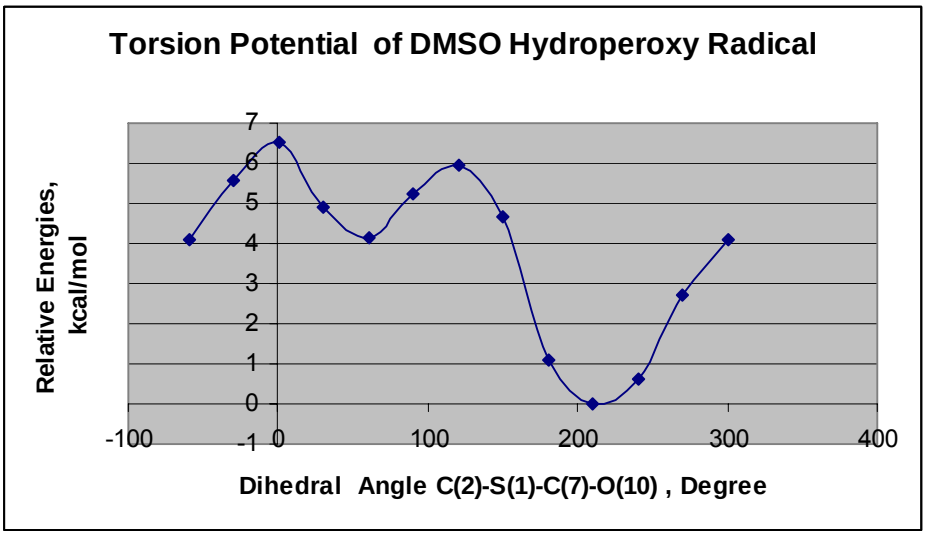
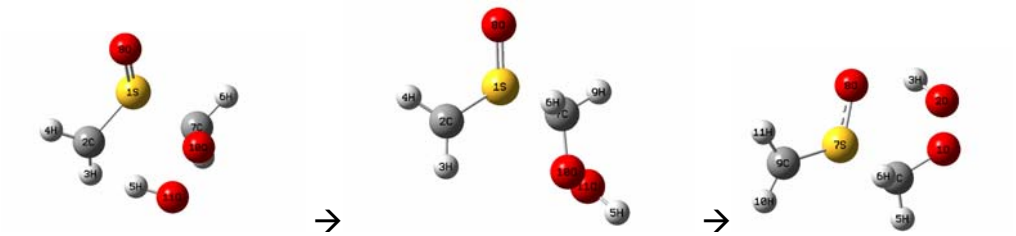
Electronic Supplementary Information





Initial Hydroperoxy Radical → **Local Minimum** → ***iso*-Hydroperoxy radical (Global Minimum)**

Fig. S1. Torsion potential for DMSO hydroperoxy radical at CBS-QB3 level using relaxed scan procedure; Rotation of CH_2OOH fragment about C-S-O-O dihedral angle leads to the formation of its isomer and further decomposition to CH_2SO+CH_2O+ OH.

Table S1. Pressure Dependent Rate Coefficients from the Chemical Activation Analysis for the Reaction of $CH_3S(=O)CH_2\bullet + O_2$ System. $k = A\ T^n \exp(-E_a/RT)$

Reaction	A	n	E_a	P
$CS(O)CJ+O_2<=>CH_2OO+CH_3SO\bullet$	1.85E+16	-1.14	1048.	0.01-10
	2.87E+16	-1.20	1160.	100
$CS(O)CJ+ O_2 <=> CJS(O)CQ$	2.93E+29	-10.72	6215.	0.01
	1.22E+31	-10.90	6164.	0.1
	1.09E+32	-10.86	5580.	1.0
	5.27E+34	-11.35	3581.	10
	5.76E+49	-15.06	7014.	100
$CS(O)CJ+O_2<=>CH_2SO+CH_2O+OH$	1.81E+14	-1.20	1255.	0.01
	1.81E+14	-1.20	1255.	0.1
	1.81E+14	-1.20	1254.	1.0
	1.78E+14	-1.20	1249.	10
	2.36E+14	-1.23	1309.	100

[a] rate constants; N_2 bath gas; P (atm). ΔE_{down} 830 cal., e/k 697.K^{-1} and σ 5.84 A^o
Units: $cm^3\ mole^{-1}\ sec^{-1}$, E_a in $cal\ mol^{-1}$

Table S2. Pressure Dependent Rate Coefficients from the Unimolecular Dissociation Analysis for the Reaction of $CH_3S(=O)CH_2\bullet + O_2$ System. $k = A\ T^n \exp(-E_a/RT)$

