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# Supporting Information

# Theoretical Studies on Mechanism and Kinetics of the Hydrogen-Abstraction Reaction of $CF_3CH_2CHO$ with OH Radicals

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**Table (S1)** Calculated frequencies (in $cm^{-1}$) of stationary points at the M06-2X/aug-cc-pVDZ level (experimental values given in parentheses)

| Species | Frequencies ($cm^{-1}$) |
|---|---|
| OH | 3733 (*3735*)[a] |
| $H_2O$ | 1614, 3867, 3977 (*1595*, *3657*, *3756*)[a] |
| *c*-$CF_3CH_2CHO$ | 105, 151, 170, 325, 354, 523, 532, 555, 739, 767, 868, 953, 1018, 1170, 1194, 1291, 1318, 1392, 1408, 1454, 1880, 3000, 3095, 3146 |
| *t*-$CF_3CH_2CHO$ | 66, 106, 181, 347, 380, 450, 530, 559, 663, 758, 879, 1002, 1063, 1148, 1193, 1278, 1293, 1373, 11413, 1436, 1874, 3006, 3100, 3171 |
| *c*-$CF_3CH_2CO$ | 89, 159, 171, 318, 347, 516, 529, 551, 730, 847, 858, 901, 1113, 1184, 1281, 1309, 1350, 1419, 2006, 3113, 3171 |
| *t*-$CF_3CH_2CO$ | 53, 144, 166, 344, 382, 414, 527, 553, 676, 778, 877, 931, 1063, 1178, 1272, 1302, 1362, 1420, 1996, 3091, 3163 |
| *c*-$CF_3CHCHO$ | 79, 165, 209, 327, 388, 522, 524, 558, 639, 778, 885, 975, 1040, 1204, 1209, 1287, 1413, 1440, 1670, 3074, 3291 |
| *t*-$CF_3CHCHO$ | 59, 141, 196, 373, 384, 427, 545, 555, 698, 712, 903, 980, 1150, 1170, 1190, 1300, 1374, 1464, 1632, 3072, 3259 |
| CR1a-1 | 38, 57, 69, 116, 169, 204, 351, 370, 383, 456, 531, 550, 582, 665, 767, 880, 1010, 1076, 1156, 1198, 1280, 1297, 1376, 1420, 1437, 1848, 3040, 3090, 3168, 3637 |
| CR1a-2 | 55, 72, 86, 121, 147, 186, 199, 346, 382, 444, 471, 530, 560, 665, 752, 877, 998, 1060, 1147, 1192, 1276, 1285, 1376, 1421, 1440, 1863, 3030, 3094, 3177, 3743 |
| CR1b-1 | 45, 69, 90, 143, 153, 203, 367, 382, 431, 453, 455, 535, 562, 686, 738, 887, 1023, 1061, 1159, 1205, 1287, 1304 1280, 1427, 1457, 1854, 3024, 3102, 3157, 3636 |
| CR1b-2 | 44, 60, 112, 147, 165, 204, 229, 353, 384, 424, 459, 530, 563, 661, 766, 876, 1002, 1063, 1145, 1195, 1265, 1296, 1370, 1409, 1433, 1871, 3007, 3100, 3175, 3730 |
| CR2a | 49, 76, 103, 104, 146, 159, 172, 234, 326, 356, 523, 532, 558, 736, 766, 869, 956, 1011, 1168, 1195, 1291, 1313, 1391, 1399, 1452, 1879, 2961, 3106, 3155, 3758 |
