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SUPPORTING INFORMATION

Theoretical Investigation on Atmospheric Chemistry of Volatile Anaesthetic Sevoflurane: Reactions with the OH Radicals and Atmospheric Fate of the Alkoxy Radical $(CF_3)_2CHOCHFO$: Thermal Decomposition vs Oxidation

Bhupesh Kumar Mishra[a], Makroni Lily[b], Arup Kumar Chakrabartty[a], Debajyoti Bhattacharjee[a], Ramesh Chandra Deka[a*] and Asit K Chandra[b**]

[a]Department of Chemical Sciences, Tezpur University, Tezpur, Assam – 784 028, India

[b]Department of Chemistry, North - Eastern Hill University, Shillong, 793 022, India

[*]Correspondence author, Email: ramesh@tezu.ernet.in; Fax: +91 3712267005; Tel: +91 3712267008

[**]Correspondence author, Email: akchandra@nehu.ac.in; Fax: +91 3642550486; Tel.: +91 3642722622

Table S1. Harmonic vibrational frequencies of reactants, reactant complexes, transition states, product complexes and products at M06-2X/6-31+G(d,p) level of theory.

Species	Vibrational frequencies (cm^{-1})
SEV 1	36, 55, 68, 97, 149, 181, 219, 293, 297, 332, 366, 449, 522, 537, 552, 580, 613, 697, 755, 905, 936, 1078, 1097, 1159, 1171, 1230, 1233, 1272, 1300, 1311, 1322, 1355, 1421, 1437, 1455, 1534, 3119, 3127, 3226
SEV 2	36, 87, 100, 113, 162, 210, 219, 295, 306, 330, 332, 477, 521, 536, 549, 569, 620, 700, 766, 886, 928, 1027, 1105, 1161, 1176, 1229, 1242, 1272, 1306, 1308, 1326, 1360, 1413, 1422, 1463, 1541, 3142, 3144, 3219,
RC1	31, 46, 59, 66, 78, 105, 126, 130, 167, 200, 230, 308, 309, 343, 348, 375, 467, 543, 558, 574, 600, 631, 722, 778, 931, 958, 1094, 1118, 1192, 1205, 1230, 1258, 1282, 1319, 1356, 1365, 1389, 1475, 1496, 1519, 1589, 3160, 3190, 3252, 3878
RC2a	34, 40, 45, 61, 88, 110, 159, 174, 197, 224, 233, 309, 314, 342, 380, 450, 464, 547, 561, 573, 586, 632, 723, 779, 933, 960, 1060, 1099, 1186, 1214, 1256, 1259, 1297, 1320, 1355, 1369, 1391, 1480, 1497, 1515, 1583, 3165, 3176, 3263, 3855
RC2b	25, 42, 67, 70, 88, 112, 116, 147, 161, 195, 226, 293, 297, 331, 364, 374, 452, 521, 536, 553, 584, 612, 698, 756, 901, 934, 1074, 1099, 1159, 1169, 1224, 1268, 1304, 1310, 1319, 1417, 1434, 1456, 1539, 3123, 3137, 3232, 3764
TS1	2118i, 36, 56, 65, 75, 119, 163, 172, 187, 232, 307, 310, 341, 348, 378, 390, 478, 561, 563, 575, 581, 637, 728, 790, 853, 979, 992, 1091, 1107, 1133, 1216, 1251, 1262, 1280, 1307, 1326, 1365, 1386, 1414, 1514, 1537, 1585, 3198, 3280, 3899
TS2a	1822i, 30, 36, 64, 80, 108, 143, 170, 199, 221, 276, 306, 310, 341, 377, 459, 545, 560, 575, 600, 634, 672, 723, 781, 856, 936, 953, 1087, 1130, 1186, 1190, 1259, 1272, 1300, 1333, 1346, 1375, 1386, 1436, 1473, 1487, 1567, 3199, 3232, 3913
TS2b	1370i, 36, 37, 60, 69, 82, 127, 150, 186, 219, 245, 280, 296, 331, 352, 445, 522, 537, 553, 570, 610, 741, 758, 845, 910, 939, 1094, 1130, 1145, 1159, 1212, 1235, 1268, 1298, 1311, 1320, 1354, 1384, 1421, 1436, 1551, 3129, 3133, 3766
PC1	35, 45, 67, 85, 102, 130, 142, 147, 180, 196, 255, 297, 318, 337, 355, 365, 378, 452, 495, 544, 547, 570, 610, 645, 711, 783, 1014, 1060, 1100,

