

SUPPORTING INFORMATION

A theoretical insight on atmospheric chemistry of HFE-7100 and Perfluoro-butyl Formate: reactions with OH radicals and Cl atoms and fate of alkoxy radical

Bhupesh Kumar Mishra^a, Makroni Lily^b, Ramesh Chandra Deka^{c*} and Asit K. Chandra^{b**}

^aDepartment of Chemistry, D. N. Government College, Itanagar, Arunachal Pradesh-791113, India

^bDepartment of Chemistry, North - Eastern Hill University, Shillong - 793 022, India

^cDepartment of Chemical Sciences, Tezpur University Tezpur, Assam - 784 028, India

*To whom correspondence should be addressed: Email-addresses: ramesh@tezu.ernet.in (R. C. Deka) & akchandra@nehu.ac.in (A. K. Chandra)

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

Species	Vibrational Frequencies (cm ⁻¹)
n-C ₄ F ₉ OCH ₃	46, 53, 64, 76, 111, 153, 166, 212, 222, 243, 248, 293, 328, 336, 338, 363, 387, 425, 513, 536, 551, 594, 607, 630, 704, 751, 801, 899, 1066, 1152, 1182, 1191, 1197, 1209, 1260, 1272, 1290, 1296, 1313, 1364, 1387, 1449, 1496, 1508, 1516, 3094, 3182, 3216
OH	3758
RC1	37, 48, 67, 71, 84, 114, 126, 142, 169, 177, 186, 214, 227, 247, 255, 296, 328, 338, 341, 366, 379, 389, 428, 512, 537, 553, 594, 607, 630, 704, 751, 802, 897, 1057, 1150, 1182, 1190, 1198, 1209, 1249, 1274, 1291, 1302, 1309, 1369, 1388, 1446, 1505, 1520, 3098, 3194, 3224, 3757
RC2	32, 44, 54, 58, 67, 84, 111, 121, 161, 176, 216, 237, 245, 270, 292, 328, 336, 341, 364, 389, 427, 514, 536, 557, 596, 608, 632, 706, 750, 802, 898, 1057, 1153, 1183, 1200, 1202, 1214, 1264, 1278, 1288, 1305, 1320, 1368, 1391, 1446, 1493, 1507, 1513, 3097, 3191, 3218
TS1	1194i, 26, 43, 45, 66, 104, 113, 147, 169, 208, 217, 224, 245, 253, 293, 302, 330, 338, 349, 364, 389, 429, 514, 536, 552, 593, 607, 630, 705, 746, 777, 805, 866, 907, 1091, 1157, 1166, 1195, 1202, 1218, 1263, 1270, 1290, 1297, 1315, 1354, 1366, 1388, 1450, 1472, 1499, 3128, 3230, 3789
TS2	730i, 15, 23, 42, 60, 66, 111, 136, 167, 210, 220, 244, 249, 292, 328, 333, 338, 364, 378, 389, 429, 514, 535, 549, 561, 593, 606, 632, 704, 751, 799, 902, 934, 976, 1122, 1180, 1200, 1207, 1225, 1232, 1265, 1276, 1290, 1293, 1315, 1365, 1379, 1447, 1483, 3146, 3277
PC1	12, 34, 39, 68, 78, 90, 117, 135, 169, 201, 214, 221, 241, 247, 249, 269, 293, 328, 334, 340, 355, 364, 391, 427, 513, 536, 551, 593, 608, 631, 703, 709, 752, 800, 906, 1118, 1175, 1195, 1206, 1212, 1262, 1271, 1294, 1297, 1316, 1365, 1383, 1448, 1488, 1621, 3205, 3356, 3857, 3983
PC2	22, 23, 43, 53, 65, 69, 110, 138, 164, 210, 223, 238, 245, 250, 292, 312, 327, 337, 342, 364, 378, 391, 427, 514, 536, 552, 595, 606, 631, 704, 742, 754, 801, 905, 1122, 1178, 1198, 1212, 1220, 1265, 1273, 1291, 1294, 1315, 1367, 1383, 1448, 1486, 2835, 3196, 3347
H ₂ O	1596, 3887, 4012
HCl	3031
n-C ₄ F ₉ OC•H ₂	43, 53, 66, 89, 111, 166, 204, 218, 222, 243, 247, 293, 330, 336, 345, 363, 388, 425, 512, 536, 551, 589, 605, 609, 631, 704, 752, 799, 906, 1118, 1175, 1194, 1206, 1208, 1262, 1275, 1292, 1301, 1315, 1366, 1385, 1448, 1482, 3200, 3355
C ₄ F ₉ OCH ₂ O•	37, 46, 56, 66, 105, 115, 165, 204, 215, 240, 249, 285, 293, 330, 336, 362, 386, 414, 483, 535, 547, 564, 604, 622, 645, 703, 748, 779, 849, 897, 1021, 1139, 1154, 1188, 1201, 1211, 1258, 1269, 1283, 1287, 1311, 1359, 1367,

