

Supplementary Material

Atmospheric fate of methyl pivalate: OH/Cl-initiated degradation and the roles of water and formic acid

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Table S1. Frequencies (Experimental values are in parentheses) (in cm^{-1}) of the reactants, products, transition states, and complexes for the reactions of methyl pivalate with hydroxyl radical and chlorine atom calculated at the B3LYP/6-311G(d,p) level.

Species	Frequencies
R1	35, 108, 131, 199, 207, 253, 260, 287, 320, 340, 363, 381, 494, 587, 778, 795, 870, 940, 946, 970, 1000, 1050, 1055, 1172, 1176, 1208, 1227, 1250, 1301, 1397, 1404, 1432, 1470, 1479, 1481, 1488, 1493, 1499, 1501, 1505, 1524, 1796, 3026, 3028, 3038, 3047, 3086, 3088, 3104, 3111, 3113, 3115, 3117, 3153
P1a	44, 125, 141, 204, 209, 246, 262, 277, 312, 326, 343, 377, 381, 495, 587, 758, 775, 853, 939, 947, 970, 1035, 1047, 1094, 1172, 1212, 1225, 1251, 1292, 1397, 1403, 1430, 1439, 1479, 1489, 1493, 1501, 1504, 1524, 1806, 3027, 3029, 3039, 3089, 3091, 3105, 3112, 3114, 3116, 3179, 3338
P1b	18, 111, 128, 146, 204, 225, 262, 278, 318, 346, 353, 372, 499, 513, 580, 773, 797, 865, 941, 947, 998, 1025, 1038, 1113, 1173, 1177, 1210, 1234, 1307, 1389, 1407, 1441, 1471, 1481, 1484, 1489, 1499, 1502, 1512, 1799, 3029, 3032, 3048, 3097, 3100, 3109, 3113, 3119, 3149, 3154, 3270
P1c	26, 84, 108, 131, 191, 230, 263, 280, 309, 326, 356, 387, 491, 548, 621, 771, 805, 878, 916, 963, 987, 1000, 1043, 1150, 1171, 1206, 1214, 1233, 1275, 1394, 1413, 1460, 1470, 1481, 1487, 1492, 1499, 1504, 1514, 1790, 3029, 3032, 3047, 3093, 3095, 3115, 3119, 3119, 3137, 3154, 3243
P1d	43, 114, 132, 151, 200, 228, 250, 275, 319, 335, 363, 383, 482, 534, 608, 772, 809, 871, 923, 963, 978, 1006, 1047, 1163, 1172, 1209, 1213, 1229, 1268, 1399, 1416, 1456, 1470, 1482, 1486, 1490, 1499, 1502, 1511, 1792, 3031, 3040, 3047, 3094, 3107, 3117, 3118, 3123, 3136, 3154, 3246
OH	3704 (3775)
H ₂ O	1637 (1595), 3812 (3657), 3909 (3756)
HCl	2929 (2991)
TS1a	900 <i>i</i> , 26, 52, 121, 164, 193, 205, 253, 263, 289, 317, 341, 361, 375, 379, 408, 496, 588, 751, 777, 819, 878, 916, 940, 948, 971, 1029, 1048, 1071, 1111, 1176, 1226, 1229, 1250, 1298, 1341, 1398, 1406, 1434, 1463, 1479, 1488, 1492, 1493, 1501, 1505, 1524, 1784, 3029, 3031, 3039, 3078, 3091, 3094, 3105, 3112, 3115, 3118, 3176, 3715
TS1b	1018 <i>i</i> , 37, 105, 123, 141, 144, 200, 231, 273, 276, 315, 328, 348, 368, 420, 467, 504, 579, 752, 780, 801, 874, 936, 945, 958, 976, 999, 1048, 1074, 1173, 1186, 1194, 1216, 1244, 1275, 1311, 1397, 1417, 1449, 1457, 1473, 1484, 1490, 1493, 1499, 1506, 1518, 1772, 3031, 3034, 3052, 3066, 3094, 3102, 3119, 3121, 3125, 3141, 3160, 3701
TS1c	610 <i>i</i> , 37, 57, 98, 123, 138, 162, 191, 239, 272, 279, 292, 323, 359, 371, 407, 491, 599, 775, 793, 811, 863, 924, 944, 978, 987, 1012, 1051, 1123, 1173, 1174, 1209, 1233, 1254, 1276, 1310, 1388, 1398, 1418, 1464, 1471, 1483, 1492, 1495, 1500, 1511, 1519, 1784, 3030, 3034, 3049, 3075, 3097, 3100, 3120, 3121, 3125, 3143, 3156, 3748
TS1d	917 <i>i</i> , 25, 106, 114, 125, 153, 199, 218, 249, 272, 311, 326, 354, 365, 374, 440, 493, 586, 747, 780, 797, 864, 916, 940, 955, 981, 1006, 1051, 1081, 1161, 1173, 1202,

- 1213, 1232, 1261, 1300, 1403, 1418, 1441, 1461, 1474, 1481, 1486, 1487, 1500, 1503, 1512, 1804, 3033, 3040, 3054, 3058, 3093, 3109, 3114, 3129, 3129, 3136, 3157, 3728
- TS1e 530i, 28, 42, 106, 123, 144, 159, 205, 234, 257, 277, 305, 341, 355, 386, 395, 491, 585, 773, 792, 825, 878, 921, 946, 954, 1000, 1037, 1047, 1129, 1174, 1184, 1211, 1225, 1254, 1303, 1321, 1392, 1411, 1417, 1454, 1472, 1483, 1485, 1493, 1499, 1500, 1517, 1801, 3027, 3036, 3050, 3065, 3095, 3105, 3108, 3123, 3127, 3143, 3156, 3747
- TS1f 501i, 38, 64, 94, 127, 141, 167, 193, 256, 258, 286, 315, 335, 361, 383, 401, 487, 601, 772, 795, 811, 869, 936, 947, 979, 991, 1020, 1058, 1163, 1172, 1178, 1210, 1231, 1252, 1281, 1327, 1396, 1406, 1421, 1467, 1472, 1483, 1490, 1496, 1499, 1510, 1517, 1797, 3035, 3042, 3049, 3063, 3104, 3110, 3118, 3120, 3121, 3136, 3156, 3746
- TS2a 589i, 27, 35, 60, 152, 205, 209, 253, 268, 288, 325, 341, 374, 375, 421, 487, 571, 592, 757, 763, 842, 919, 940, 948, 956, 972, 1024, 1048, 1075, 1176, 1190, 1224, 1230, 1249, 1288, 1399, 1407, 1435, 1447, 1480, 1489, 1494, 1503, 1506, 1525, 1837, 3032, 3034, 3042, 3095, 3099, 3100, 3108, 3114, 3117, 3121, 3229
- TS2b 292i, 18, 42, 81, 120, 141, 199, 231, 258, 269, 316, 338, 362, 392, 422, 492, 582, 709, 771, 800, 805, 838, 877, 933, 950, 993, 1009, 1038, 1137, 1173, 1186, 1215, 1248, 1305, 1331, 1390, 1416, 1442, 1471, 1483, 1484, 1490, 1498, 1502, 1515, 1797, 3030, 3041, 3053, 3103, 3108, 3110, 3113, 3128, 3131, 3161, 3214
- TS2c 192i, 37, 46, 66, 120, 134, 196, 230, 266, 281, 316, 339, 354, 365, 399, 493, 588, 728, 771, 777, 798, 834, 875, 922, 967, 985, 1002, 1052, 1160, 1172, 1208, 1224, 1242, 1267, 1403, 1416, 1441, 1461, 1472, 1483, 1490, 1496, 1499, 1511, 1516, 1779, 3036, 3039, 3052, 3102, 3104, 3110, 3125, 3126, 3129, 3160, 3208
- TS2d 263i, 29, 36, 70, 116, 141, 199, 226, 259, 276, 316, 342, 357, 377, 413, 491, 584, 714, 771, 803, 812, 828, 873, 933, 952, 979, 1012, 1038, 1146, 1173, 1181, 1213, 1249, 1295, 1353, 1389, 1417, 1450, 1473, 1483, 1484, 1491, 1498, 1499, 1515, 1806, 3031, 3042, 3054, 3103, 3107, 3110, 3116, 3129, 3132, 3162, 3213
- TS2e 246i, 34, 45, 66, 112, 134, 192, 225, 252, 274, 314, 332, 359, 378, 414, 484, 588, 720, 773, 799, 807, 827, 865, 926, 966, 974, 1003, 1051, 1166, 1171, 1203, 1211, 1230, 1268, 1363, 1403, 1425, 1459, 1471, 1482, 1488, 1490, 1498, 1507, 1512, 1803, 3039, 3046, 3052, 3101, 3107, 3114, 3123, 3123, 3125, 3161, 3202
- ER1a 24, 44, 90, 131, 153, 163, 214, 221, 255, 276, 292, 324, 343, 371, 382, 444, 498, 586, 606, 781, 798, 877, 941, 947, 970, 989, 1049, 1055, 1169, 1192, 1227, 1227, 1250, 1310, 1397, 1404, 1432, 1479, 1480, 1488, 1494, 1495, 1502, 1502, 1506, 1526, 1762, 3028, 3031, 3039, 3051, 3090, 3092, 3105, 3112, 3115, 3119, 3131, 3166, 3563
- ER1b 27, 72, 76, 125, 156, 161, 216, 222, 269, 283, 301, 321, 350, 381, 381, 480, 518, 565, 590, 781, 802, 877, 939, 952, 971, 994, 1053, 1055, 1172, 1192, 1218, 1222, 1251, 1307, 1350, 1407, 1439, 1466, 1471, 1482, 1487, 1490, 1497, 1504, 1508, 1526, 1751, 3025, 3028, 3037, 3055, 3092, 3093, 3096, 3101, 3111, 3111, 3130, 3163, 3531
- ER1c 26, 35, 52, 89, 119, 135, 149, 203, 224, 250, 279, 290, 320, 327, 345, 364, 387, 494, 590, 778, 795, 870, 942, 947, 970, 1001, 1050, 1052, 1173, 1176, 1209, 1227, 1249, 1296, 1395, 1398, 1428, 1471, 1472, 1482, 1482, 1493, 1499, 1500, 1512, 1523,

