Electronic Supplementary Information for

High-Accuracy Theoretical Studies on the Gas-Phase Reaction Mechanisms of Sulfur Mustard with Reactive Oxygen Species ($OH/O_2/HO_2/O$)

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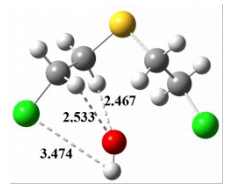

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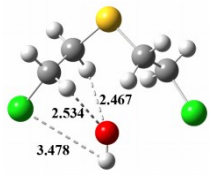

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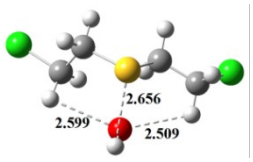

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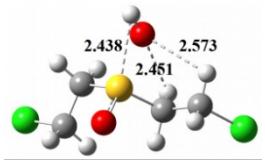

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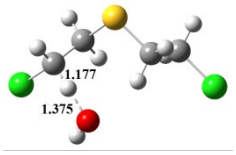

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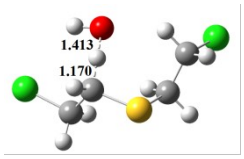

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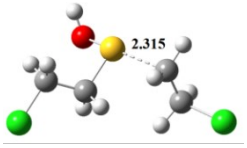

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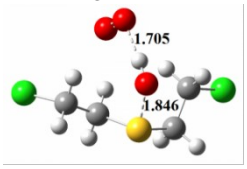

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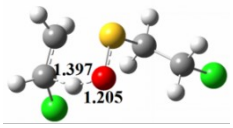

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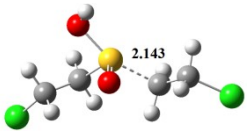

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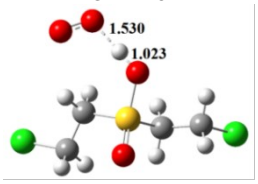

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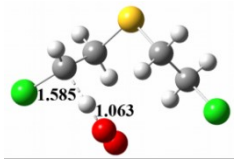

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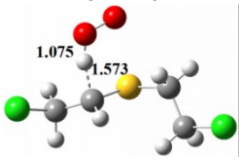

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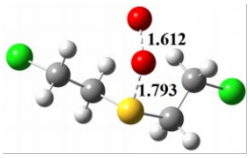

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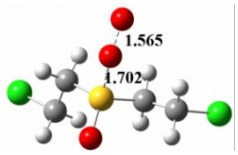

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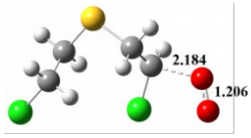

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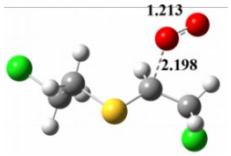

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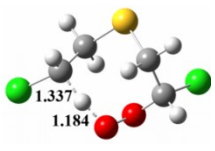

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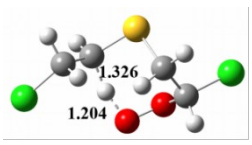

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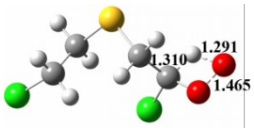

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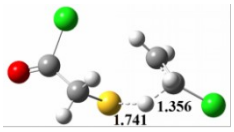

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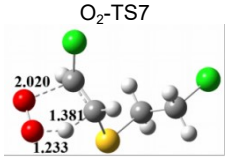

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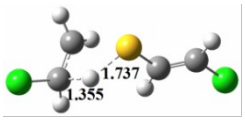

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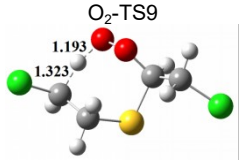

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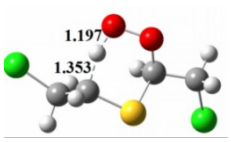

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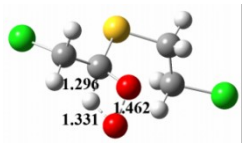

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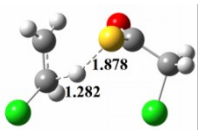

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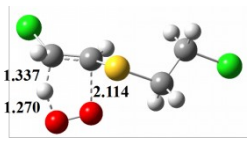

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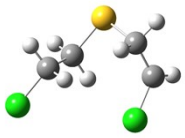

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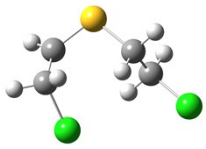

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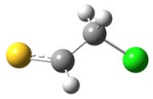

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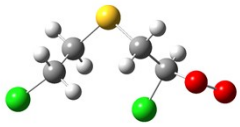

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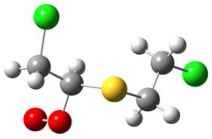

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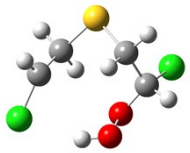

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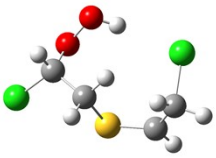

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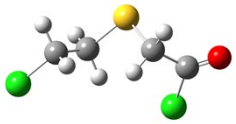

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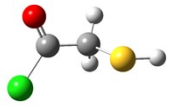

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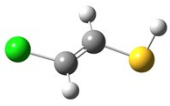
O_2-IM7



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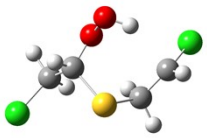

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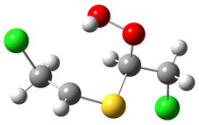

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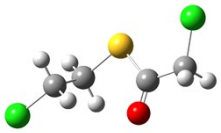

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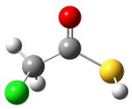

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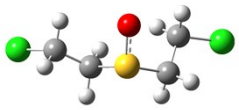