	1376, 1429, 1445, 3017, 3077
TS3	647i, 36, 42, 66, 91, 102, 135, 160, 192, 210, 233, 246, 262, 289, 302, 331, 347, 366, 387, 425, 499, 514, 544, 584, 597, 630, 691, 724, 749, 783, 924, 1134, 1164, 1198, 1209, 1230, 1250, 1262, 1281, 1288, 1313, 1351, 1367, 1433, 1471, 1610, 3058, 3155
TS4	1018i, 39, 45, 60, 92, 129, 157, 190, 214, 241, 243, 290, 294, 329, 334, 363, 386, 422, 475, 505, 539, 556, 585, 595, 607, 621, 648, 718, 751, 826, 942, 1028, 1084, 1158, 1202, 1216, 1259, 1266, 1285, 1292, 1316, 1366, 1375, 1392, 1445, 1787, 3097
TS5	1673i, 21, 33, 48, 55, 62, 83, 107, 138, 160, 165, 191, 216, 242, 245, 287, 293, 330, 338, 364, 386, 425, 455, 479, 514, 539, 576, 585, 596, 614, 639, 714, 750, 820, 925, 988, 1056, 1148, 1180, 1188, 1202, 1255, 1263, 1285, 1291, 1298, 1315, 1360, 1368, 1392, 1444, 1626, 1695, 3034,
C ₄ F ₉ O•	53, 72, 73, 126, 174, 209, 232, 240, 291, 299, 328, 330, 359, 383, 407, 496, 527, 551, 576, 596, 627, 695, 702, 776, 919, 1086, 1176, 1202, 1233, 1267, 1270, 1297, 1302, 1318, 1360, 1421
CH ₂ O•	1212, 1275, 1547, 1881, 2976, 3049
C ₄ F ₉ OC(O)H	38, 45, 61, 92, 98, 139, 154, 188, 214, 241, 289, 292, 329, 335, 363, 386, 425, 488, 512, 539, 589, 596, 619, 648, 720, 751, 829, 949, 1033, 1057, 1163, 1203, 1226, 1259, 1267, 1286, 1294, 1317, 1367, 1374, 1433, 1448, 1949, 3143
HO• ₂	1266, 1459, 3710
TS6	1221i, 29, 44, 58, 61, 81, 99, 119, 161, 196, 213, 221, 242, 245, 269, 290, 293, 330, 336, 364, 387, 427, 448, 512, 537, 580, 592, 615, 637, 704, 739, 753, 775, 834, 950, 1024, 1049, 1160, 1204, 1225, 1264, 1270, 1288, 1300, 1318, 1367, 1374, 1414, 1447, 1986, 3780
TS7	1093i, 30, 40, 50, 56, 70, 91, 100, 158, 190, 212, 242, 243, 270, 290, 297, 311, 332, 338, 365, 386, 426, 509, 518, 539, 589, 600, 622, 654, 724, 751, 830, 918, 942, 1089, 1097, 1168, 1198, 1236, 1265, 1272, 1295, 1299, 1320, 1363, 1373, 1446, 2007
C ₄ F ₉ OC(O)	38, 42, 60, 89, 94, 153, 186, 195, 213, 240, 242, 285, 291, 329, 336, 363, 386, 425, 482, 511, 539, 587, 593, 618, 643, 718, 751, 827, 935, 1033, 1153, 1201, 1244, 1255, 1268, 1289, 1295, 1318, 1363, 1370, 1443, 2007

Table S2 Relative energies ΔE (in kJ mol^{-1}) with zero-point energy correction for the reactants, reaction complexes, transition states, product complexes and products at M06-2X/6-31+G(d,p) level of theory.

Species	M06-2X/6-311++G(d,p)	M06-2X/6-31+G(d,p)	Species	M06-2X/6-311++G(d,p)	M06-2X/6-31+G(d,p)
n-C ₄ F ₉ OCH ₃ + OH	0.00	0.00	TS3	144.92	148.01
RC1	-13.41	-12.58	TS4	105.16	92.71
TS1	10.66	9.32	TS5	76.50	39.17
PC1	-72.31	-69.97	C ₄ F ₉ O• + CH ₂ O•	108.38	112.10
n-C ₄ F ₉ OC•H ₂ + H ₂ O	-66.33	-64.70	C ₄ F ₉ OC(O)H + H	55.42	59.90
n-C ₄ F ₉ OCH ₃ + Cl	0.00	0.00	C ₄ F ₉ OC(O)H + HO• ₂	-137.85	-137.27
RC2	-14.88	-12.83	C ₄ F ₉ OC(O)H + OH/Cl	0.00	0.00
TS2	4.38	5.18	TS6	8.07	6.60
PC2	-8.61	-4.01	TS7	5.73	7.19
n-C ₄ F ₉ OC•H ₂ + HCl	-2.00	2.92	C ₄ F ₉ OC(O) + H ₂ O	-81.00	-79.04
n-C ₄ F ₉ OCH ₂ O• + O ₂	0.00	0.00	C ₄ F ₉ OC(O) + HCl	-16.72	-11.37