1792, 2955, 3024, 3030, 3047, 3073, 3087, 3093, 3109, 3113, 3117, 3118, 3153, 3709

ER1d 16, 43, 69, 122, 135, 150, 205, 217, 249, 282, 290, 326, 344, 368, 370, 392, 488, 589, 630, 773, 794, 865, 940, 949, 972, 987, 1048, 1055, 1149, 1172, 1209, 1226, 1250, 1293, 1398, 1407, 1436, 1471, 1481, 1482, 1488, 1488, 1500, 1504, 1511, 1523, 1809, 3030, 3031, 3040, 3056, 3091, 3093, 3107, 3113, 3116, 3120, 3134, 3159, 3588

ER2b 22, 37, 59, 120, 131, 139, 200, 217, 260, 273, 293, 321, 342, 364, 396, 496, 585, 775, 798, 872, 912, 943, 961, 996, 1037, 1042, 1168, 1173, 1186, 1211, 1236, 1283, 1291, 1327, 1392, 1418, 1450, 1472, 1483, 1486, 1491, 1499, 1503, 1515, 1797, 2364, 3030, 3036, 3051, 3076, 3097, 3102, 3110, 3124, 3127, 3145, 3158

ER2c 33, 39, 45, 103, 109, 132, 210, 223, 263, 268, 302, 319, 349, 361, 380, 493, 588, 775, 794, 858, 931, 936, 966, 991, 1017, 1048, 1171, 1172, 1207, 1211, 1241, 1262, 1280, 1300, 1399, 1421, 1459, 1470, 1482, 1488, 1495, 1498, 1506, 1518, 1779, 2371, 3031, 3034, 3051, 3081, 3094, 3097, 3119, 3123, 3123, 3143, 3158

ER2d 21, 30, 44, 116, 133, 142, 199, 224, 258, 279, 293, 326, 341, 365, 387, 493, 584, 774, 799, 868, 908, 945, 960, 992, 1034, 1039, 1172, 1174, 1185, 1211, 1238, 1257, 1280, 1329, 1393, 1420, 1451, 1471, 1482, 1485, 1490, 1499, 1500, 1513, 1801, 2314, 3030, 3040, 3052, 3071, 3099, 3105, 3115, 3125, 3126, 3146, 3159

ER2e 34, 37, 45, 97, 124, 145, 206, 225, 256, 284, 313, 327, 350, 364, 384, 487, 590, 771, 793, 859, 937, 944, 967, 981, 1017, 1052, 1172, 1174, 1211, 1218, 1230, 1258, 1282, 1323, 1402, 1427, 1465, 1471, 1483, 1487, 1491, 1498, 1504, 1515, 1793, 2377, 3033, 3043, 3052, 3070, 3099, 3109, 3114, 3121, 3126, 3143, 3161

EP1a 23, 53, 96, 139, 142, 196, 210, 223, 248, 259, 272, 274, 300, 328, 350, 379, 382, 465, 498, 572, 597, 759, 784, 861, 939, 947, 970, 1036, 1047, 1097, 1170, 1225, 1228, 1249, 1295, 1397, 1405, 1433, 1469, 1479, 1488, 1494, 1502, 1506, 1524, 1664, 1776, 3029, 3031, 3040, 3091, 3093, 3106, 3113, 3115, 3119, 3158, 3327, 3748, 3871

EP1b 29, 53, 103, 122, 131, 148, 156, 208, 232, 255, 274, 284, 319, 329, 346, 356, 373, 493, 524, 575, 588, 779, 804, 872, 946, 952, 996, 1025, 1043, 1121, 1173, 1189, 1221, 1233, 1317, 1394, 1413, 1450, 1473, 1483, 1486, 1494, 1498, 1505, 1525, 1663, 1765, 3027, 3036, 3054, 3097, 3102, 3116, 3119, 3128, 3144, 3161, 3259, 3739, 3869

EP1c 30, 47, 70, 102, 117, 132, 140, 184, 203, 245, 253, 286, 292, 316, 336, 357, 384, 412, 495, 583, 680, 772, 806, 882, 915, 967, 987, 1004, 1053, 1159, 1172, 1208, 1215, 1239, 1273, 1396, 1418, 1457, 1471, 1482, 1491, 1498, 1499, 1515, 1517, 1634, 1785, 3032, 3034, 3049, 3100, 3103, 3120, 3122, 3125, 3127, 3155, 3229, 3723, 3873

EP1d 30, 58, 90, 114, 123, 131, 142, 193, 220, 231, 258, 277, 306, 329, 332, 362, 367, 479, 556, 573, 602, 772, 804, 864, 941, 958, 980, 1014, 1044, 1143, 1173, 1177, 1211, 1238, 1280, 1398, 1416, 1459, 1472, 1482, 1482, 1489, 1500, 1505, 1521, 1656, 1806, 3030, 3038, 3055, 3094, 3111, 3113, 3123, 3130, 3131, 3161, 3236, 3757, 3878

EP1e 19, 31, 85, 115, 131, 159, 159, 216, 260, 280, 303, 313, 346, 356, 377, 490, 515, 556, 575, 606, 627, 774, 803, 861, 935, 958, 973, 1011, 1040, 1148, 1168, 1174, 1208, 1256, 1283, 1391, 1412, 1449, 1468, 1481, 1487, 1493, 1499, 1504, 1523, 1680, 1800, 3016, 3021, 3050, 3085, 3092, 3116, 3121, 3125, 3149, 3161, 3260, 3552,