| CR2b | 46, 73, 92, 134, 163, 184, 201, 251, 321, 350, 355, 519, 530, 556, 731, 846, 859, 906, 1111, 1187, 1279, 1301, 1356, 1404, 1614, 2007, 3124, 3177, 3832, 3956 |
| CP1a-1 | 50, 71, 103, 138, 165, 180, 208, 233, 324, 359, 385, 422, 529, 553, 674, 796, 871, 938, 1071, 1183, 1265, 1291, 1358, 1426, 1619, 1996, 3104, 3179, 3852, 3964 |
| CP1a-2 | 47, 58, 76, 99, 119, 173, 213, 232, 281, 345, 384, 421, 528, 556, 675, 788, 875, 934, 1068, 1187, 1274, 1297, 1364, 1422, 1645, 2014, 3094, 3165, 3845, 3960 |
| CP1b-1 | 28, 81, 103, 159, 166, 178, 226, 354, 383, 389, 441, 535, 555, 559, 700, 770, 910, 990, 1173, 1185, 1195, 1305, 1373, 1468, 1611, 1641, 3075, 3247, 3760, 3959 |
| CP1b-2 | 51, 68, 95, 143, 172, 183, 205, 236, 266, 380, 388, 431, 545, 560, 694, 701, 903, 971, 1152, 1165, 1175, 1304, 1379, 1462, 1615, 1677, 3084, 3266, 3862, 3976 |
| CP2a | 47, 73, 92, 134, 163, 184, 205, 257, 321, 350, 355, 519, 530, 556, 731, 846, 858, 907, 1111, 1188, 1279, 1301, 1357, 1404, 1615, 2008, 3124, 3177, 3831, 3955 |
| CP2b | 34, 75, 89, 122, 151, 166, 218, 289, 331, 355, 416, 524, 534, 561, 642, 777, 881, 983, 1046, 1197, 1201, 1289, 1412, 1441, 1620, 1667, 3034, 3274, 3850, 3957 |
| TS1a-1 | 519i, 40, 56, 85, 132, 195, 245, 348, 369, 421, 534, 547, 648, 660, 780, 881, 985, 1012, 1146, 1192, 1255, 1299, 1362, 1380, 1428, 1788, 1910,3096, 3172, 3735 |
| TS1a-2 | 491i, 17, 72, 120, 165, 197, 274, 342, 381, 427, 528, 556, 643, 674, 739, 877, 994, 1016, 1128, 1192, 1259, 1289, 1366, 1389, 1437, 1648, 1909, 3096, 3165, 3766 |
| TS1b-1 | 1632i, 50, 69, 103, 171, 190, 342, 378, 403, 472, 488, 533, 568, 694, 750, 860, 919, 1018, 1076, 1170, 1193, 1219, 1292, 1366, 1406, 1455, 1843, 3017, 3137, 3722 |
| TS1b-2 | 1269i, 60, 84, 105, 133, 187, 233, 330, 386, 432, 535, 555, 651, 659, 792, 867, 902, 1033, 1094, 1150, 1204, 1234, 1281, 1354, 1414, 1444, 1847, 3031, 3175, 3758 |
| TS2a | 460i, 29, 59, 94, 154, 178, 260, 324, 350, 521, 529, 542, 622, 740, 770, 853, 922, 999, 1084, 1157, 1198, 1283, 1304, 1387, 1437, 1900, 2170, 3106, 3156, 3743 |
| TS2b | 1372i, 59, 96, 108, 164, 173, 318, 327, 330, 523, 25, 553, 697, 772, 815, 854, 909, 967, 1057, 1110, 1200, 1253, 1282, 1378, 1407, 1467, 1852, 3034, 3145, 3740 |

