	0.95	3.03E-21	6.91E-21	0.44
375	2.96E-16	2.99E-16	0.99	1.03E-20	1.91E-20	0.54
400	4.63E-16	4.56E-16	1.02	3.03E-20	4.85E-20	0.62
450	1.01E-15	9.64E-16	1.05	1.90E-19	2.50E-19	0.76
500	1.95E-15	1.84E-15	1.06	8.54E-19	1.00E-18	0.85
550	3.46E-15	3.25E-15	1.06	3.03E-18	3.32E-18	0.91
600	5.73E-15	5.38E-15	1.07	8.93E-18	9.39E-18	0.95
650	8.98E-15	8.46E-15	1.06	2.29E-17	2.34E-17	0.98
700	1.35E-14	1.27E-14	1.06	5.23E-17	5.26E-17	0.99
750	1.95E-14	1.85E-14	1.05	1.09E-16	1.09E-16	1.00
800	2.74E-14	2.61E-14	1.05	2.11E-16	2.09E-16	1.01
850	3.75E-14	3.58E-14	1.05	3.84E-16	3.77E-16	1.02
900	5.01E-14	4.80E-14	1.04	6.61E-16	6.48E-16	1.02
950	6.56E-14	6.31E-14	1.04	1.09E-15	1.06E-15	1.03
1000	8.46E-14	8.15E-14	1.04	1.72E-15	1.68E-15	1.02
1050	1.07E-13	1.04E-13	1.03	2.63E-15	2.57E-15	1.02
1100	1.34E-13	1.30E-13	1.03	3.90E-15	3.81E-15	1.02
1150	1.66E-13	1.61E-13	1.03	5.63E-15	5.51E-15	1.02
1200	2.03E-13	1.97E-13	1.03	7.93E-15	7.77E-15	1.02
1250	2.45E-13	2.39E-13	1.03	1.10E-14	1.07E-14	1.03
1300	2.94E-13	2.87E-13	1.02	1.48E-14	1.45E-14	1.02
1350	3.49E-13	3.42E-13	1.02	1.97E-14	1.94E-14	1.02

1400	4.12E-13	4.03E-13	1.02	2.59E-14	2.54E-14	1.02
1450	4.82E-13	4.73E-13	1.02	3.34E-14	3.29E-14	1.02
1500	5.61E-13	5.51E-13	1.02	4.27E-14	4.20E-14	1.02
1550	6.49E-13	6.38E-13	1.02	5.38E-14	5.29E-14	1.02
1600	7.46E-13	7.34E-13	1.02	6.71E-14	6.61E-14	1.02
1650	8.54E-13	8.41E-13	1.02	8.28E-14	8.16E-14	1.01
1700	9.72E-13	9.57E-13	1.02	1.01E-13	9.99E-14	1.01
1750	1.10E-12	1.09E-12	1.01	1.23E-13	1.21E-13	1.02
1800	1.24E-12	1.23E-12	1.01	1.48E-13	1.46E-13	1.01
1850	1.40E-12	1.38E-12	1.01	1.77E-13	1.74E-13	1.02
1900	1.56E-12	1.54E-12	1.01	2.09E-13	2.07E-13	1.01
1950	1.74E-12	1.72E-12	1.01	2.47E-13	2.44E-13	1.01
2000	1.94E-12	1.92E-12	1.01	2.89E-13	2.86E-13	1.01

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