3638

- EP1f 38, 49, 63, 101, 124, 136, 150, 195, 204, 253, 262, 267, 300, 321, 341, 363, 384, 396, 484, 584, 652, 774, 811, 873, 922, 966, 979, 1007, 1054, 1168, 1172, 1210, 1213, 1229, 1269, 1401, 1418, 1455, 1471, 1483, 1488, 1495, 1500, 1512, 1515, 1633, 1795, 3035, 3044, 3048, 3104, 3115, 3120, 3120, 3123, 3125, 3156, 3231, 3735, 3875
- EP2a 19, 21, 48, 83, 156, 203, 208, 245, 270, 283, 323, 326, 343, 375, 379, 479, 495, 521, 589, 732, 759, 767, 845, 939, 948, 970, 1029, 1047, 1081, 1186, 1216, 1224, 1249, 1289, 1399, 1405, 1433, 1443, 1479, 1489, 1493, 1502, 1505, 1525, 1826, 2463, 3031, 3033, 3040, 3093, 3096, 3107, 3113, 3115, 3119, 3138, 3285
- EP2b 20, 26, 46, 81, 112, 133, 203, 231, 268, 273, 276, 319, 341, 367, 376, 443, 466, 500, 580, 711, 772, 801, 871, 942, 948, 994, 1014, 1038, 1128, 1173, 1184, 1213, 1244, 1307, 1389, 1413, 1447, 1471, 1482, 1485, 1491, 1498, 1503, 1515, 1797, 2537, 3031, 3037, 3051, 3101, 3106, 3109, 3125, 3125, 3131, 3159, 3244
- EP2c 26, 34, 38, 66, 106, 131, 201, 230, 253, 265, 287, 314, 340, 354, 383, 492, 496, 499, 592, 758, 771, 811, 881, 918, 964, 984, 999, 1046, 1157, 1171, 1207, 1219, 1239, 1272, 1398, 1417, 1461, 1471, 1482, 1489, 1495, 1498, 1507, 1515, 1784, 2424, 3033, 3036, 3051, 3098, 3100, 3121, 3121, 3124, 3124, 3159, 3224
- EP2d 12, 22, 30, 84, 115, 138, 202, 225, 255, 266, 278, 317, 342, 358, 379, 470, 477, 497, 583, 732, 773, 807, 869, 935, 954, 979, 1011, 1036, 1146, 1173, 1180, 1213, 1255, 1289, 1389, 1415, 1451, 1473, 1483, 1484, 1490, 1499, 1500, 1512, 1804, 2470, 3029, 3040, 3053, 3100, 3105, 3118, 3125, 3127, 3128, 3160, 3236
- EP2e 28, 37, 43, 64, 123, 140, 202, 222, 251, 275, 292, 320, 338, 361, 382, 472, 482, 492, 594, 725, 777, 816, 871, 921, 964, 976, 1003, 1049, 1165, 1172, 1206, 1211, 1229, 1270, 1402, 1421, 1458, 1471, 1483, 1487, 1490, 1499, 1504, 1511, 1799, 2471, 3036, 3044, 3050, 3101, 3113, 3118, 3119, 3123, 3123, 3159, 3225
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Table S2. Relative energies (Er) of main species for reactions R1 and R2 at the B3LYP/6-311G(d,p), CCSD(T) and QCISD(T)/6-311++G(d,p)//B3LYP/6-311G(d,p) levels (in kcal/mol) with the ZPE corrections (in Hartree).

	Species	ZPE	B3LYP	CCSD(T)//B3LYP	QCISD(T)//B3LYP
Er (R1)	R1+OH	0.182093	0.00	0.00	0.00
	ER1a	0.185313	-6.55	-3.93	-3.97
	TS1a	0.180679	-4.34	2.07	1.81
	EP1a	0.183669	-22.79	-19.30	-19.70
	P1a+H ₂ O	0.179950	-16.97	-16.42	-16.53
	ER1b	0.185122	-6.46	-4.03	-4.06
	TS1b	0.180736	-4.70	1.74	1.52
	EP1b	0.183621	-18.68	-17.11	-17.21
	P1b+H ₂ O	0.180040	-13.01	-13.39	-13.45
	ER1c	0.183435	-1.89	-0.003	-0.02
	TS1c	0.180149	-2.32	3.97	3.75
	EP1c	0.182942	-15.28	-13.99	-14.08
	P1c+H ₂ O	0.180061	-11.97	-12.77	-12.83
	ER1d	0.184929	-4.68	-3.35	-3.37
	TS1d	0.180318	-3.29	2.82	2.58
	EP1d	0.183269	-17.62	-16.84	-16.94
	TS1e	0.180296	-1.88	4.01	3.78
	EP1e	0.183882	-15.16	-14.45	-14.58
TS1f	0.180631	-2.44	4.10	3.86	
EP1f	0.183026	-16.62	-15.13	-15.27	
P1d+H ₂ O	0.180290	-13.54	-14.02	-14.12	
Er (R2)	R1+Cl	0.173653	0.00	0.00	0.00
	TS2a	0.166818	-5.88	0.43	0.27
	EP2a	0.168149	-6.22	-2.92	-3.02
	P1a+HCl	0.165298	-4.80	-1.36	-1.42
	ER2b	0.171826	-3.28	-0.25	-0.32
	TS2b	0.166960	-2.32	0.92	0.82
	EP2b	0.167844	-2.51	-1.08	-1.12
	P1b+HCl	0.165388	-0.84	1.68	1.66
	ER2c	0.171646	-3.37	-0.50	-0.56
	TS2c	0.167219	-1.61	1.63	1.55
	EP2c	0.16782	-1.59	-0.03	-0.07
	P1c+HCl	0.165409	0.20	2.29	2.27
	ER2d	0.171581	-3.48	-0.55	-0.62
	TS2d	0.166964	-2.49	0.31	0.20
	EP2d	0.167727	-2.54	-1.52	-1.58
	ER2e	0.171937	-4.28	-0.30	-0.40
	TS2e	0.166953	-2.96	0.82	0.67
	EP2e	0.167921	-2.88	-1.15	-1.23
P1d+HCl	0.165638	-1.36	1.03	1.00	

Table S3a. Relative energies (Er) of main species for reactions R1 and R2 at the CCSD(T) and QCISD(T)/6-311++G(d,p)//B3LYP/6-311G(d,p), and CCSD(T)/6-311++G(d,p)//MP2/6-311G(d,p) and) levels (kcal/mol) with the ZPE corrections.

	Species	CCSD(T)//B3LYP	QCISD(T)//B3LYP	CCSD(T)//MP2
Er (R1)	R1+OH	0.00	0.00	0.00
	TS1a	2.07	1.81	2.03
	P1a+H ₂ O	-16.42	-16.53	-16.25
	TS1b	1.74	1.52	1.77
	P1b+H ₂ O	-13.39	-13.45	-13.35
	TS1c	3.97	3.75	3.89
	P1c+H ₂ O	-12.77	-12.83	-12.58
	TS1d	2.82	2.58	2.86
	TS1e	4.01	3.78	3.60
	TS1f	4.10	3.86	3.77
	P1d+H ₂ O	-14.02	-14.12	-13.99
Er (R2)	R1+Cl	0.00	0.00	0.00
	TS2a	0.43	0.27	0.29
	P1a+HCl	-1.36	-1.42	-1.09
	TS2b	0.92	0.82	0.43
	P1b+HCl	1.68	1.66	1.81
	TS2c	1.63	1.55	1.33
	P1c+HCl	2.29	2.27	2.58
	TS2d	0.31	0.20	0.34
	TS2e	0.82	0.67	0.77
	P1d+HCl	1.03	1.00	1.16

Table S3b. The activation energy (ΔE) and free energy barrier (ΔG) (kcal/mol) for the reaction pathways R1a-R1f and R2a-R2e at 298 K obtained at the CCSD(T)/6-311++G(d,p)//B3LYP/6-311G(d,p) level.