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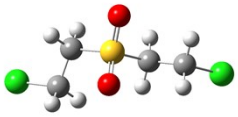

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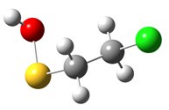

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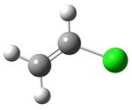

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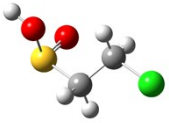

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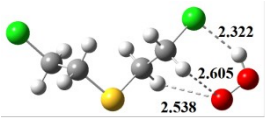

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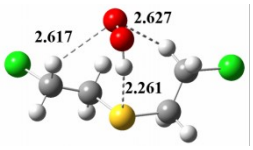

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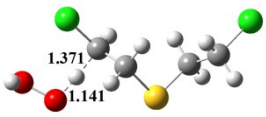

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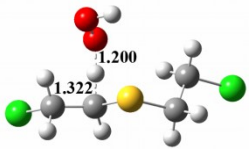

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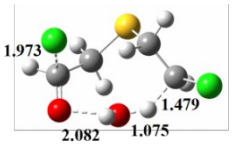

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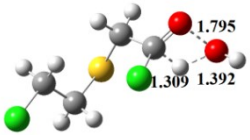

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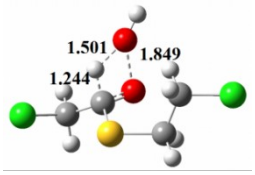

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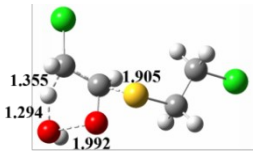

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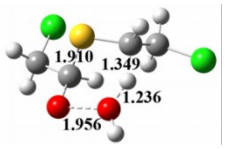

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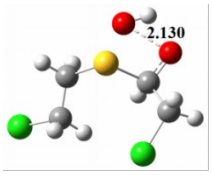
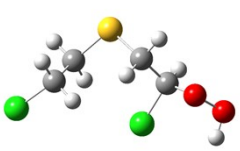
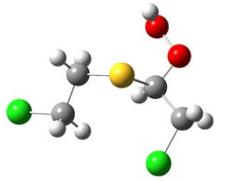


HO_2-TS8



HO_2-IM1



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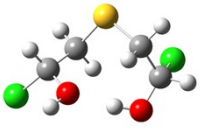
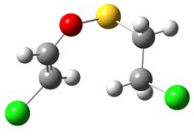
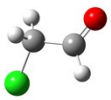
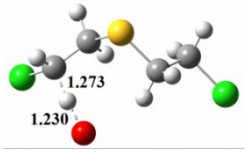








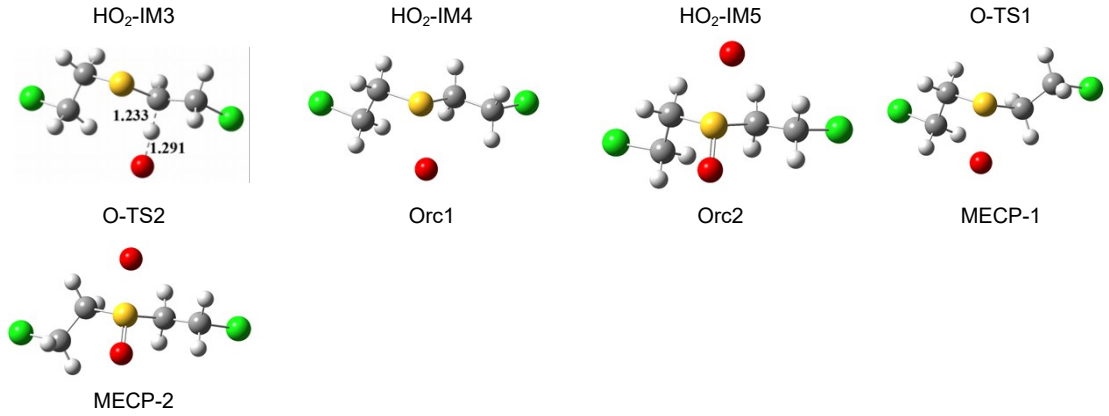
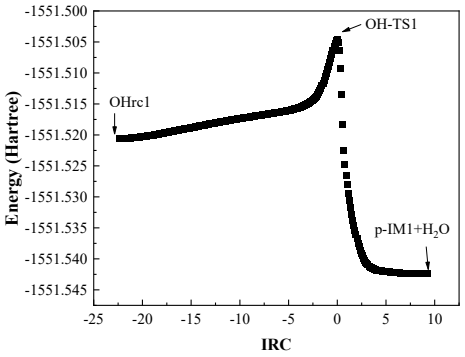
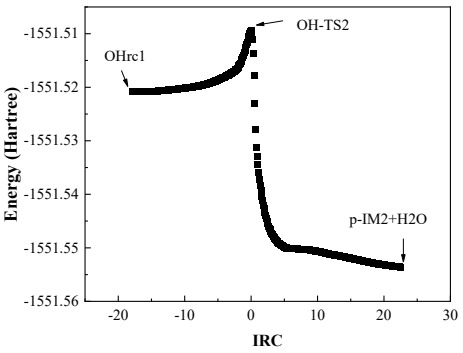


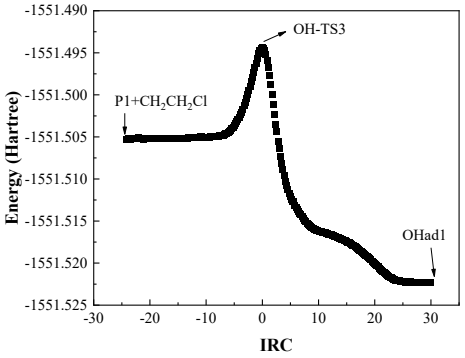
Figure S1 Optimized minimum-energy structures and transition-state structures of the reaction system calculated at the M06-2X/6-311+G(d,p) level of theory. Color scheme: white = hydrogen (H), gray = carbon (C), yellow = sulfur (S), green = chlorine (Cl), red = oxygen (O).