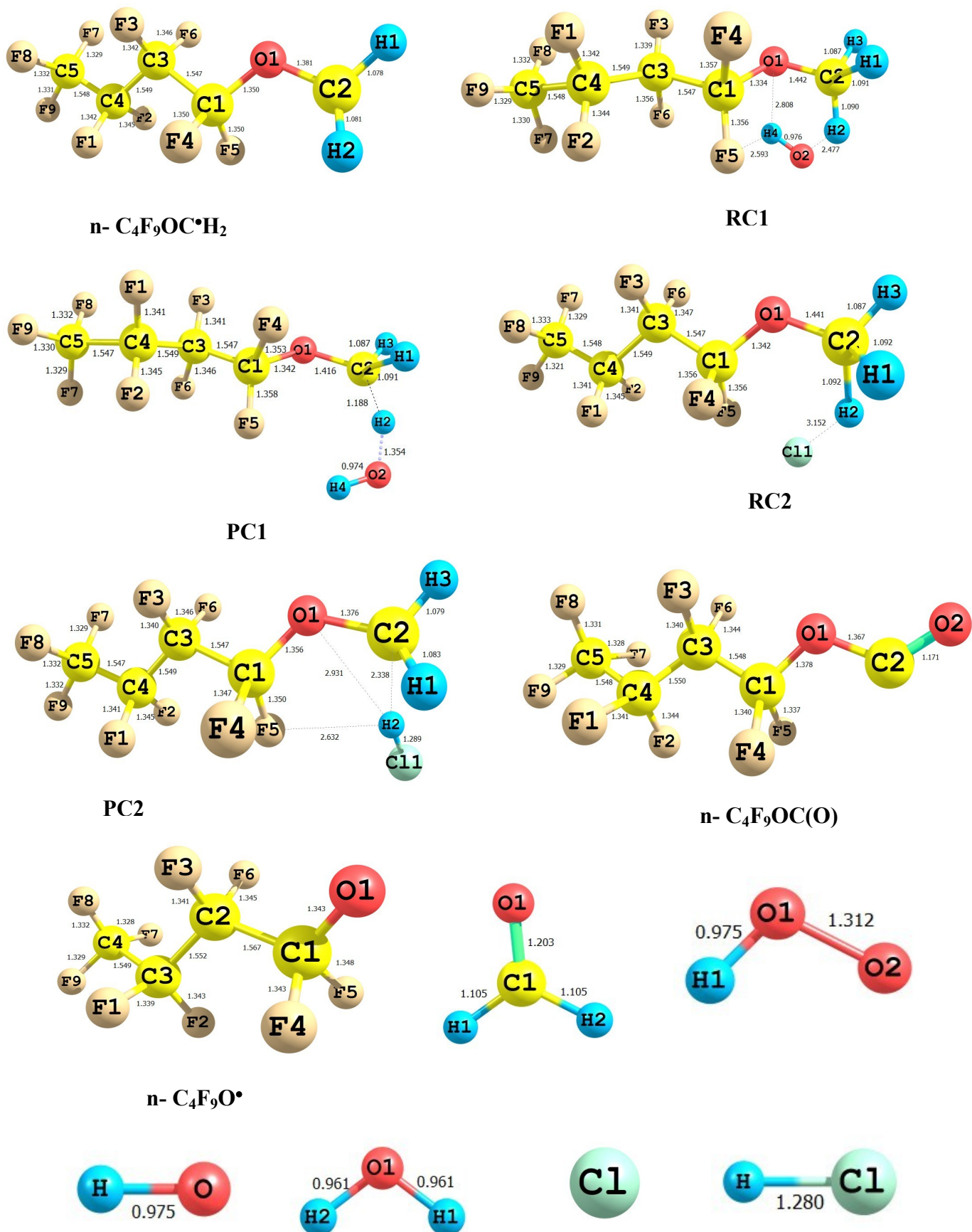


Fig. S1. Optimized geometries of reactant complexes, product complexes and products at M06-2X/6-31+G(d,p) level of theory. Bond lengths are in Angstroms.