Species	ΔE	ΔG
R1+OH	0.00	0.00
TS1a	2.07	10.71
TS1b	1.74	10.73
TS1c	3.97	12.16
TS1d	2.82	11.45
TS1e	4.01	11.97
TS1f	4.10	12.40
R1+Cl	0.00	0.00
TS2a	0.43	7.43
TS2b	0.92	7.67
TS2c	1.63	8.70
TS2d	0.31	7.16
TS2e	0.82	7.73

Table S4. $\Delta H_{f,298}^{\theta}$ (in kcal/mol) for the reactant (R1) and products (P1, P2, P3, and P4) at various levels.

Species	B3LYP/6-311G(d,p)		CCSD(T)/6-311++G(d,p) //B3LYP/6-311G(d,p)		QCISD(T)/6-311++G(d,p) //B3LYP/6-311G(d,p)	
	$\Delta H_{f,298}^{\theta}$	average	$\Delta H_{f,298}^{\theta}$	average	$\Delta H_{f,298}^{\theta}$	average
R1	-111.48		-117.39		-117.44	
	-110.99	-110.99	-118.73	-118.73	-118.76	-118.76
	-110.51		-120.08		-120.09	
P1a	-65.82		-70.11		-70.22	
	-65.34	-65.29	-71.46	-70.27	-71.54	-70.36
	-64.72		-69.24		-69.32	
P1b	-61.82		-67.04		-67.09	
	-61.33	-61.29	-68.38	-67.19	-68.42	-67.24
	-60.71		-66.16		-66.20	
P1c	-60.73		-66.38		-66.43	
	-60.24	-60.20	-67.72	-66.40	-67.75	-66.57
	-59.62		-65.50		-65.54	
P1d	-62.39		-67.72		-67.81	
	-61.91	-61.86	-69.07	-67.88	-69.13	-67.95
	-61.29		-66.85		-66.92	

Table S5. Reaction enthalpies ($\Delta H_{r,298}^\theta$) and Gibbs free energies ($\Delta G_{r,298}^\theta$)(in kcal/mol)for R1 and R2 at different levels.

		CCSD(T)/6-311G++(d,p)		QCISD(T)/6-311G++(d,p)
Reactions		B3LYP/6-311G(d,p)	//B3LYP/6-311G(d,p)	//B3LYP/6-311G(d,p)
$\Delta H_{r,298}^\theta$	R1a	-16.97	-15.93	-16.04
	R1b	-13.01	-12.85	-12.91
	R1c	-11.97	-12.19	-12.25
	R1d,e,f	-13.06	-13.54	-13.63
	R2a	-4.02	-0.57	-0.64
	R2b	-0.01	2.50	2.49
	R2c	1.08	3.16	3.15
	R2d,e,f	-0.03	1.82	1.77
$\Delta G_{r,298}^\theta$	R1a	-17.73	-17.17	-17.28
	R1b	-14.44	-14.81	-14.88
	R1c	-13.44	-14.24	-14.30
	R1d,e,f	-14.46	-14.94	-15.03
	R2a	-6.49	-3.05	-3.10
	R2b	-3.20	-0.69	-0.70
	R2c	-2.20	-0.12	-0.13
	R2d,e,f	-0.003	-0.81	-0.86

Table S6. The rate constants for the decomposition reaction (k_{dec}) of $(\text{CH}_3)_3\text{CCOOCH}_3 \rightarrow (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{HCOOCH}_3$ and reactions of OH/Cl radical-attack on $(\text{CH}_3)_3\text{CCOOCH}_3$ between 200 and 2000 K. ($[\text{OH}]=1 \times 10^6 \text{ molecule cm}^{-3}$, $[\text{Cl}]=1.3 \times 10^5 \text{ molecule cm}^{-3}$)

T (K)	$k_{\text{dec}} (\text{s}^{-1})$	$k_{\text{OH}} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$k_{\text{OH}}[\text{OH}] (\text{s}^{-1})$	$k_{\text{Cl}} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$k_{\text{Cl}}[\text{Cl}] (\text{s}^{-1})$
200	4.59×10^{-94}	6.89×10^{-13}	6.89×10^{-7}	3.07×10^{-11}	3.99×10^{-6}
220	2.96×10^{-84}	7.03×10^{-13}	7.03×10^{-7}	3.17×10^{-11}	4.12×10^{-6}
230	5.47×10^{-80}	7.14×10^{-13}	7.14×10^{-7}	3.25×10^{-11}	4.23×10^{-6}
250	1.78×10^{-72}	7.45×10^{-13}	7.45×10^{-7}	3.44×10^{-11}	4.47×10^{-6}
272	1.73×10^{-65}	7.89×10^{-13}	7.89×10^{-7}	3.71×10^{-11}	4.82×10^{-6}
298	1.49×10^{-58}	8.55×10^{-13}	8.55×10^{-7}	4.08×10^{-11}	5.30×10^{-6}
330	1.63×10^{-51}	9.55×10^{-13}	9.55×10^{-7}	4.12×10^{-11}	5.36×10^{-6}
370	2.03×10^{-44}	1.11×10^{-12}	1.11×10^{-6}	4.71×10^{-11}	6.12×10^{-6}
400	5.02×10^{-40}	1.26×10^{-12}	1.26×10^{-6}	5.12×10^{-11}	6.66×10^{-6}
500	3.64×10^{-29}	1.93×10^{-12}	1.93×10^{-6}	5.57×10^{-11}	7.24×10^{-6}
600	6.68×10^{-22}	2.98×10^{-12}	2.98×10^{-6}	6.33×10^{-11}	8.23×10^{-6}
800	8.85×10^{-13}	6.78×10^{-12}	6.78×10^{-6}	9.45×10^{-11}	1.23×10^{-5}
1000	2.83×10^{-07}	1.41×10^{-11}	1.41×10^{-5}	1.35×10^{-10}	1.76×10^{-5}
1200	1.37×10^{-03}	2.66×10^{-11}	2.66×10^{-5}	2.41×10^{-10}	3.13×10^{-5}
1500	$6.95 \times 10^{+00}$	5.86×10^{-11}	5.86×10^{-5}	3.77×10^{-10}	4.90×10^{-5}
1800	$2.10 \times 10^{+03}$	1.10×10^{-10}	1.10×10^{-4}	5.39×10^{-10}	7.01×10^{-5}
2000	$3.67 \times 10^{+04}$	1.58×10^{-10}	1.58×10^{-4}	8.16×10^{-10}	1.06×10^{-4}

Table S7. Computed activation energy barrier ($\Delta E_{r,298}^\theta$), reaction enthalpies ($\Delta H_{r,298}^\theta$), and reaction Gibbs free energies ($\Delta G_{r,298}^\theta$) with the ZPE or thermal corrections to enthalpies or Gibbs free energies for thermal decomposition of the alkoxy radicals at B3LYP/6-311G(d,p) and CCSD(T)/6-311++G(d,p)//B3LYP/6-311G(d,p) levels of theory

Reactions	B3LYP/6-311G(d,p)			CCSD(T)//B3LYP		
	$\Delta E_{r,298}^\theta$	$\Delta H_{r,298}^\theta$	$\Delta G_{r,298}^\theta$	$\Delta E_{r,298}^\theta$	$\Delta H_{r,298}^\theta$	$\Delta G_{r,298}^\theta$
R3a	14.46	-28.84	-29.75	11.26	-31.60	-32.52
R3b	7.04	-4.62	-16.08	13.63	-8.02	-19.48
R3c	22.71	6.81	10.81	20.42	12.65	5.26
R4a	7.46	-25.87	-26.93	11.59	-27.15	-28.21
R4b	24.91	21.16	13.63	23.32	17.10	9.57
R4c	7.46	-3.75	-17.55	10.94	4.10	-9.71
R4d	30.46	6.38	6.72	35.91	10.64	10.98
R5a	8.37	-1.82	-14.01	7.39	-1.40	-13.60
R5b	13.61	5.83	-6.76	11.20	4.10	-8.50

Table S8. Frequencies (cm^{-1}) of the reactants, products, and transition states for the oxidation and decomposition pathways of alkoxy radicals calculated at the B3LYP/6-311G(d,p) level.