	1172, 1180, 1215, 1225, 1241, 1299, 1310, 1405, 1444, 1488, 1536, 1622, 3170, 3258, 3862, 3983
PC2a	26, 40, 52, 65, 85, 133, 145, 152, 193, 215, 221, 228, 292, 294, 297, 333, 366, 448, 522, 536, 554, 591, 619, 696, 755, 902, 934, 985, 1090, 1154, 1161, 1236, 1268, 1274, 1309, 1317, 1351, 1375, 1431, 1441, 1619, 3167, 3234, 3873, 3995
PC2b	29, 44, 64, 80, 82, 134, 147, 170, 181, 202, 225, 261, 298, 320, 332, 354, 451, 521, 537, 553, 600, 625, 701, 757, 895, 941, 950, 1079, 1167, 1189, 1241, 1243, 1267, 1309, 1314, 1330, 1351, 1413, 1436, 1606, 3147, 3237, 3872, 3999
$(CF_3)_2COCH_2F$	51, 54, 71, 124, 162, 175, 210, 305, 310, 333, 353, 465, 498, 544, 552, 581, 613, 671, 726, 788, 1016, 1084, 1132, 1179, 1188, 1205, 1248, 1259, 1299, 1321, 1408, 1448, 1509, 1549, 3146, 3234
$(CF_3)_2CHOCHF$	35, 44, 71, 105, 151, 181, 223, 291, 295, 332, 364, 447, 522, 537, 554, 593, 593, 620, 697, 757, 901, 934, 981, 1095, 1162, 1166, 1242, 1263, 1273, 1313, 1320, 1347, 1366, 1419, 1434, 3133, 3245
OH	3757
H_2O	1596, 3887, 4012

Table S2. Relative energies in kcal mol^{-1} with zero-point energy correction for the reactants, reactant complexes, transition states, product complexes and products.

Species	**M06-2X/6-311++G(d,p)**
$(CF_3)_2CHOCH_2F + OH$	0.00
RC1	-3.91
RC2a	-4.88
RC2b	-4.69
TS1	1.52
TS2a	1.42
TS2b	3.50
PC1	-23.18
PC2a	-22.64
PC2b	-19.00
$(CF_3)_2COCH_2F + H_2O$	-16.52
$(CF_3)_2CHOCHF + H_2O$	-16.77

Table S3. Harmonic vibrational frequencies of reactants, transition states and products involved in the thermal decomposition and oxidation reactions of $(CF_3)_2CHOCHFO$ at M06-2X/6-31+G(d,p) level of theory.

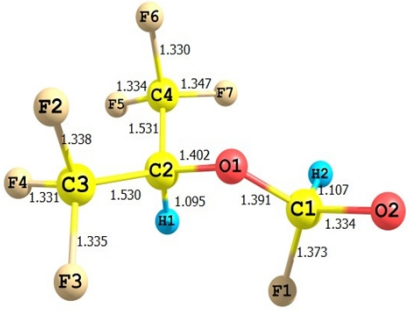
Species	Vibrational frequencies (cm^{-1})
$(CF_3)_2CHOCHFO$	43, 55, 69, 82, 139, 158, 232, 268, 297, 327, 346, 354, 503, 520, 537, 553, 563, 602, 663, 700, 755, 907,937, 982, 1116, 1146, 1159, 12310, 1232, 1269, 1297, 1305, 1325, 1362, 1380, 1426, 1441, 3014, 3143
TS3	673i, 42, 60, 69, 91, 137, 166, 197, 227, 294, 299, 331, 379, 450, 481, 533, 537, 553, 602, 679, 694, 754, 888, 926, 1045, 1120, 1245, 1258, 1292, 1309, 1334, 1360, 1361, 1419, 1565, 3125, 3216
TS4	564i, 40, 53, 69, 86, 137, 163, 178, 258, 294, 302, 334, 351, 437, 454, 524, 537, 554, 599, 694, 729, 783, 920, 1007, 1091, 1163, 1246, 1257, 1273, 1314, 1315, 1384, 1424, 1425, 1564, 3164, 3214
TS5	1087i, 31, 41, 66, 74, 134, 160, 246, 259, 296, 329, 341, 375, 513, 537, 540, 552, 584, 609, 683, 690, 700, 755, 807, 917, 941, 975, 1162, 1172, 1226, 1245, 1275, 1309, 1323, 1362, 1424, 1433, 1811, 3165
TS6	1128i, 29, 39, 53, 64, 83, 128, 140, 145, 159, 220, 252, 285, 299, 330, 352, 367, 504, 511, 538, 540, 554, 597, 651, 700, 735, 783, 907, 938, 1026, 1082, 1160, 1168, 1198, 1236, 1239, 1276, 1300, 1324, 1357, 1425, 1432, 1639, 1722, 3146
$(CF_3)_2CHO$	32, 87, 149, 240, 248, 293, 321, 409, 463, 521, 540, 566, 611, 735, 744, 868, 923, 1169, 1175, 1242, 1265, 1291, 1305, 1334, 1382, 3090, 5412
CHFO	673, 1041, 1129, 1389, 1950, 3196
$(CF_3)_2CHOCHO$	14, 41, 70, 142, 144, 163, 263, 299, 311, 340, 353, 390, 525, 538, 551, 562, 698, 730, 759, 916, 940, 1034, 1139, 1163, 1205, 1243, 1268, 1305, 1326, 1362, 1416, 1424, 1450, 1937, 3076, 3096
$(CF_3)_2CHOCFO$	27, 63, 67, 79, 137, 156, 251, 262,297, 330, 342, 387, 516, 537, 552, 555, 630, 674, 703, 754, 770, 908, 947, 963, 1167, 1189, 1246, 1265, 1284, 1319, 1326, 1367, 1425, 1429, 2011, 3174
HO_2	1266, 1459, 3710
O_2	1774

