Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Theoretical Investigation on the Atmospheric Fate of $CF_3C(O)OCH(O)CF_3$ Radical: Alpha-ester Rearrangement vs Oxidation

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Table S1 Harmonic vibrational frequencies of reactants, transition states and products at MPWB1K/6-31+G(d,p) and M06-2X/6-31+G(d,p) (italic values in parenthesis) level of theories.

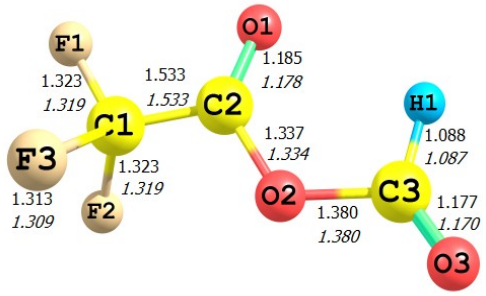
Species	Vibrational Frequencies (cm^{-1})
$CF_3C(O)OCH(O)CF_3$	13, 29, 47, 53, 130, 199, 214, 260, 262, 334, 381, 421, 454, 523, 535, 568, 600, 649, 701, 766, 807, 873, 943, 1058, 1135, 1208, 1238, 1282, 1291, 1325, 1339, 1345, 1354, 1461, 1963, 3030 *(22, 37, 49, 54, 137, 199, 218, 261, 271, 329, 35, 416, 452, 513, 524, 557, 588, 632, 694, 752, 787, 856, 919, 1044, 1114, 1180, 1211, 1263, 1264, 1297, 1314, 1323, 1330, 1426, 1927, 3003)*
TS1	1548i, 77, 86, 100, 105, 107, 139, 191, 220, 254, 278, 296, 306, 333, 381, 420, 464, 486, 526, 536, 559, 602, 651, 735, 744, 801, 807, 882, 935, 961, 1131, 1168, 1214, 1237, 1249, 1267, 1279, 1392, 1520, 1593, 1759, 1906 *(1743i, 27, 44, 51, 63, 82, 110, 165, 177, 198, 219, 264, 275, 301, 334, 386, 423, 464, 515, 523, 548, 567, 613, 662, 734, 760, 788, 867, 927, 1022, 104, 1187, 1262, 1270, 1293, 106, 1315, 1370, 1423, 1630, 1684, 1921)*
TS2	1131i, 18, 47, 54, 99, 151, 201, 220, 264, 273, 348, 381, 437, 465, 503, 542, 592, 614, 678, 753, 778, 824, 922, 949, 1227, 1273, 1297,1302, 1315, 1324, 1341, 1591, 1692, 1777, 1796 *(1059i, 31, 48, 57, 102, 152, 204, 219, 261, 274, 352, 374, 429, 465, 494, 525, 536, 583, 607, 675, 742, 766, 806, 905, 938, 1209, 1250, 1277, 1283, 1289, 1302, 1316, 1553, 1662, 1732, 1756)*
TS3	742i, 27, 40, 48, 93, 141, 195, 236, 254, 269, 338, 396, 419, 457, 470, 525, 529, 533, 581, 622, 686, 726, 780, 793, 853, 916, 1086, 1199, 1281, 1284, 1333, 1343, 1372, 1430, 1904, 1978 *(930i, 37, 44, 56, 70, 112, 211, 222, 249, 272, 321, 372, 420, 444, 509, 519, 539, 558, 576, 611, 681, 738, 768, 781, 847, 922, 1095, 1146, 1260, 1271, 1311, 1317, 1352, 1392, 1820, 1966)*
TS4	365i, 22, 27, 44, 117, 141, 154, 184, 199, 260, 316, 354, 376, 427, 528, 533, 538, 552, 637, 682, 763, 815, 927, 979, 1038, 1119, 1214, 1279, 1336, 1363, 1384, 1397, 1450, 1721, 1963, 3157