Reaction	A	n	E_a	P
CS(O)COOJ <=> CS(O)CJ+ O_2	6.57E-20	6.82	19583.	0.01
	3.75E-04	2.22	23643.	0.1
	2.74E-18	7.13	18651.	1.0
	2.73E-09	4.69	18705.	10
	9.90E+36	-8.63	32076.	100
CS(O)COOJ<=>CH_2OO + $CH_3SO\bullet$	1.18E-10	5.72	9031.	0.01
	7.43E+05	1.12	13215.	0.1
	2.63E+01	2.99	12038.	1.0
	4.66E+01	3.28	12428.	10
	2.09E+33	-6.34	23026.	100
CS(O)COOJ <=> CJS(O)CQ	7.18E-06	4.41	9415.	0.01
	5.36E+01	2.54	11881.	0.1
	6.06E+14	-1.41	16341.	1.0
	8.81E+06	1.16	14134.	10
	1.40E+28	-5.34	21215.	100
CJS(O)CQ<=>CH_2SO+CH_2O+OH	4.54E+01	2.20	7247.	0.01
	4.48E+02	2.20	7246.	0.1
	3.94E+03	2.22	7236.	1.0
	8.95E+03	2.44	7125.	10
	4.28E-09	6.42	2228.	100
CJS(O)CQ<=> CS(O)COOJ	1.10E+00	2.24	7230.	0.01
	1.08E+01	2.24	7229.	0.1
	9.56E+01	2.26	7220.	1.0
	2.24E+02	2.47	7112.	10
	3.00E-11	6.63	2044.	100

[a] Rate constants; N_2 bath gas; see table S1 for L-J parameters
Units: sec^{-1}, E_a in cal mol^{-1}, P in atm

Table S3. Calculated Ideal Gas- Phase Thermodynamic Properties [a]

Species	$\Delta H_f^{o}{}_{298}$ [b]	$S^{\circ}{}_{298}$ [c]	$C_{p(300)}$ [c]	$C_{p(400)}$ [c]	$C_{p(500)}$ [c]	$C_{p(600)}$ [c]	$C_{p(800)}$ [c]	$C_{p(1000)}$ [c]	$C_{p(1500)}$ [c]
CS(O)C•	13.00	72.91	21.61	25.49	28.64	31.18	35.06	37.97	42.67
CS(O)COO•	-16.70	85.02	26.63	31.72	36.01	39.48	44.65	48.31	53.87
CH_2OO	26.70	58.19	11.32	13.40	15.16	16.60	18.74	20.26	22.57
CH_3SO•	-18.95	65.32	14.01	16.29	18.28	19.95	22.53	24.44	27.46
C•S(O)CQ	-2.75	86.53	28.71	33.87	37.92	41.09	45.70	48.99	54.11
CH_2SO	-7.10	61.14	12.34	14.53	16.25	17.57	19.46	20.79	22.84
$HOCH_2SO$	-55.22	72.49	16.93	19.94	22.47	24.51	27.55	29.70	32.99
IC•S(O)CQ	-5.77	84.90	28.55	33.74	37.81	40.98	45.61	48.91	54.06
TS0	13.5	95.00	28.97	33.21	36.71	39.57	43.94	47.16	52.25
TS1	0.39	80.83	25.25	30.94	35.52	39.11	44.26	47.76	52.85
TS2	17.17	82.94	26.52	31.99	36.17	39.37	43.95	47.17	52.19
TS3	-1.00	85.96	26.96	32.18	36.22	39.34	43.88	47.12	52.18
TS4	1.65	91.56	26.93	31.55	35.44	38.60	43.35	46.77	52.07

[a] Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1 atm.
[b] Units in kcal mol^{-1}. [c] Units in cal mol^{-1} K^{-1}.

Table S4. $\Delta H_f^{o}{}_{298}$ Values by Isodesmic Reaction Analysis at CBS- QB3 level [a]