Table S4 Thermochemical data for the thermal decomposition and oxidation pathways of $(CF_3)_2CHOCHFO$ radical calculated at M06-2X/6-31+G(d,p) level of theory. All values are in $kcal.mol^{-1}$.

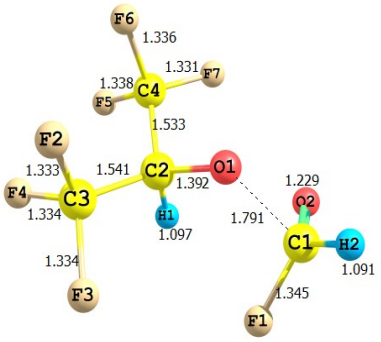
Reaction channels	**$\Delta_rH°_{298}$**	**$\Delta_rG°_{298}$**	**$\Delta G^{\#}$**
Reaction 3	14.67	1.86	16.17
Reaction 4	28.10	18.12	25.36
Reaction 5	6.60	-1.14	15.38
Reaction 6	-41.48	-42.74	14.84

Table S5. Calculated energy barriers (in kcal mol^{-1}) for the thermal decomposition and oxidation pathways of $(CF_3)_2CHOCHFO$ radical.

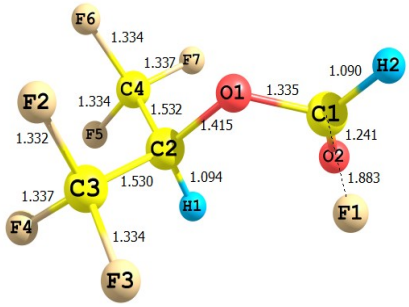
Reaction Channels	**M06-2X/ 6-311++G(d,p)**
TS3 (C-O bond scission)	15.51
TS4 (C-F bond scission)	24.90
TS5 (C-H bond scission)	15.36
TS6 (Reaction with O_2)	4.91