	(379i, 15, 40, 48, 77, 140, 148, 159, 199, 260, 314, 341, 371, 420, 520, 525, 529, 545, 627, 662, 750, 793, 906, 944, 1011, 1088, 1184, 1263, 1314, 1333, 1354, 1366, 1415, 1690, 1933, 3118)
TS5	632i, 63, 79, 90, 106, 116, 131, 205, 248, 257, 277, 349, 395, 435, 452, 519, 536, 566, 597, 611, 701, 783, 791, 838, 873, 1135, 1208, 1235, 1247, 1267, 1313, 1325, 1373, 1659, 1822, 2791
	(723i, 38, 48, 62, 87, 89, 135, 203, 241, 253, 275, 345, 401, 435, 447, 517, 535, 566, 587, 611, 695, 766, 783, 825, 875, 1140, 1189, 1258, 1265, 1288, 1300, 1330, 1381, 1687, 1844, 2820)
$CF_3C(O)OC(O)CF_3$	20, 31, 39, 72, 99, 204, 230, 247, 269, 328, 366, 435, 452, 524, 531, 580, 609, 686, 768, 791, 804, 864, 928, 1141, 1166, 1279, 1285, 1341, 1342, 1410, 1419, 1970, 2047
	(27, 38, 46, 71, 100, 211, 225, 239, 269, 323, 363, 426, 446, 517, 523, 572, 598, 676, 751, 777, 783, 847, 908, 1118, 1133, 1260, 1265, 1316, 1318, 1377, 1388, 1942, 2018)
HO_2	1284, 1490, 3787
	(1268, 1459, 3713)
$CF_3C(O)OH$	27, 239, 243, 401, 435, 517, 605, 615, 685, 817, 836, 1213, 1263, 1274, 1339, 1503, 1972, 3912
	(29, 240, 243, 394, 429, 510, 595, 598, 676, 798, 821, 1187, 1244, 1253, 1317, 1467, 1940, 3814)
$CF_3C(O)$	144, 251, 412, 417, 542, 551, 685, 805, 1198, 1248, 1266, 2031
	(70, 242, 404, 416, 538, 549, 672, 805, 1198, 1269, 1287, 2045)
$CF_3C(O)OCH(O)$	26, 66, 111, 140, 258, 299, 359, 423, 530, 551, 638, 765, 807, 935, 1072, 1087, 1207, 1283, 1338, 1410, 1446, 1956, 1989, 3213
	(44, 102, 121, 144, 260, 302, 352, 417, 521, 544, 628, 751, 791, 916, 1048, 1059, 1178, 1263, 1313, 1392, 1417, 1927, 1960, 3178)

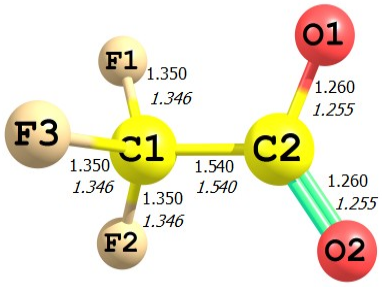
CF_3	517, 517, 716, 1138, 1342, 1343 *(510, 510, 701, 1120, 1312, 1315)*
$CF_3C(O)O$	279, 297, 309, 363, 433, 492, 524, 563, 727, 855, 1009, 1181, 1198, 1345, 1544 *(270, 294, 308, 368, 432, 509, 523, 566, 734, 850, 1022, 1211, 1225, 1354, 1707)*
$CF_3C(O)H$	78, 258, 314, 442, 538, 539, 727, 885, 1013, 1262, 1272, 1388, 1443, 1959, 3093 *(94, 258, 318, 435, 530, 532, 714, 866, 993, 1242, 1250, 1360, 1416, 1924, 3063)*

Table S2 Harmonic vibrational frequencies of reactants, transition states and products at MPWB1K/6-311++G(d,p) level of theory.