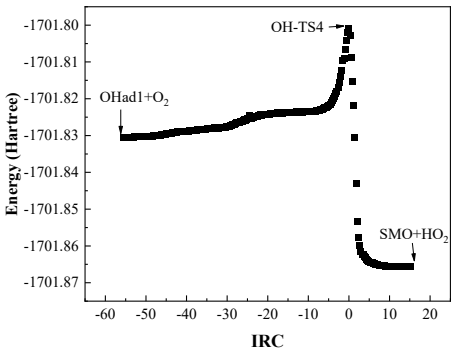
OH-TS1, *-1061.66*



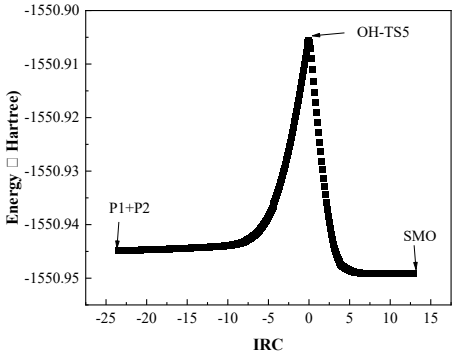
OH-TS2, *-959.38*



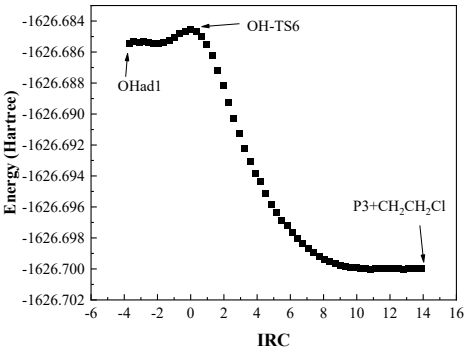
OH-TS3, *-338.81*



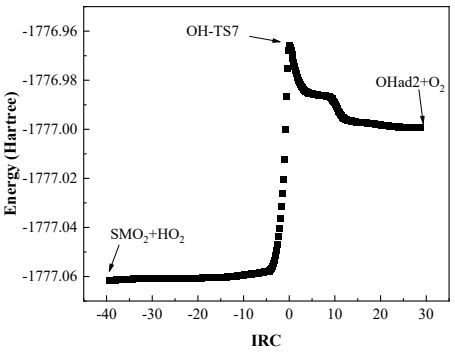
OH-TS4, *-971.59*



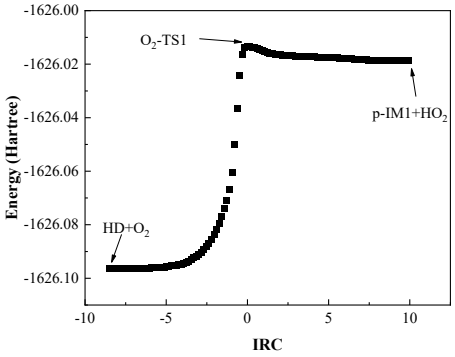
OH-TS5, *-1139.65*



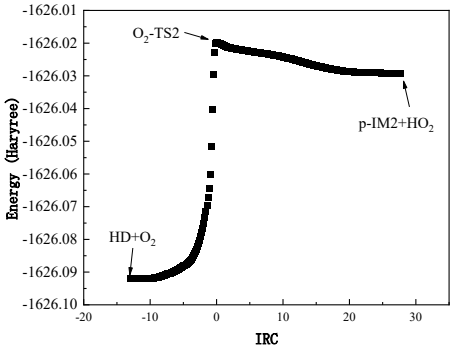
OH-TS6,*-214.21*



OH-TS7, *-1179.49*



O_2-TS1, *-681.34*



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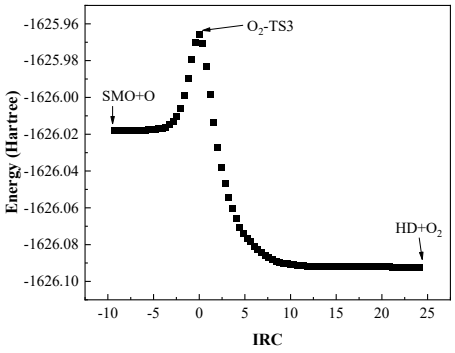
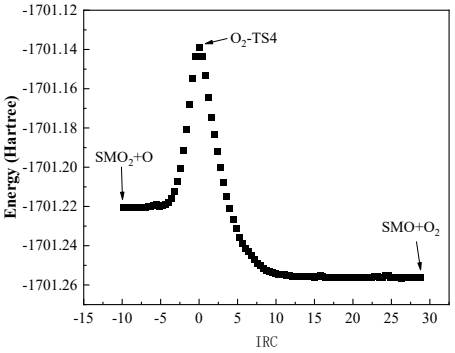
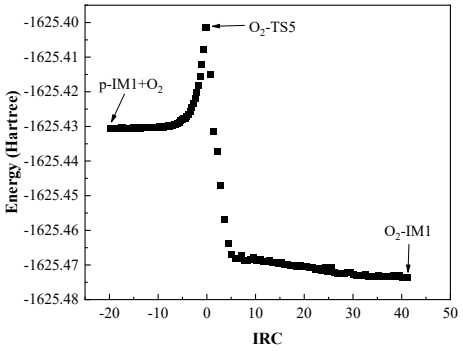