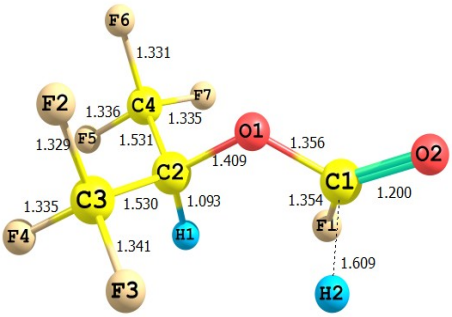
$(CF_3)_2CHOCHFO$



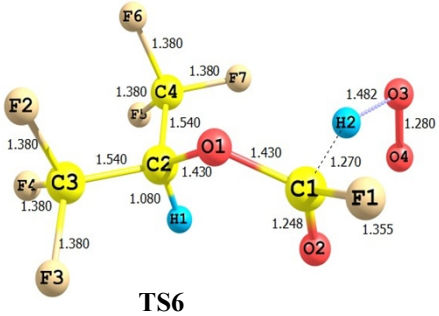
TS3



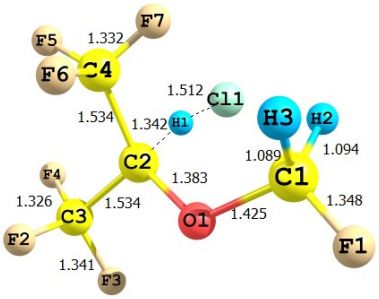
TS4



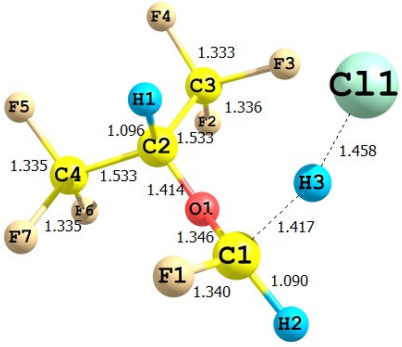
TS5



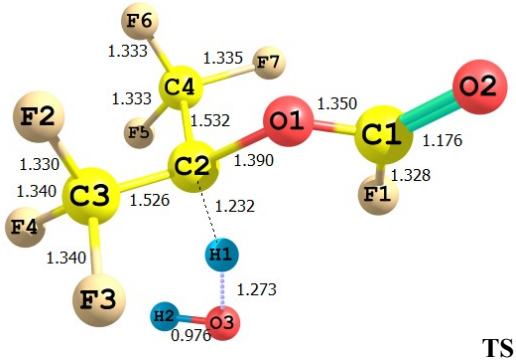
TS6



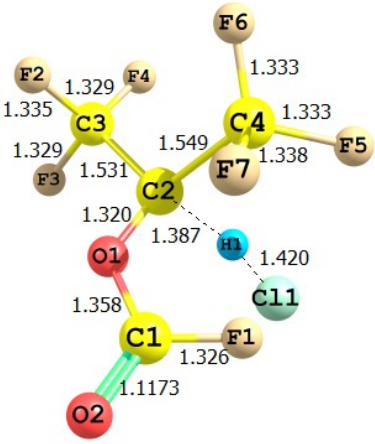
TS7



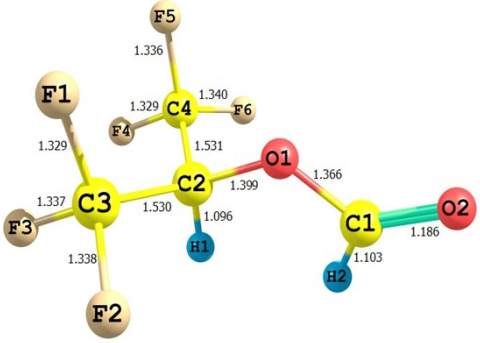
TS8



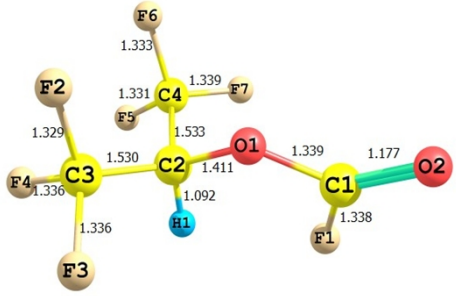
TS9



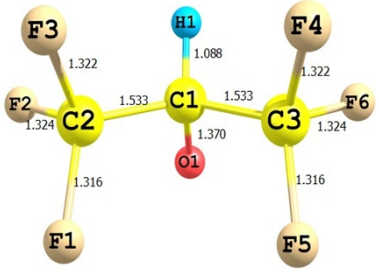
TS10



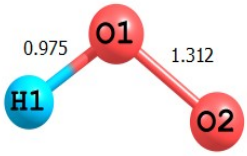
$(CF_3)_2CHOC(O)H$

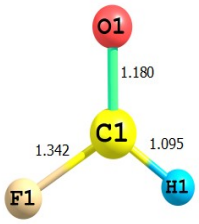


$(CF_3)_2CHOC(O)F$



$(CF_3)_2CHO$





C(O)HF

Fig. S1 Optimized geometries of reactants, transition states and products involved in thermal decomposition and oxidation of alkoxy radical at M06-2X/6-31+G(d,p) method. Bond lengths are in angstroms.