No	Reaction	$\Delta H_f^{o}{}_{298}$ [b]	Mean
V	$(CH_3)_2S + SO_3 \rightarrow$ **$CH_3S(=O)CH_3$** $+ SO_2$	-35.85	-35.97±0.3
VI	$(CH_3)_2S + SO_2 \rightarrow$ **$CH_3S(=O)CH_3$** $+ SO$	-36.53	(-36.1±0.3) [c]
VII	$(CH_3)_2S + CH_3S(=O)OH \rightarrow$ **$CH_3S(=O)CH_3$** $+ CH_3SOH$	-36.15	
VIII	$CH_3S(=O)OH + CH_3S(=O)OH \rightarrow$ **$CH_3S(=O)CH_3$** $+ H_2SO_3$	-35.90	
IX	**$CH_3S(O)CH_2$•** $+ CH_3C(O)CH_3 \rightarrow CH_3S(O)CH_3 + CH_3C(O)CH_2$•	13.20	13.0±0.3[d]
X	**$CH_3S(O)CH_2$•** $+ CH_3SCH_3 \rightarrow CH_3S(O)CH_3 + CH_3SCH_2$ •	13.23	
XI	**CH_2OO** $+ CH_3CH_2OOH = CH_3OO + CH_2CH_2OOH$	24.78	25.3±0.7
XII	**CH_2OO**$+ CH_3S$•$=O = CH_2=S=O +$ CH_3OO•	25.80	
XIII	**$CH_3S(O)CH_2OOH$** $+ C_2H_6 = C_2H_5OOH + CH_3S(O)CH_3$	-52.04	-52.0±0.5
XIV	**$CH_3S(O)CH_2OO$•** $+ C_2H_5OOH = CH_3S(O)CH_2OOH + C_2H_5OO$•	-16.07	-16.0±0.5

[a] Units in kcal mol^{-1}.
[b] $\Delta H_f^{o}{}_{298}$ are evaluated for species in bold.
[c] Including reaction V, see text.
[d] G3MP2 values 13.1 and 12.8 kcal mol^{-1}, respectively.

TABLE S5. Moments of Inertia and Harmonic Frequencies for Stable Species and Transition States of DMSO radical+O2 System Calculated at CBS-QB3 (B3LYP/6-311(2d,d,p) Level of Theory

==========

DMSO - (CH3)2SO

Moments of Inertia
262.26561 267.26824 438.02553

Rotational symmetry number =1
Frequencies and Mode Symmetries

A"	A'	A'
168.8949	218.8175	283.5035
A"	A'	A'
307.1042	364.0445	621.6439
A"	A"	A"
647.4632	888.6718	919.5535
A'	A'	A'
949.0905	1023.6540	1081.8654
A"	A'	A"
1311.6987	1335.3925	1440.1104
A'	A"	A'
1454.1967	1461.4659	1479.7128
A"	A'	A"
3033.8264	3036.5707	3131.3974
A'	A"	A'
3136.1891	3140.1328	3140.9399

CH2S(=O)CH3 radical

Moments of Inertia
240.64071 256.25362 429.87763

Rotational symmetry number =1
Frequencies , cm^{-1}

182.6354	199.6671	276.1630
315.7265	351.2717	532.5719
612.3649	698.4518	873.0149
934.8898	962.2079	1101.1821
1313.2021	1376.1867	1445.6841
1466.4446	3045.1619	3128.3437
3147.6541	3155.7291	3260.2330

CH2OO Criegee Intermediate

Moments of Inertia
22.14098 145.78404 167.92502

Rotational symmetry number =1
Frequencies , cm^{-1}

534.6725	674.6157	909.0898
934.7144	1241.3275	1397.0314
1527.0600	3120.8985	3277.7258

CH3SO Radical

Moments of Inertia
66.50653 217.35652 272.35890

Rotational symmetry number = 1
Frequencies , cm^{-1}

127.7150	324.4862	653.8976
892.9507	943.9439	1024.2449
1324.6069	1445.0163	1463.2263
3032.6082	3127.3942	3129.0256

DMSO- HydroPeroxy Radical

Moments of Inertia
370.67203 843.07657 998.47360

Rotational symmetry number =1
Frequencies , cm^{-1}

73.2460	165.0182	187.5140
251.8186	267.8310	294.8649
386.5278	439.5818	485.9551
564.6362	632.0443	719.0699
851.7171	899.2047	944.6762
1068.2105	1110.8811	1260.8332
1281.7296	1378.5498	1423.9531
1428.6596	3047.9899	3120.4260
3134.9645	3246.1662	3595.5035

DMSO-Peroxy Radical

Moments of Inertia
314.18672 945.55132 1149.89038

Rotational symmetry number =1

Frequencies , cm^{-1}
40.0695 129.0916 186.2374
214.5887 281.4950 294.0743
357.8490 513.2647 627.9165
673.3358 873.3470 923.5972
943.9897 1007.5110 1072.9164
1127.5916 1241.4755 1280.6893
1328.4677 1440.8372 1447.6534
1467.0573 3041.5609 3079.8831
3142.6453 3150.1064 3167.9708

Criegee Complex

Moments of Inertia
365.4473 1310.1965 1589.4898

Rotational symmetry number =1

Frequencies , cm^{-1}
22.6250 53.0778 71.5629
99.6911 118.2841 131.5234
141.5722 329.5168 530.0592
659.5145 674.8720 901.0576
907.6049 943.2509 959.4638
1014.1488 1237.8170 1317.8025
1403.5007 1457.8062 1461.2647
1540.8498 3036.5002 3124.5742
3125.9319 3149.6405 3278.4835