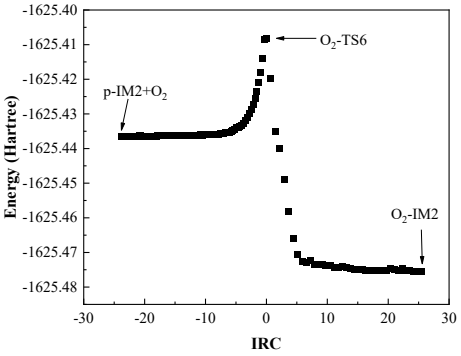
O_2-TS3, *-1256.86*



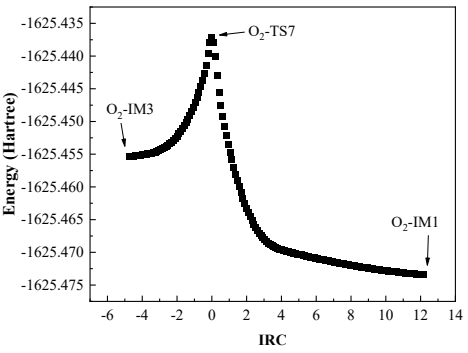
O_2-TS4, *-1218.40*



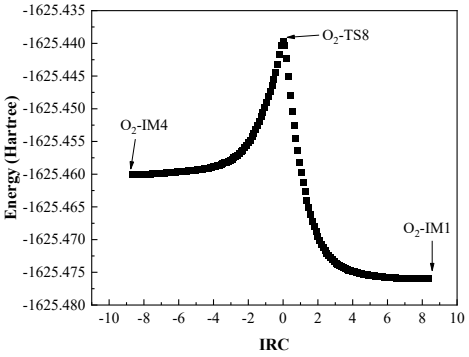
O_2-TS5, *-297.48*



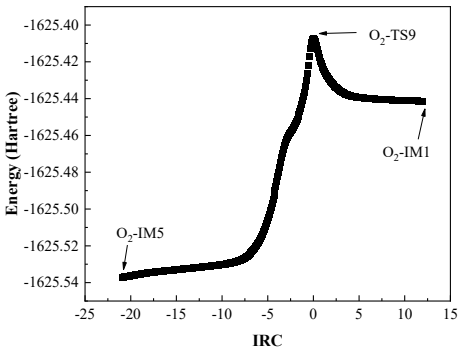
O_2-TS6, *-258.39*



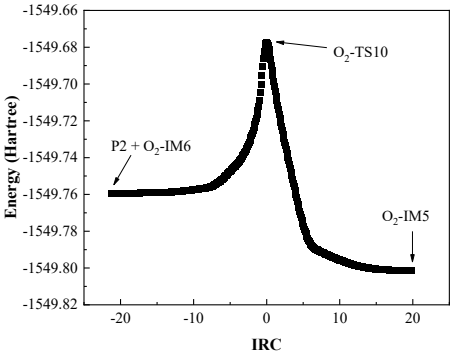
O_2-TS7, *-1885.78*



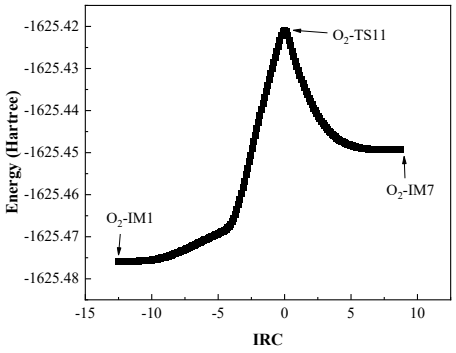
O_2-TS8, *-1946.52*



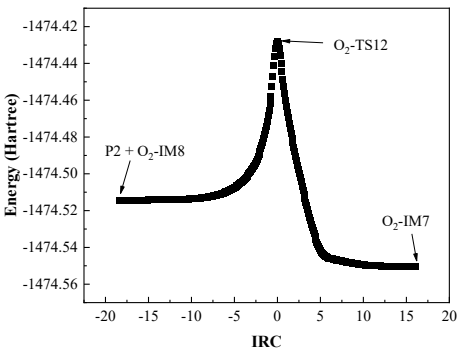
O_2-TS9, *-1879.29*



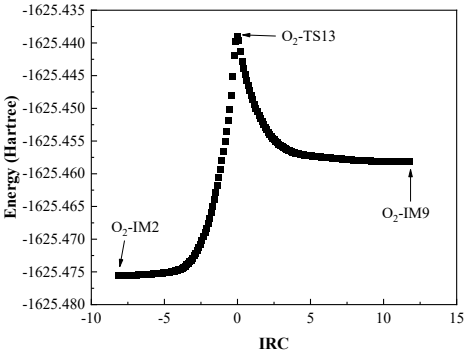
O_2-TS10, *-2111.69*



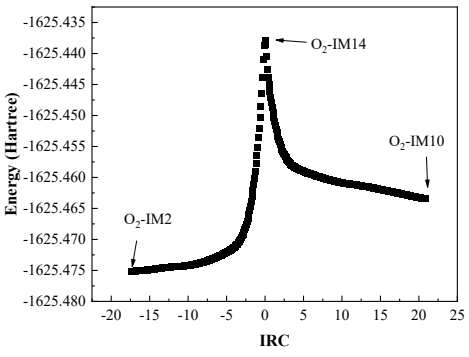
O_2-TS11, *-1079.61*



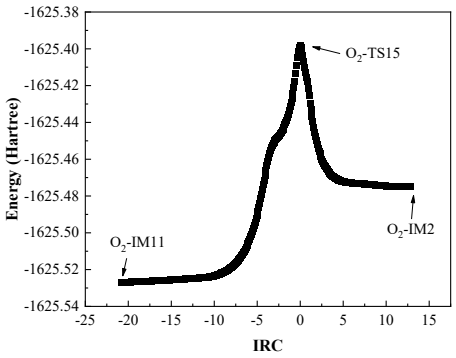
O_2-TS12, *-2105.21*



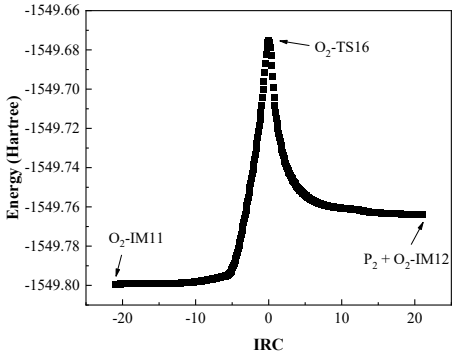
O_2-TS13, *-1901.86*



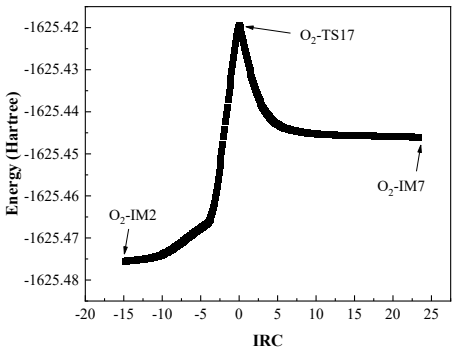
O_2-TS14, *-1780.86*



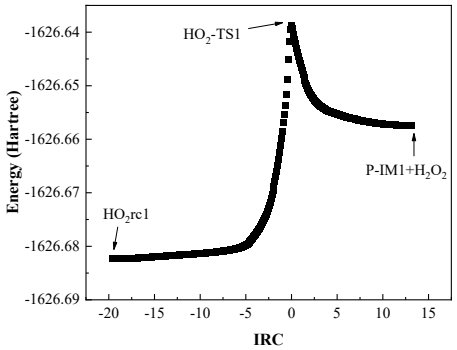
O_2-TS15, *-1733.49*