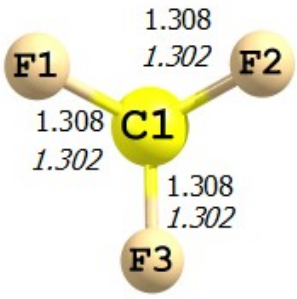
Species	Vibrational Frequencies (cm^{-1})
$CF_3C(O)OCH(O)CF_3$	15, 32, 48, 56, 129, 201, 216, 260, 265, 336, 384, 423, 459, 532, 544, 576, 605, 655, 705, 773, 815, 872, 944, 1052, 1130, 1196, 1231, 1267, 1282, 1313, 1329, 1334, 1349, 1447, 1960, 3012
TS1	1570i, 81, 103, 109, 116, 117, 147, 194, 231, 263, 292, 306, 321, 339, 384, 423, 468, 481, 532, 542, 562,602, 653, 737, 743, 796, 816, 873, 930, 954, 1129, 1151, 1183, 1209, 1224, 1235, 1259, 1373, 1492, 1540, 1751, 1858
TS2	1207i, 81, 94, 104, 131, 159, 220, 230, 275, 289, 354, 379, 432, 465, 490, 534, 543, 587, 607, 679, 743, 763, 837, 895, 930, 1192, 1213, 1226, 1230, 1261, 1271, 1285, 1512, 1599, 1691, 1724
TS3	741i, 27, 41, 48, 91, 141, 193, 237, 256, 271, 339, 396, 420, 470, 482, 516, 535, 539, 586, 627, 691, 733, 787, 801, 854, 918, 1071, 1187, 1265, 1269, 1318, 1327, 1359, 1416, 1901, 1976
TS4	365i, 22, 28, 39, 116, 140, 155, 177, 202, 262, 318, 358, 378, 431, 537, 542, 549, 560, 641, 686, 768, 817, 922, 968, 1022, 1123, 1205, 1265, 1320, 1353, 1377, 1387, 1437, 1711,, 1958, 3127
TS5	632i, 66, 82, 91, 106, 117, 135, 210, 252, 267, 287, 356, 395, 432, 458, 521, 536, 566, 597, 611, 701, 783, 791, 838, 873, 1135, 1208, 1235, 1247, 1267, 1318, 1335, 1393, 1719, 1862, 2831
$CF_3C(O)OC(O)CF_3$	20, 31, 39, 72, 99, 204, 230, 247, 269, 328, 366, 435, 452, 524, 531, 580, 609, 686, 768, 791, 804, 864, 928, 1141, 1166, 1279, 1285, 1341, 1342, 1410, 1419, 1970, 2047
HO_2	1277, 1488, 3780
$CF_3C(O)OH$	29, 240, 246, 403, 440, 524, 608, 610, 693, 824, 838, 1209, 1260, 1261, 1327, 1490, 1969, 3908
$CF_3C(O)$	63, 238, 411, 431, 556, 565, 695, 833, 1226, 1276, 1294, 2081
$CF_3C(O)OCH(O)$	28, 55, 108, 141, 261, 301, 359, 427, 539, 557, 642, 771, 814, 934, 1072, 1073, 1198, 1268, 1323, 1410, 1439, 1953, 1986, 3186
CF_3	528, 528, 725, 1133, 1331, 1332
$CF_3C(O)O$	18, 218, 241, 301, 432, 528, 540, 624, 778, 824, 1227, 1266, 1298, 1366, 1845
$CF_3C(O)H$	79, 257, 315, 445, 544, 548, 733, 883, 1013, 1249, 1262, 1377, 1439, 1957, 3061



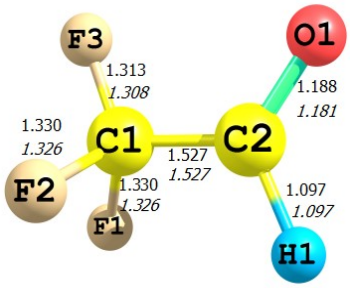
$CF_3C(O)OCH(O)$



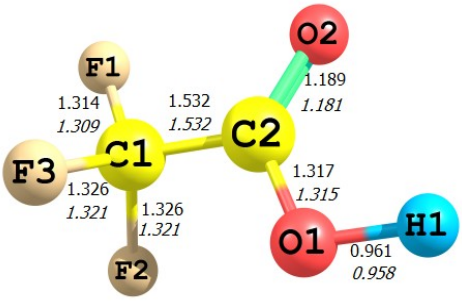
$CF_3C(O)O$



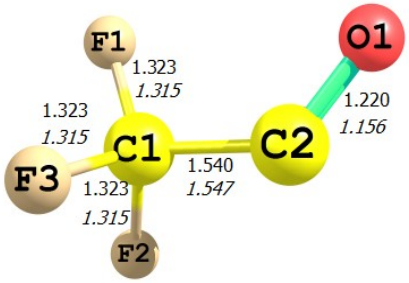
CF_3



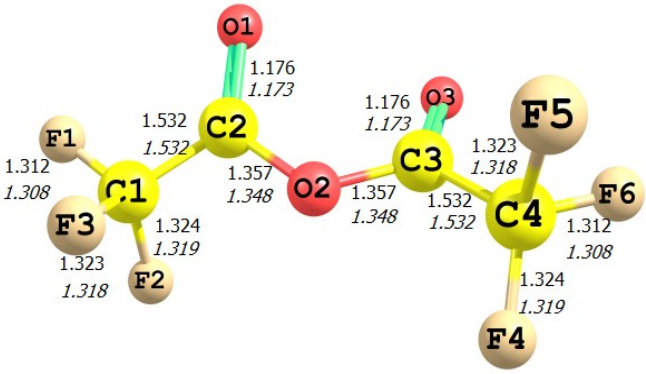
$CF_3CH(O)$



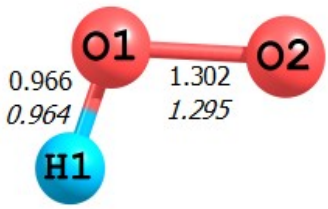
$CF_3C(O)OH$



CF_3CO



$CF_3C(O)OC(O)CF_3$



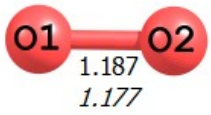


Fig. S1 Optimized geometries of products obtained at MPWB1K/6-31+G(d,p) and MPWB1K/6-311++G(d,p) (italic values) levels of theory. Bond lengths are in angstroms.