[a] from ref 38.

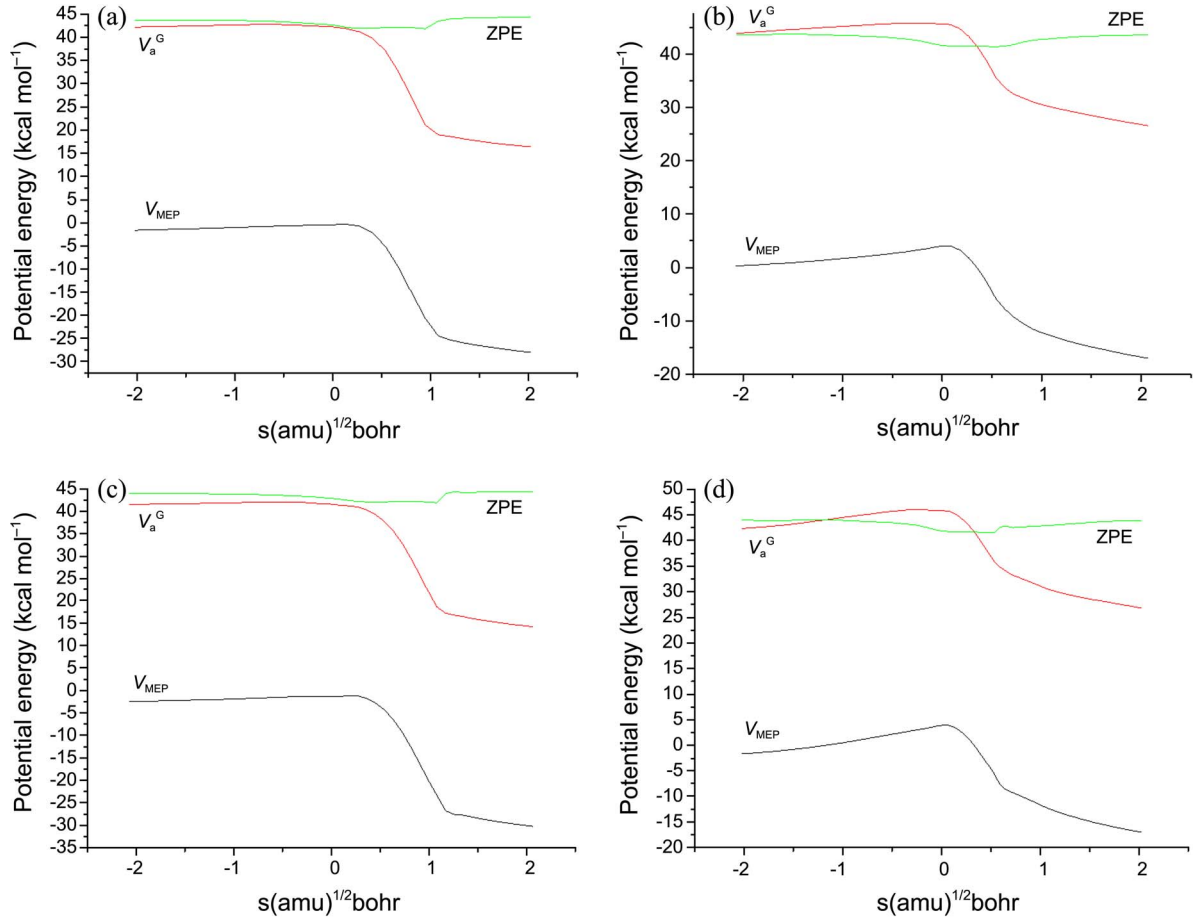



**Figure S1.** Classical potential energy curves ($V_{MEP}$), ground-state vibrationally adiabatic energy curves ($V_a^G$), and zero-point energy curve (ZPE) as functions of $s$ (amu)$^{1/2}$ bohr at the MCG3-MPWB//M06-2X/aug-cc-pVDZ level: (a) for R1a-2, (b) for R1b-2, (c) for R2a, and (d) for R2b.

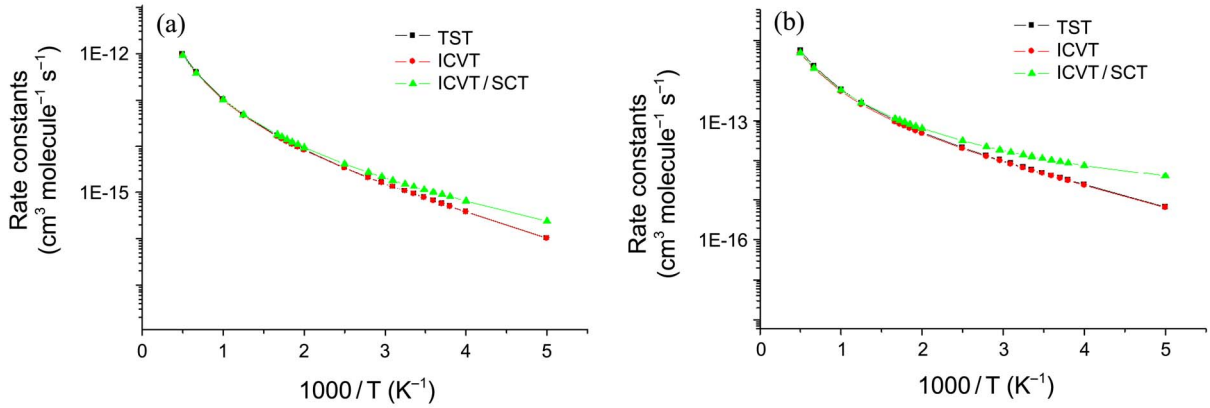



**Figure S2.** The TST, ICVT, and ICVT/SCT rate constants calculated at the MCG3-MPWB//M06-2X/aug-cc-pVDZ level versus 1000/$T$ between 200 and 2000 K: (a) for R1b-2 and (b) for R2b.