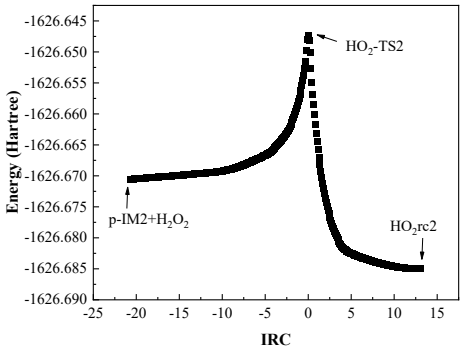
O_2-TS16, *-1592.59*



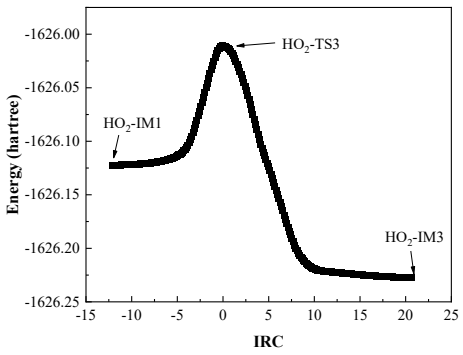
O_2-TS17, *-1135.03*



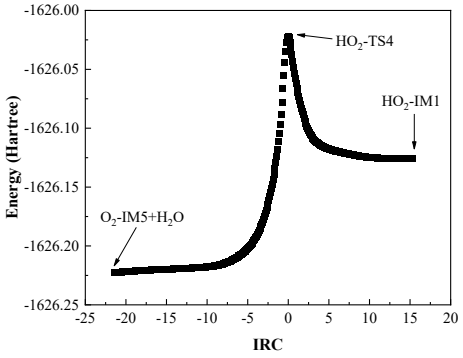
HO_2-TS1, *-1777.44*



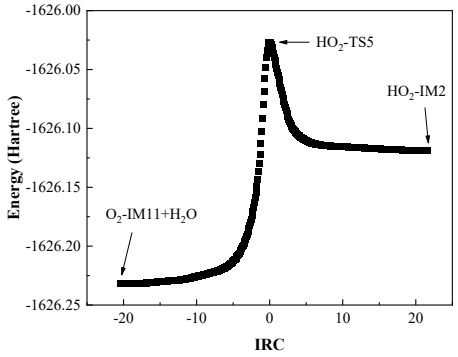
HO_2-TS2, *-1844.72*



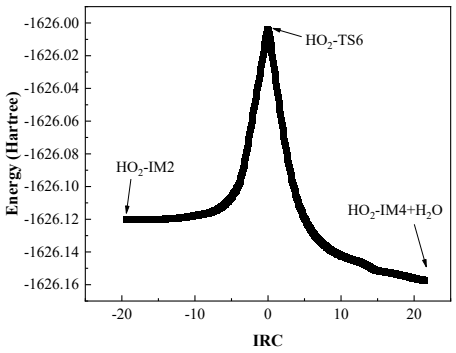
HO_2-TS3, *-716.02*



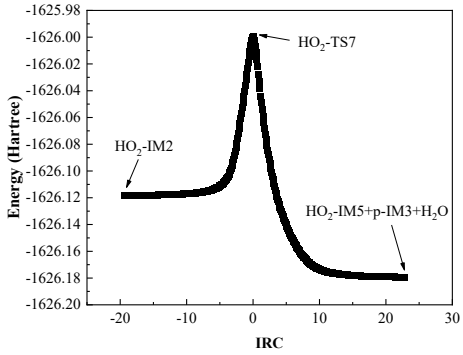
HO_2-TS4, *-2506.80*



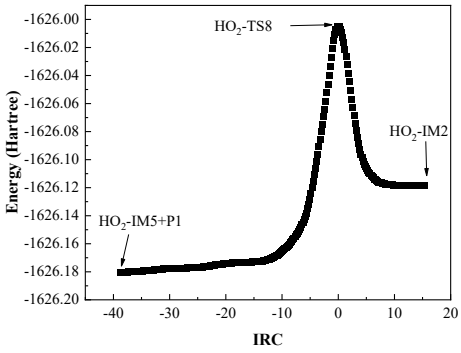
HO_2-TS5, *-1747.58*



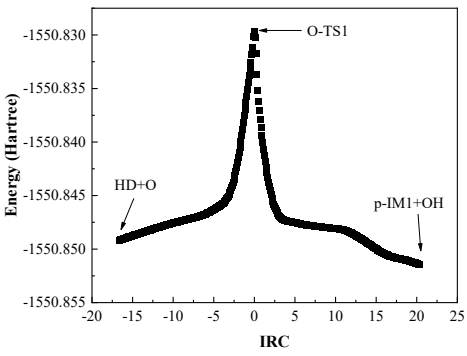
HO_2-TS6, *-1810.05*



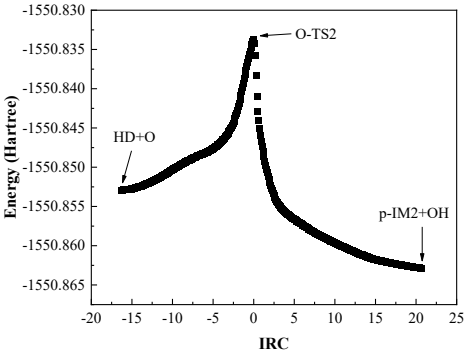
HO_2-TS7, *-1852.72*



HO_2-TS8, *-881.07*



O-TS1, *-1629.20*



O-TS2, *-1360.48*

Figure S2 The Intrinsic Reaction Coordinate (IRC) diagram of the transition state in the reaction system, with the italicized numbers indicating the imaginary frequencies of the transition state.