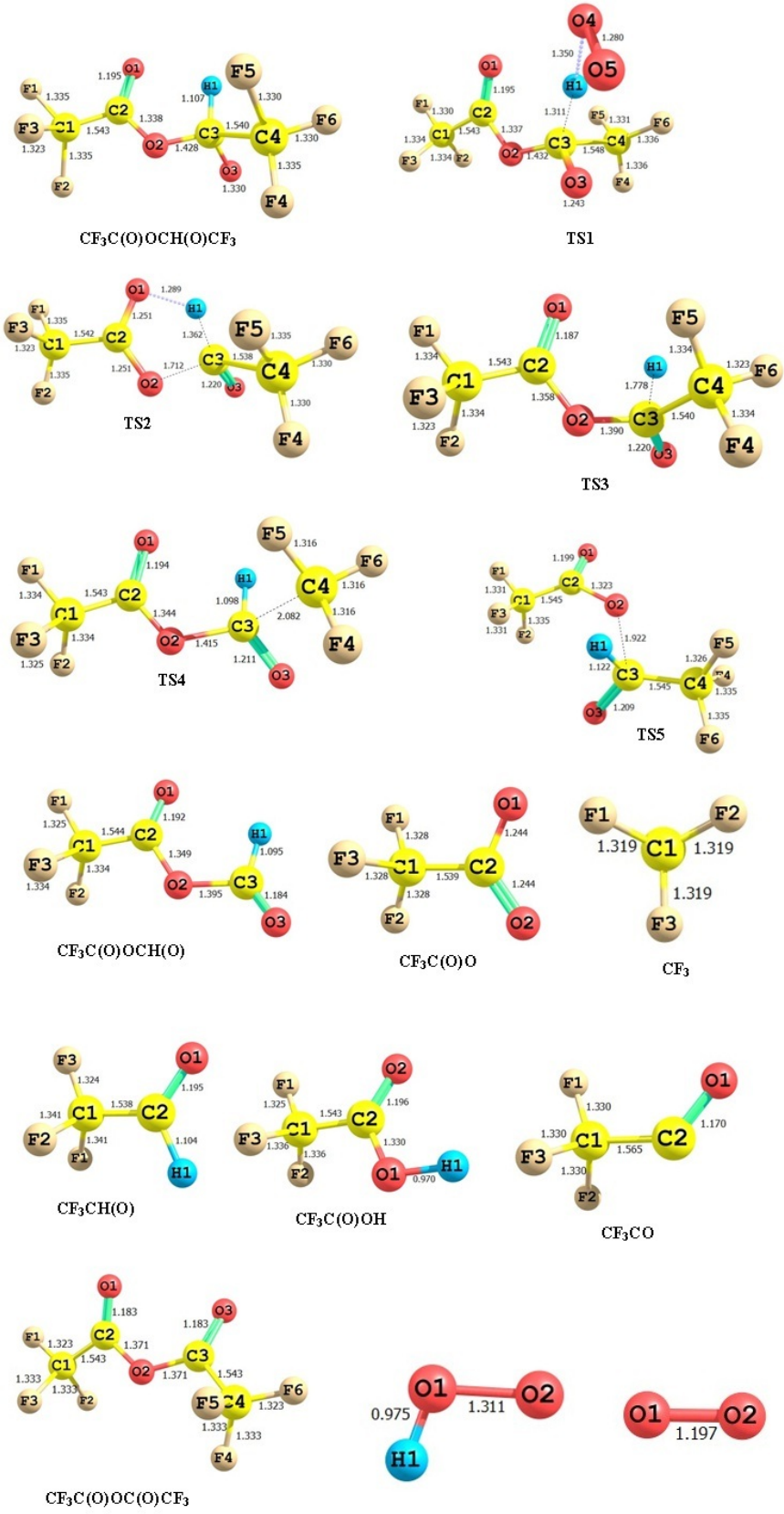


Fig. S2 Optimized geometries of reactants, transition states and products obtained at M06-2X/6-31+G(d,p) level of theory. Bond lengths are in angstroms.