Species	Frequencies
R2	35, 54, 82, 181, 204, 240, 258, 280, 309, 323, 362, 377, 459, 581, 586, 763, 776, 825, 905, 921, 940, 949, 971, 1045, 1049, 1114, 1170, 1187, 1226, 1248, 1285, 1344, 1352, 1398, 1406, 1435, 1479, 1489, 1493, 1501, 1504, 1524, 1782, 2864, 2946, 3028, 3030, 3039, 3089, 3092, 3104, 3113, 3116, 3119
R3	28, 98, 119, 156, 199, 220, 236, 262, 281, 324, 336, 352, 473, 529, 562, 686, 780, 815 883, 940, 957, 1000, 1029, 1072, 1097, 1172, 1176, 1201, 1217, 1255, 1286, 1342, 1356, 1398, 1423, 1471, 1482, 1488, 1491, 1498, 1503, 1515, 1785, 2886, 2924, 3028, 3034, 3051, 3092, 3101, 3106, 3124, 3125, 3159
R4	25, 117, 136, 189, 200, 241, 280, 312, 328, 347, 393, 486, 580, 751, 816, 869, 907, 947, 1001, 1010, 1086, 1147, 1173, 1188, 1206, 1243, 1371, 1402, 1468, 1471, 1480, 1484, 1488, 1498, 1506, 1799, 3046, 3050, 3050, 3122, 3123, 3126, 3131, 3152, 3161
P2a	37, 46, 167, 172, 202, 233, 258, 263, 279, 330, 351, 375, 476, 551, 661, 744, 832, 837, 940, 945, 970, 1019, 1030, 1047, 1067, 1081, 1224, 1247, 1284, 1396, 1404, 1406, 1434, 1480, 1489, 1493, 1502, 1505, 1524, 1813, 1891, 3031, 3032, 3032, 3041, 3093 3095, 3107, 3112, 3114, 3121
P2b	39, 204, 231, 254, 271, 277, 346, 357, 375, 509, 572, 610, 724, 786, 859, 941, 949, 969, 1043, 1049, 1140, 1227, 1242, 1271, 1349, 1397, 1407, 1436, 1478, 1489, 1494, 1500, 1505, 1525, 1816, 3028, 3030, 3038, 3090, 3091, 3104, 3111, 3114, 3118, 3759
P3a	51, 84, 104, 128, 191, 214, 227, 248, 313, 330, 344, 350, 465, 552, 570, 778, 839, 886, 941, 956, 967, 1010, 1052, 1172, 1178, 1189, 1214, 1230, 1289, 1399, 1405, 1429, 1472, 1483, 1483, 1491, 1498, 1502, 1516, 1801, 1822, 2854, 3033, 3039, 3051, 3095, 3104, 3125, 3128, 3129, 3158
P3b	48, 84, 86, 115, 150, 212, 314, 343, 351, 493, 573, 712, 811, 944, 952, 967, 1036, 1040, 1167, 1172, 1206, 1287, 1361, 1396, 1409, 1464, 1470, 1473, 1479, 1489, 1499, 1501, 1692, 2984, 2992, 3022, 3027, 3041, 3108, 3137, 3145, 3147
P3c	67, 86, 159, 175, 204, 210, 228, 243, 262, 306, 332, 347, 404, 467, 554, 602, 730, 766 809, 845, 952, 963, 996, 1035, 1152, 1165, 1190, 1199, 1210, 1262, 1350, 1356, 1400, 1420, 1455, 1483, 1484, 1486, 1496, 1498, 1504, 1515, 1617, 2942, 3032, 3040, 3041, 3097, 3107, 3113, 3113, 3125, 3128, 3154
P4a	29, 110, 142, 154, 195, 324, 394, 442, 463, 625, 722, 826, 972, 997, 1039, 1147, 1172, 1212, 1256, 1389, 1459, 1464, 1470, 1483, 1497, 1817, 1829, 3040, 3052, 3099, 3125, 3146, 3163
P4b	35, 133, 376, 488, 535, 779, 881, 881, 1082, 1117, 1230, 1382, 1385, 1460, 1466, 1470, 1487, 1804, 3024, 3031, 3079, 3086, 3139, 3140
O ₂ (³ P)	1641
HO ₂	1163, 1428, 3605

HCO	1202, 1270, 1538, 1826, 2869, 2919
CH ₃	506, 1402, 1403, 3103, 3281, 3283
HCOH	632, 701, 1058, 1132, 1310, 1411, 1836, 3043, 3736
COOCH ₃	93, 272, 384, 761, 877, 1133, 1147, 1188, 1453, 1482, 1488, 1846, 3057, 3140, 3177
TS3a	1340 <i>i</i> , 11, 30, 54, 63, 71, 108, 161, 196, 233, 254, 258, 275, 326, 351, 366, 381, 472, 552, 578, 656, 768, 790, 850, 917, 940, 949, 971, 973, 1040, 1048, 1094, 1124, 1226, 1247, 1288, 1319, 1354, 1398, 1407, 1435, 1471, 1478, 1488, 1492, 1501, 1505, 1523, 1651, 1805, 2880, 3029, 3031, 3039, 3090, 3094, 3104, 3113, 3115, 3118
TS3b	360 <i>i</i> , 21, 70, 189, 210, 232, 258, 267, 282, 291, 337, 375, 393, 484, 510, 596, 787, 794, 829, 912, 940, 945, 963, 970, 1048, 1051, 1124, 1227, 1243, 1253, 1328, 1386, 1396, 1407, 1440, 1478, 1488, 1493, 1501, 1503, 1524, 1532, 1674, 1746, 2971, 3028, 3030, 3038, 3090, 3092, 3102, 3113, 3116, 3120
TS3c	900 <i>i</i> , 40, 53, 113, 164, 198, 235, 255, 256, 278, 329, 353, 375, 470, 481, 497, 561, 667, 750, 822, 841, 940, 946, 971, 992, 1031, 1047, 1071, 1082, 1225, 1247, 1285, 1374, 1398, 1406, 1435, 1479, 1489, 1493, 1501, 1505, 1524, 1700, 1849, 3019, 3031 3032, 3040, 3094, 3095, 3107, 3112, 3114, 3119
TS4a	1700 <i>i</i> , 27, 32, 49, 89, 114, 136, 146, 181, 210, 229, 240, 265, 280, 329, 336, 355, 481, 542, 561, 609, 778, 823, 874, 921, 954, 997, 999, 1016, 1040, 1170, 1172, 1184, 1209, 1222, 1253, 1302, 1336, 1399, 1418, 1447, 1471, 1482, 1486, 1487, 1497, 1502, 1514, 1570, 1787, 2811, 3030, 3036, 3053, 3093, 3102, 3117, 3126, 3127, 3160
TS4b	723 <i>i</i> , 23, 79, 111, 135, 202, 205, 212, 246, 259, 328, 335, 358, 415, 471, 483, 544, 568, 782, 834, 880, 923, 958, 982, 1002, 1042, 1172, 1184, 1187, 1210, 1222, 1285, 1379, 1398, 1422, 1471, 1482, 1483, 1489, 1496, 1500, 1512, 1698, 1794, 2854, 3032 3036, 3053, 3094, 3098, 3121, 3127, 3136, 3160
TS4c	460 <i>i</i> , 60, 80, 117, 136, 191, 196, 199, 217, 234, 290, 337, 347, 383, 495, 577, 693, 757, 820, 926, 945, 1001, 1012, 1021, 1157, 1171, 1186, 1217, 1238, 1256, 1314, 1397, 1409, 1415, 1468, 1470, 1477, 1482, 1490, 1495, 1499, 1561, 1764, 2885, 2961, 3008, 3015, 3051, 3078, 3082, 3125, 3137, 3147, 3160
TS4d	1033 <i>i</i> , 37, 121, 127, 168, 194, 214, 228, 234, 262, 327, 340, 424, 469, 513, 577, 675, 701, 805, 918, 949, 958, 972, 990, 1025, 1152, 1168, 1178, 1195, 1228, 1316, 1393, 1401, 1411, 1461, 1483, 1484, 1487, 1495, 1500, 1504, 1528, 1558, 2061, 2832, 3028, 3036, 3054, 3094, 3098, 3102, 3123, 3132, 3171
TS5a	364 <i>i</i> , 30, 82, 105, 141, 170, 203, 221, 238, 299, 364, 376, 503, 576, 740, 778, 890, 907, 947, 1035, 1070, 1138, 1155, 1200, 1205, 1379, 1392, 1448, 1461, 1468, 1471, 1483, 1488, 1490, 1522, 1857, 3024, 3032, 3059, 3089, 3101, 3140, 3142, 3143, 3178
TS5b	418 <i>i</i> , 40, 111, 129, 137, 180, 191, 205, 214, 328, 379, 413, 468, 575, 603, 637, 728, 821, 938, 975, 997, 1031, 1131, 1172, 1208, 1227, 1392, 1415, 1429, 1466, 1472, 1475, 1482, 1499, 1551, 1817, 3034, 3050, 3091, 3106, 3123, 3149, 3159, 3256, 3267