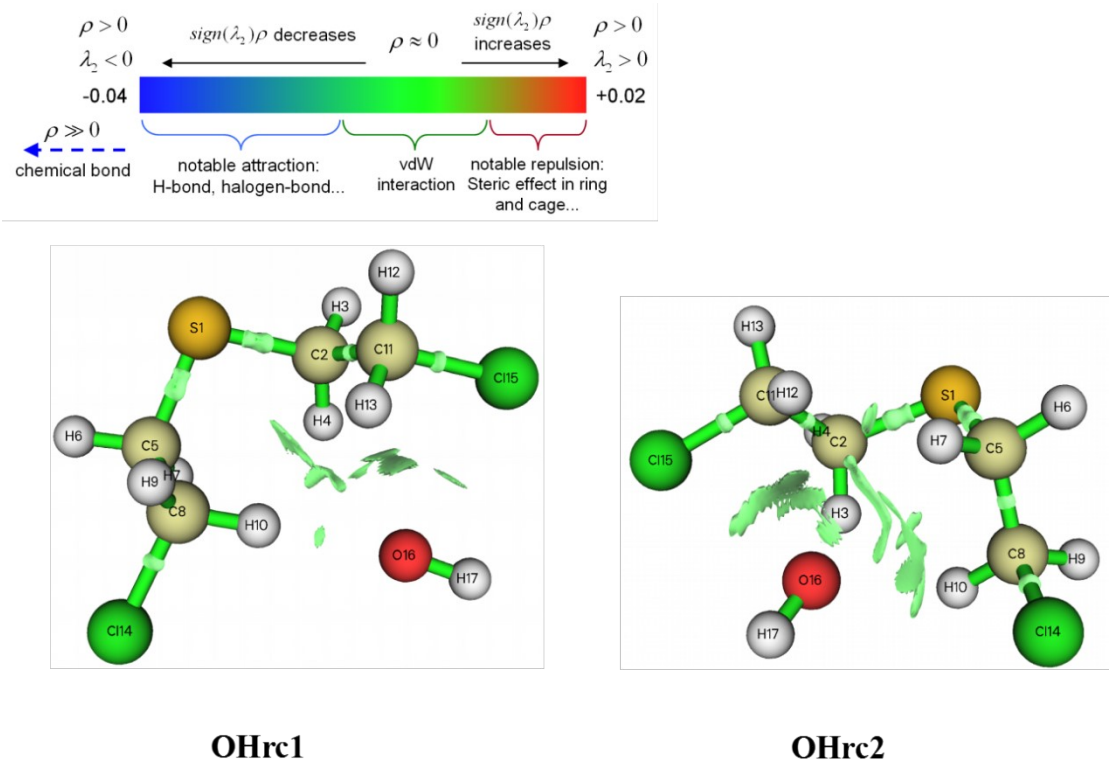
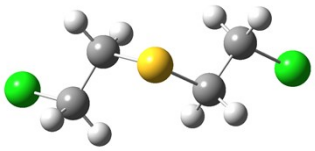
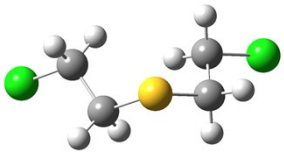
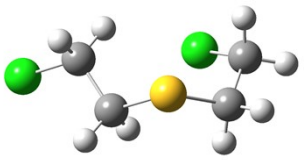
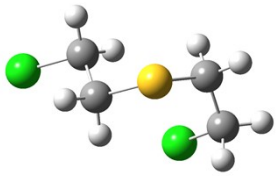
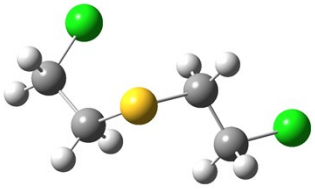
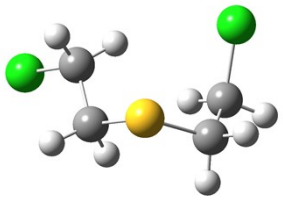
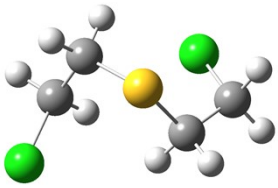
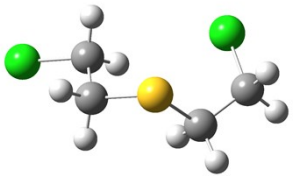
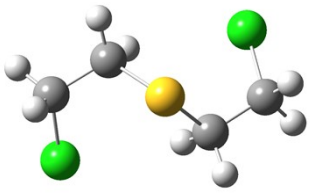
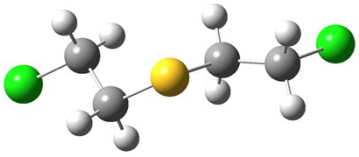
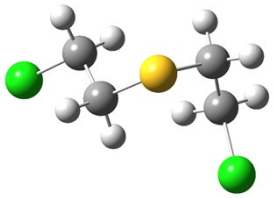
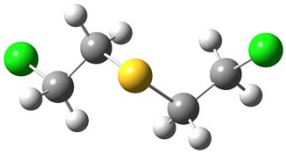
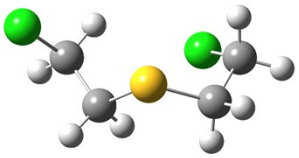
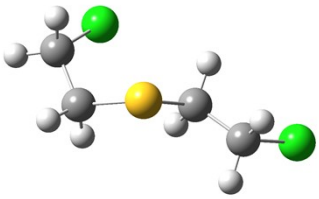
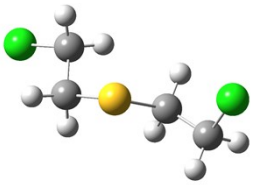
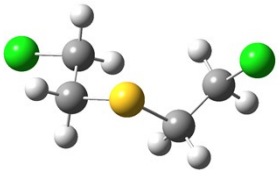
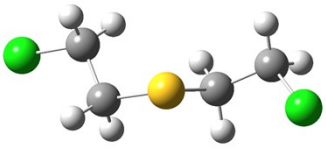
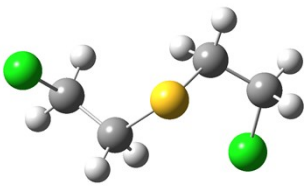
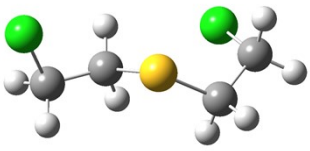