TS0 B3LYP/6-31G(d,p)

Moments of Inertia
285.43164 1503.35777 1675.22884

Rotational symmetry number =1
Frequencies , cm^{-1}

-53.7730 18.3002 36.3096
74.2805 159.0016 219.3531
262.4058 293.1510 311.8120
381.2916 642.2069 667.1626
740.3567 883.2967 957.2252
1000.8743 1055.6929 1343.5690
1412.2391 1461.3681 1478.6991
1583.0002 3058.6813 3137.5511
3164.1625 3169.0556 3272.4715

TS3

Moments of Inertia
345.13759 950.17998 1116.50476

Rotational symmetry number =1
Frequencies , cm^{-1}

-133.1409 39.5471 155.7290
217.3997 234.2900 306.6027
381.6247 487.4728 547.7513
611.6223 666.1437 682.6401
842.6242 868.4682 922.5385
944.8599 1046.5453 1176.6544
1226.6492 1385.9893 1444.6839
1515.2704 3099.9572 3137.6448
3235.3980 3265.9754 3383.4550

TS1

Moments of Inertia
365.54394 780.18029 939.61041

Rotational symmetry number =1

Frequencies , cm^{-1}
-1420.4367 100.4786 222.0136
305.3335 342.4053 411.6133
456.6230 462.9131 551.6904

TS4

Moments of Inertia
341.72291 1261.46435 1486.67946

Rotational symmetry number =1

Frequencies , cm^{-1}
-74.8706 39.2476 93.7262
116.1029 133.9727 152.4811
246.0159 339.9794 526.2031

617.3079 691.8962 883.7910	655.8439 701.6367 854.7111
934.0215 960.4311 979.4012	906.3579 920.1838 961.4358
1065.1988 1114.7808 1156.9182	1034.7590 1224.6086 1290.3056
1252.5794 1258.8339 1384.1413	1338.1959 1449.1456 1460.8131
1437.0556 1589.0079 3050.6530	1478.7499 3018.1445 3115.3092
3083.2885 3152.1970 3188.4822	3130.5319 3134.1357 3286.3569

TS2

Moments of Inertia
438.65621 654.87975 771.01003

Rotational symmetry number =1
Frequencies , cm^{-1}

-1270.6050 49.8236 214.3457	-193.5984 33.9878 74.2263
290.3236 291.9888 391.7651	90.5684 134.1590 185.8056
409.4249 475.3226 517.7121	273.9336 338.0006 531.7436
578.4372 602.6344 670.6509	536.5105 657.3941 667.3450
772.5047 868.7722 935.9450	907.1489 935.4982 947.2166
1029.1443 1063.8853 1107.9908	1084.9111 1203.1560 1257.7271
1213.0008 1258.9671 1379.4292	1317.9861 1444.5311 1455.0249
1445.9966 2997.0669 3068.0889	1461.6582 3041.6034 3137.4399
3123.4995 3255.1753 3714.6578	3146.7801 3148.5328 3303.7495

TS5

Moments of Inertia
352.79215 1063.98452 1239.44861

Rotational symmetry number =1
Frequencies , cm^{-1}

Table S6 Thermochemical Parameters Calculated at CBS-QB3 Level

	ΔG^{o}_{298} * Hartrees	ΔH^{o}_{298} Hartrees	ΔS^{o}_{298} cal mol^{-1} K^{-1}
Peroxy Radical	**-702.082606**	**-702.040996**	**87.386**
TS4	**-702.055647**	**-702.011909**	**91.862**
VdW Criegee	**-702.061535**	**-702.013817**	**100.219**
CH_2OO+CH_3SO	-702.067021	-702.006538	127.202
CH_2OO	-189.367160	-189.338845	59.560
CH_3SO	-512.699861	-512.667693	67.642
TS5	**-702.046565**	**-702.002452**	**92.646**
$CH_3SO_2+CH_2O$	**-702.202522**	**-702.142932**	**125.32**
CH_3SO_2	-587.836731	-587.802610	71.721
CH_2O	-114.365791	-114.340322	53.599

*- Gibbs Free Energies $\Delta G^{o}_{298} = \Delta H^{o}_{298} - T\Delta S^{o}_{298}$ calculated at 298.15 K

ΔG^{o}_{298} (TS4) = -702.011909 + (298.15K x 91.862 cal/mol-K)/ 1000 x 627.5 =
-702.011909 + 0.043647 = -702.055556 (Gaussian exact output = -702.055647)