Table S9. Gibbs free energy barriers (ΔG^\ddagger) (in kcal/mol) and the corresponding C–H BDE for the reaction of OH with different esters at different levels.

	B3LYP		M06-2X		ω B97XD	
	BDE	ΔG^\ddagger	BDE	ΔG^\ddagger	BDE	ΔG^\ddagger
(CH ₃) ₃ COOCH ₃	96.32	4.30	98.32	6.93	97.61	5.12
CH ₃ COOCH ₃	96.32	4.38	98.56	7.32	97.51	5.25
CH ₂ FCOOCH ₃	96.88	5.02	99.13	9.27	98.17	6.14
CF ₂ HCOOCH ₃	97.05	5.43	99.29	8.57	98.32	6.33
CF ₃ COOCH ₃	97.35	6.31	99.48	9.39	98.67	7.08
CH ₂ ClCOOCH ₃	96.66	5.03	99.00	7.89	98.04	6.34
CHCl ₂ COOCH ₃	97.07	5.91	99.47	9.10	98.37	6.32
CCl ₃ COOCH ₃	97.37	6.31	99.59	9.10	98.71	7.11
CF ₂ ClCOOCH ₃	97.33	6.07	99.68	9.45	98.68	6.85
CFCl ₂ COOCH ₃	97.35	6.25	99.59	9.01	98.73	7.50

Table S10. The calculated distortion (E_{dis}), interaction (E_{int}) energies, and Gibbs free energy barriers (ΔG^\ddagger) (in kcal/mol) for $(\text{CH}_3)_3\text{CCOOCH}_3$, $\text{CH}_3\text{COOCH}_3$, and $\text{CH}_2\text{FCOOCH}_3$ at different levels.

Energies	B3LYP			M06-2X			ω B97XD		
	E_{dis}	E_{int}	ΔG^\ddagger	E_{dis}	E_{int}	ΔG^\ddagger	E_{dis}	E_{int}	ΔG^\ddagger
$(\text{CH}_3)_3\text{CCOOCH}_3$	4.67	8.13	4.30	3.96	4.48	6.93	4.64	7.17	5.12
$\text{CH}_3\text{COOCH}_3$	4.77	8.12	4.38	4.00	4.38	7.32	4.73	7.05	5.25
$\text{CH}_2\text{FCOOCH}_3$	5.24	7.76	5.02	4.33	3.99	9.27	5.12	6.67	6.14

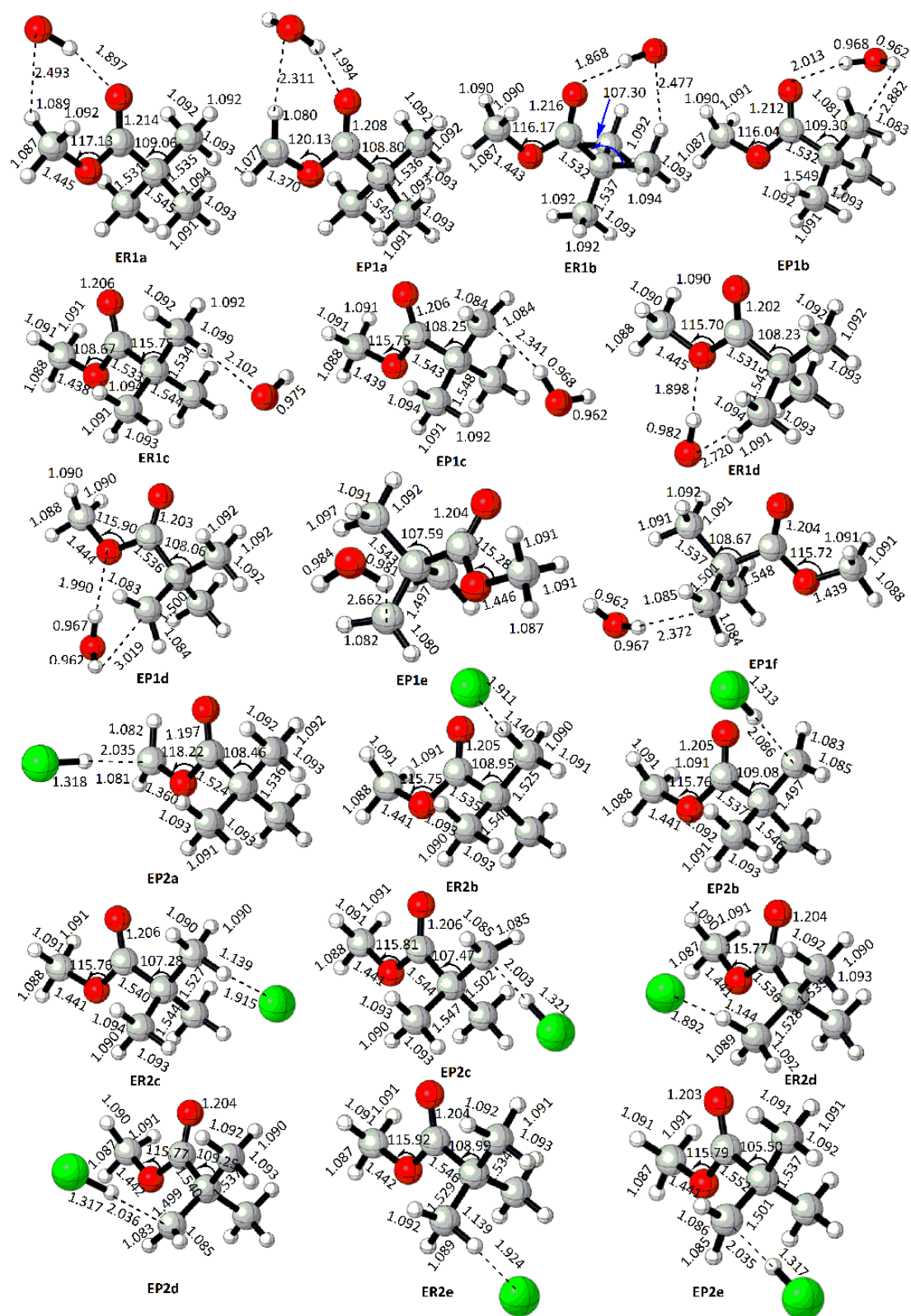


Figure S1. Optimized geometries of the reactants, products, transition states, and complexes at the B3LYP/6-311G(d,p) level, and the limited experimental values (in parentheses). Bond lengths are in angstroms and angles in degrees.