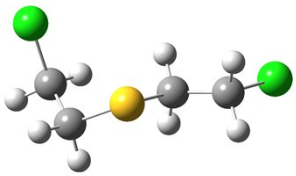
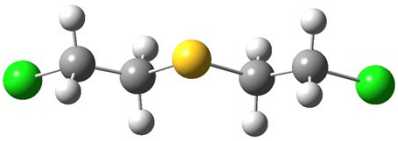
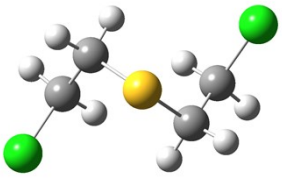
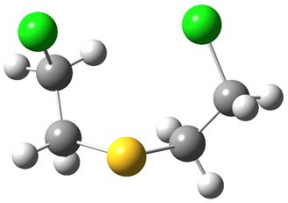
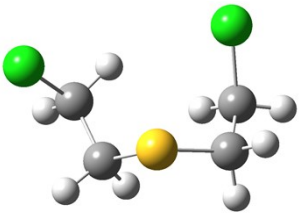
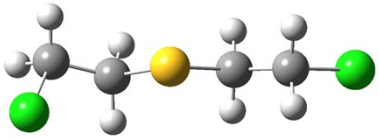
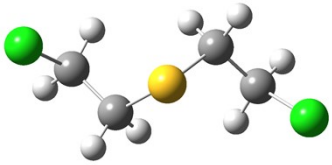
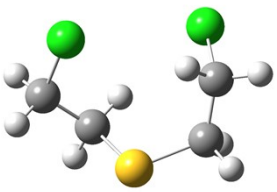
Figure S3 The interaction region indicator (IRI) for the HD-OH prereactive complexes.

Table S1 Conformational distribution of HD.

Serial number	conformation	Relative energies (kcal • mol^{-1})	Boltzmann distribution at 298.15 K (%)
1		0.00	26.73
2		0.47	12.15

3		0.67	8.59
4		0.77	7.33
5		0.83	6.60
6		0.91	5.73
7		1.06	4.48
8		1.09	4.25
9		1.11	4.08
10		1.15	3.87

11		1.18	3.63
12		1.47	2.23
13		1.65	1.65
14		1.65	1.64
15		1.82	1.25
16		1.90	1.08
17		2.01	0.89
18		2.09	0.79
19		2.20	0.66

20		2.41	0.45
21		2.43	0.44
22		2.49	0.40
23		2.60	0.33
24		2.87	0.21
25		3.12	0.14
26		3.24	0.11
27		3.35	0.09

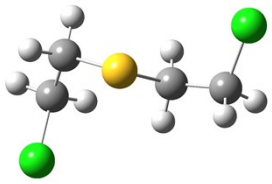
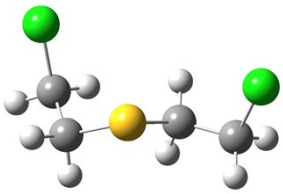
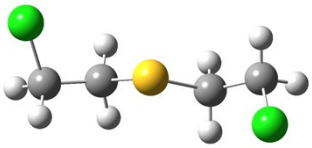
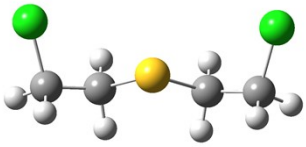
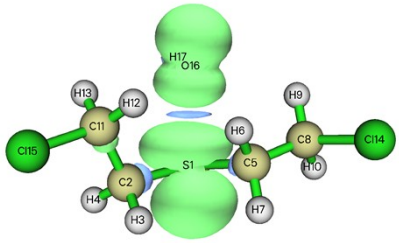
28		3.42	0.08
29		3.57	0.06
30		3.93	0.04
31		4.30	0.02

Table S2 T1 diagnostics for all stationary points in the reaction system at the CCSD(T) level.

Species	HD	OH-TS1	OH-TS2	OH-TS3
T1 diagnostics values	0.009	0.015	0.016	0.016
Species	OH-TS4	OH-TS5	OH-TS6	OH-TS7
T1 diagnostics values	0.059	0.017	0.018	0.051
Species	O_2-TS1	O_2-TS2	O_2-TS3	O_2-TS4
T1 diagnostics values	0.020	0.022	0.029	0.026
Species	O_2-TS5	O_2-TS6	O_2-TS7	O_2-TS8
T1 diagnostics values	0.016	0.017	0.017	0.019
Species	O_2-TS9	O_2-TS10	O_2-TS11	O_2-TS12
T1 diagnostics values	0.020	0.023	0.020	0.024
Species	O_2-TS13	O_2-TS14	O_2-TS15	O_2-TS16
T1 diagnostics values	0.017	0.020	0.023	0.025
Species	O_2-TS17	p-IM1	p-IM2	p-IM3
T1 diagnostics values	0.022	0.013	0.016	0.015
Species	O_2-IM1	O_2-IM2	O_2-IM3	O_2-IM4
T1 diagnostics values	0.018	0.018	0.016	0.016
Species	O_2-IM5	O_2-IM6	O_2-IM7	O_2-IM8
T1 diagnostics values	0.013	0.014	0.011	0.011
Species	O_2-IM9	O_2-IM10	O_2-IM11	O_2-IM12

T1 diagnostics values	0.013	0.015	0.014	0.015
Species	SMO	SMO_2	P1	P2
T1 diagnostics values	0.014	0.014	0.011	0.011
Species	P3	HO_2-TS1	HO_2-TS2	HO_2-TS3
T1 diagnostics values	0.016	0.016	0.017	0.017
Species	HO_2-TS4	HO_2-TS5	HO_2-TS6	HO_2-TS7
T1 diagnostics values	0.016	0.017	0.023	0.019
Species	HO_2-TS8	HO_2-IM1	HO_2-IM2	HO_2-IM3
T1 diagnostics values	0.030	0.016	0.011	0.011
Species	HO_2-IM4	HO_2-IM5	O-TS1	O-TS2
T1 diagnostics values	0.012	0.014	0.014	0.017

Table S3 Structural and Electronic Characterization of OHad1.

Analysis Method	**Detection Result**	**Interpretation & Implication**
Wiberg Bond Order	Total = 0.399 α-spin = –0.0596 β-spin = 0.459	Bonding is dominated by β-spin electrons, consistent with a one-electron covalent interaction. The total bond order ≈ 0.4 suggests a weak but non-negligible covalent character, typical of 2c-3e bonds.
Spin Density Visualization	 S and O atoms show green isosurfaces (β-spin enrichment) Bond axis shows thin blue region (α-spin)	The unpaired electron (β-spin) is localized on S and O atoms — characteristic of σ* orbital occupancy in 2c-3e systems. The minor α-density along the bond is due to spin polarization, not bonding delocalization.
Localized Orbital Analysis	Occupancy ≈ 1.00 S contribution: 55.6% O contribution: 31.7%	The singly occupied orbital is localized over the S–O region (S: 55.6%, O: 31.7%) and exhibits σ symmetry. Its single occupancy and antibonding character (evidenced by reduced bond order and spin localization) are consistent with the σ* orbital in the canonical 2c-3e bonding scheme.

Mulliken Spin Population (Atom-level)	S: Spin pop. = –0.437 O: Spin pop. = –0.594 Sum = –1.03	The unpaired electron (spin = 1.0) is almost entirely distributed over S and O, confirming their role as radical centers. This matches the expected spin distribution for a 2c-3e system where the odd electron resides in an antibonding σ* orbital.

Table S4 Input conditions for computational modeling of the roles of reactive oxygen species in the degradation of HD during incineration.

Items	Value
Reactive species	C_2H_4, 0.048; N_2, 0.758; O_2, 0.194
Reaction time	0.2 s
Reaction temperature	973-1573 K
Reaction pressure	1 atm
Equivalence Ratio	Fuel:O_2=1:4

Table S5 Elementary reactions contributing to the total rate constant of each oxygen-containing species

Reactive oxygen species	Reactions	Rate constant		
OH	$ClCH_2CH_2SCH_2CH_2Cl+OH=ClCH_2CH_2SCH_2CHCl+H_2O$	1.21E03	3.11	-657
	$ClCH_2CH_2SCH_2CH_2Cl+OH=ClCH_2CH_2SCHCH_2Cl+H_2O$	7.63E03	2.83	-1016
O_2	$ClCH_2CH_2SCH_2CH_2Cl+O_2=ClCH_2CH_2SCH_2CHCl+HO_2$	3.44E01	3.45	45535
	$ClCH_2CH_2SCH_2CH_2Cl+O_2=ClCH_2CH_2SCHCH_2Cl+HO_2$	3.22E01	3.22	38750
	$ClCH_2CH_2SCH_2CH_2Cl+O_2=ClCH_2CH_2SOCH_2CH_2Cl+O$	3.85E01	2.97	75151
HO_2	$ClCH_2CH_2SCH_2CH_2Cl+HO_2=ClCH_2CH_2SCH_2CHCl+H_2O_2$	5.45E-03	4.41	13031
	$ClCH_2CH_2SCH_2CH_2Cl+HO_2=ClCH_2CH_2SCHCH_2Cl+H_2O_2$	1.72E-03	4.29	8028
O	$ClCH_2CH_2SCH_2CH_2Cl+O=ClCH_2CH_2SCH_2CHCl+OH$	1.09E06	2.34	3996
	$ClCH_2CH_2SCH_2CH_2Cl+O=ClCH_2CH_2SCHCH_2Cl+OH$	3.68E00	3.87	-1588