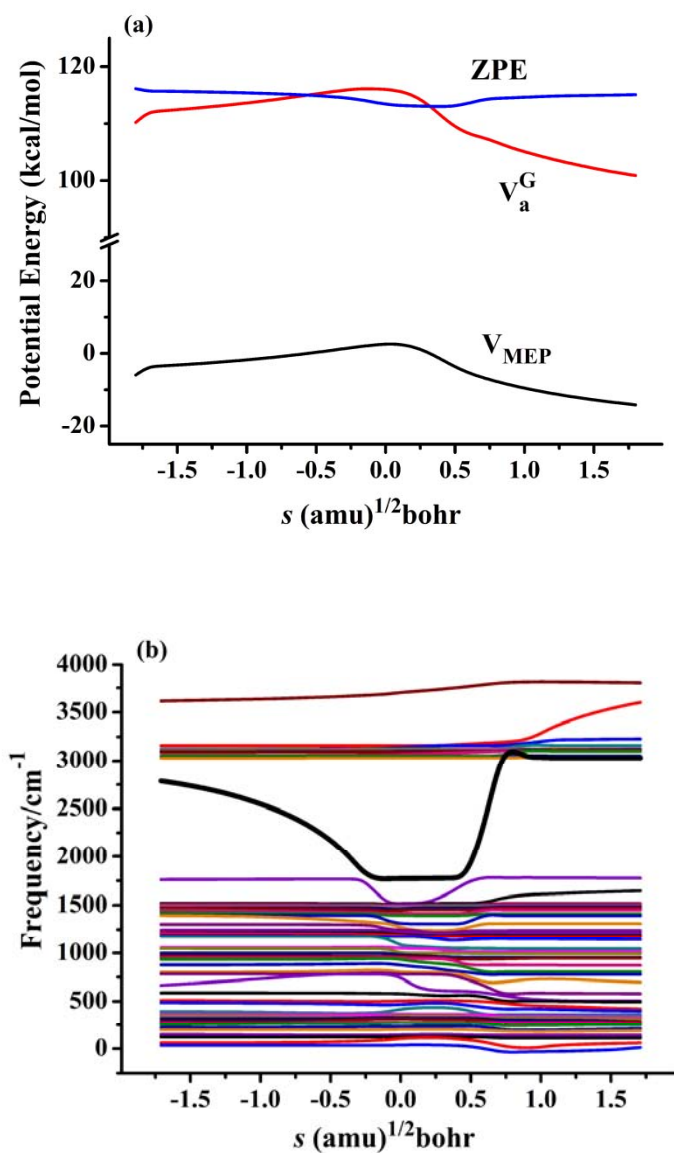


Figure S2. Classical potential energy curve (V_{MEP}), ground-state vibrational adiabatic energy curve (V_a^G), zero-point energy curve (ZPE) (a) and changes of generalized normal-mode vibrational frequencies as functions of s ($(\text{amu})^{1/2}\text{bohr}$) at the CCSD(T)/6-311++G(d,p)//B3LYP/6-311G(d,p) level for the reaction R1b (b).

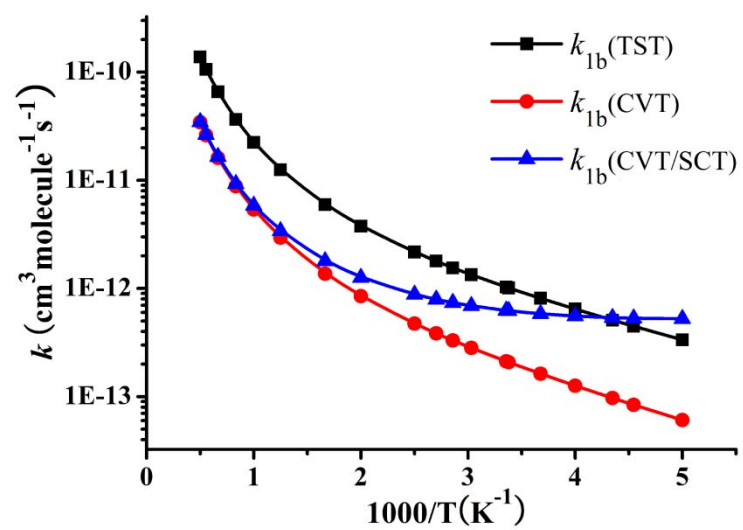


Figure S3. Calculated TST, CVT, and CVT/SCT rate constants for reaction R1b as functions of $1000/T$ in the temperature range of 200–2000 K.

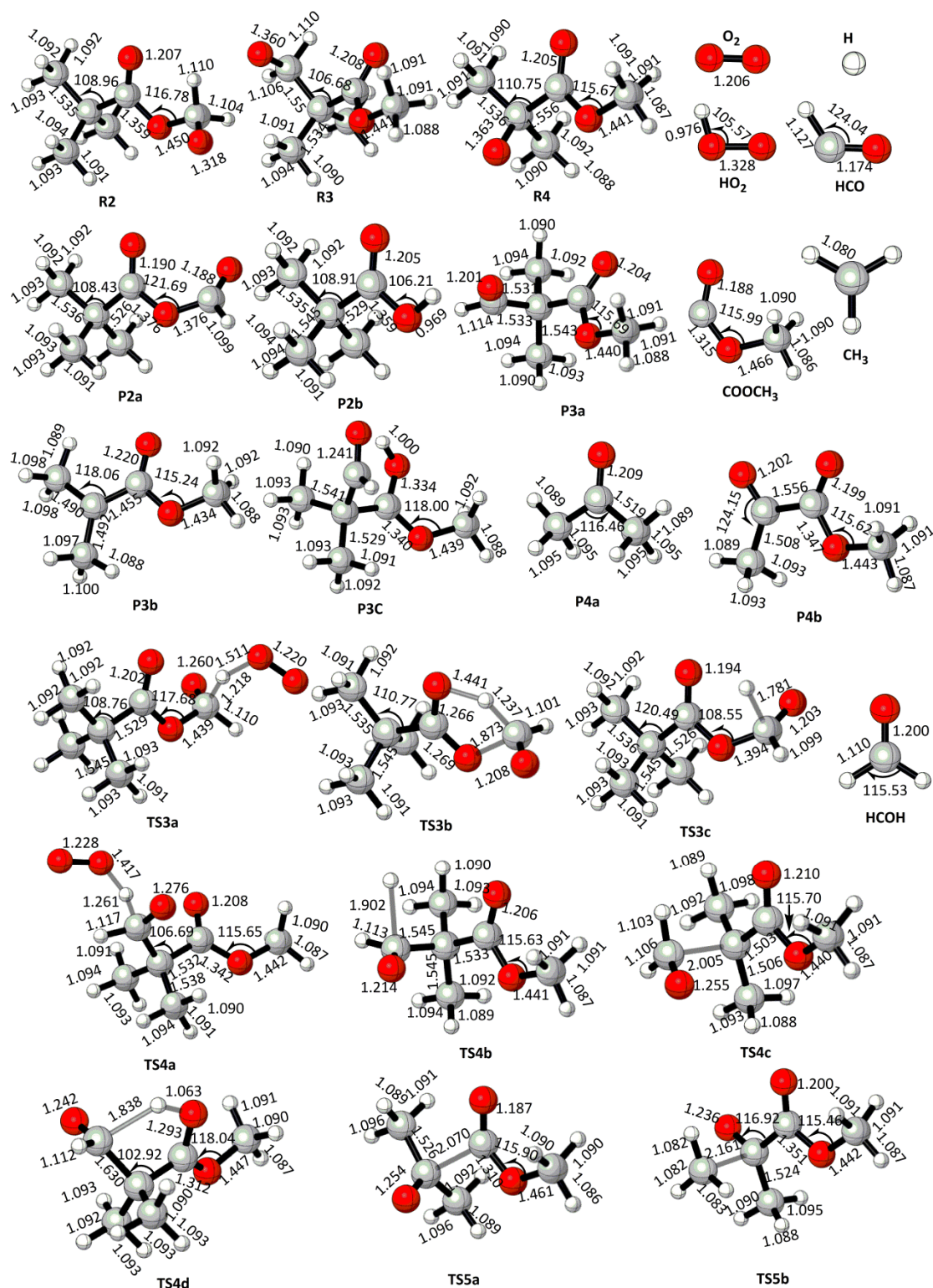
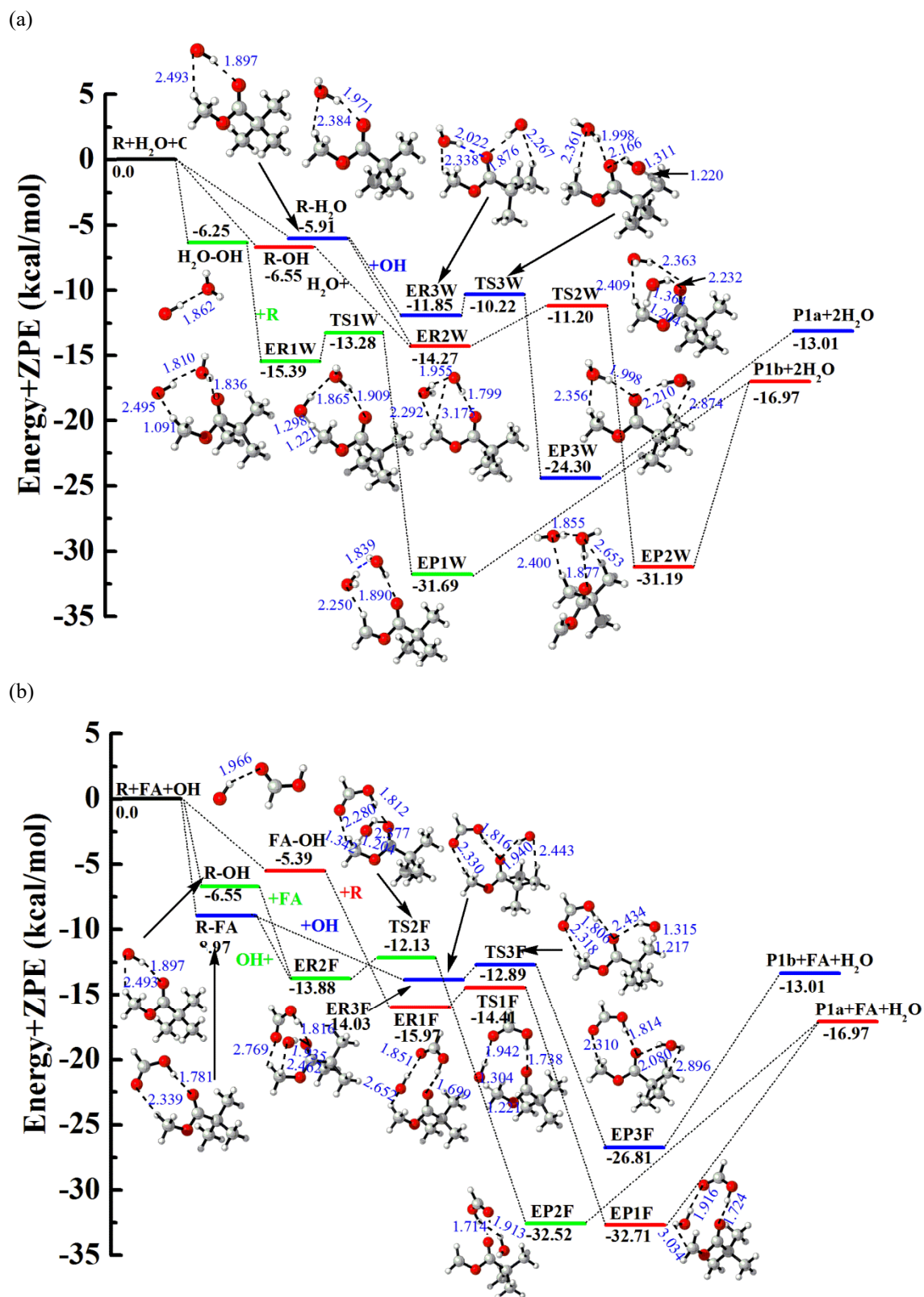
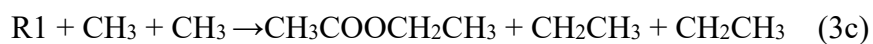
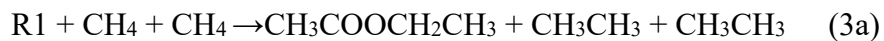


Figure S4. Optimized geometries of reactants, products, and transition states for the oxidation and decomposition channels of alkoxy radicals at the B3LYP/6-311G(d,p) level.



The enthalpies of formation for $(\text{CH}_3)_3\text{CCOOCH}_3$ (R1), $(\text{CH}_3)_3\text{CCOOCH}_2\bullet$ (P1a), $\bullet\text{CH}_2(\text{CH}_3)_2\text{CCOOCH}_3$ (P1b, P1c, and P1d) are computed through the following reactions:



The kinetics calculation section

The canonical variational theory rate constant for the temperature T , $k^{CVT}(T)$, is based on the thought of varying the dividing surface along a reference path to minimize the rate constant. The $k^{GT}(T,s)$, with respect to the dividing surface at s is given as follows:

$$k_s^{CVT}(T) = \min k^{GT}(T, s) \quad (1)$$

$$k^{GT}(T, s) = \frac{\sigma Q^{GT}(T, s)}{\beta h Q^R(T)} \exp(-\beta V_{MEP}(s)) \quad (2)$$

The s is the location of the generalized transition state on the IRC; σ is the symmetry factor; β equals $(k_B T)^{-1}$ where k_B is Boltzmann's constant; h is Planck's constant; and Q^{GT} and Q^R are partition functions for the generalized transition state and reactants, respectively.

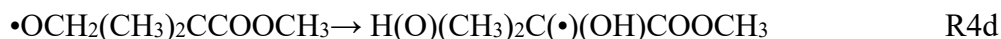
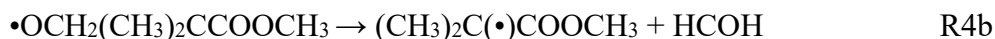
The two electronic states of the OH radicals, with a 140 cm^{-1} splitting in the $^2\Pi$ ground state, are included. The two electronic states of the OH radicals, with a 140 cm^{-1} splitting in the $^2\Pi$ ground state, are included. The hindered-rotor approximation of Truhlar and Chuang is used for computing the partition functions of the lower modes associated with the torsion. All the vibrational modes are considered as quantum-mechanical separable harmonic oscillator approximation except for the lowest one.

The corresponding possible processes (R3a-R3c, R4a-R4d, R5a-R5b) for subsequent reactions of the alkoxy radicals:

Theoretical calculations at the CCSD(T)/6-311++G(d,p)//B3LYP/6-311G(d,p) level are carried out to explore the mechanism for the oxidation and decomposition of $(\text{CH}_3)_3\text{CCOOCH}_2\text{O}\cdot$, $\cdot\text{OCH}_2(\text{CH}_3)_2\text{CCOOCH}_3$ and $\cdot\text{O}(\text{CH}_3)_2\text{CCOOCH}_3$. There are three possible processes proposed as follows:



Four possible channels (R4a–R4d) are found for $\cdot\text{OCH}_2(\text{CH}_3)_2\text{CCOOCH}_3$:



The $\cdot(\text{CH}_3)_2\text{CCOOCH}_3$ radical (produced through R4b) can be transformed into

$\cdot\text{O}(\text{CH}_3)_2\text{CCOOCH}_3$ via reaction with O_2 in the presence of NO. The formed radical

$\cdot\text{O}(\text{CH}_3)_2\text{CCOOCH}_3$ can be further degraded by R5a and R5b:

