Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

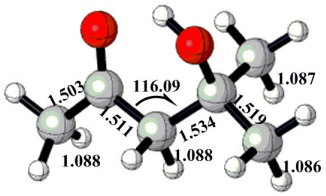
Supplementary Information

Theoretical investigations of the mechanism, kinetics and subsequent degradation products of the NO_3 radical initiated oxidation of 4-hydroxy-3-hexanone

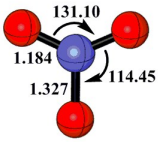
Ning Zhang[a], Fengyang Bai[b], Xiumei Pan[a]*

[a]Institute of Functional Material Chemistry, National & Local United Engineering Lab for Power Battery, Faculty of Chemistry, Northeast Normal University, 130024 Changchun, People's Republic of China

[b]Institute of Catalysis for Energy and Environment, College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang, 110034, People's Republic of China



4H4M2P



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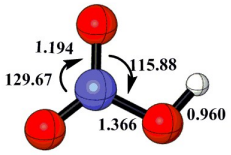

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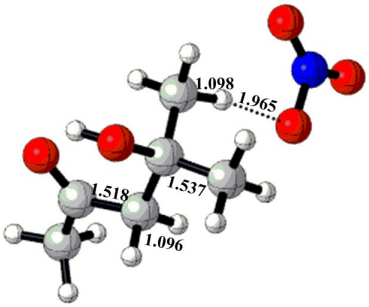

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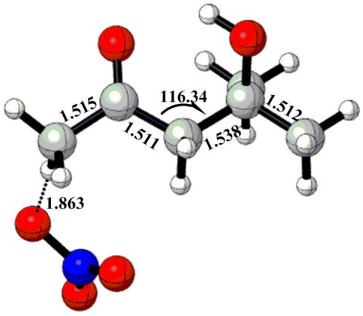

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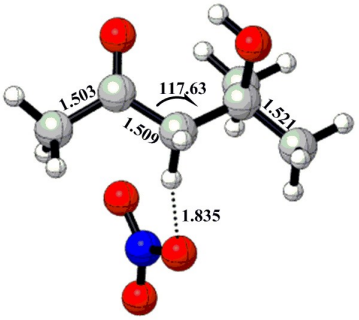

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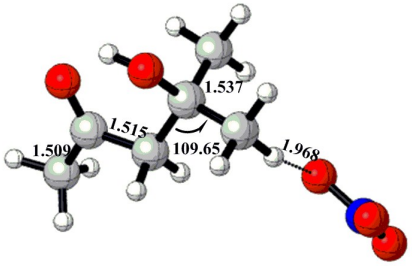

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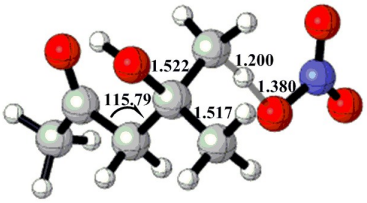
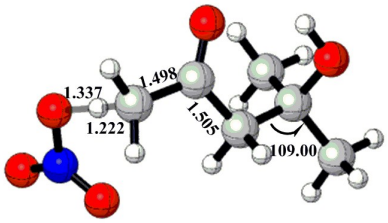


TS1



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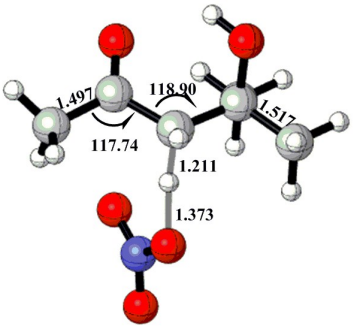

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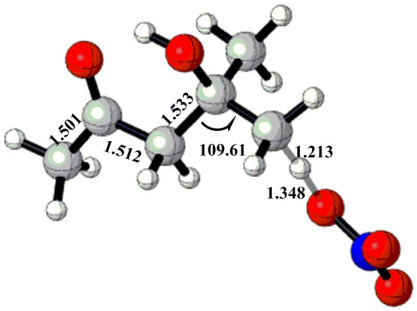

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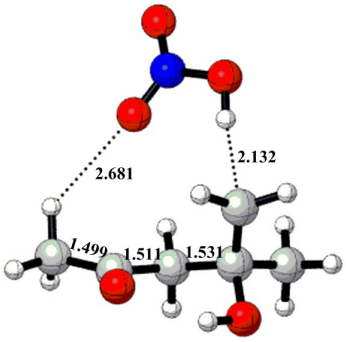
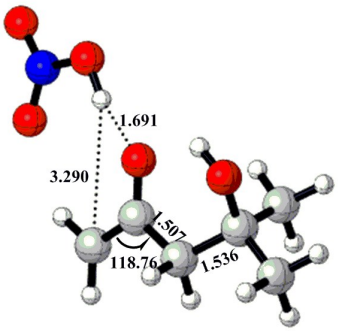


EP1



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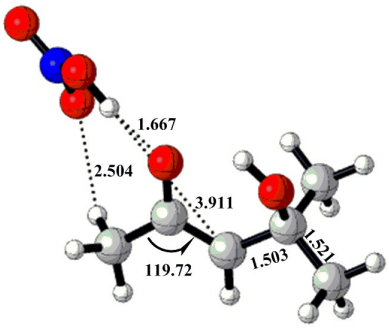

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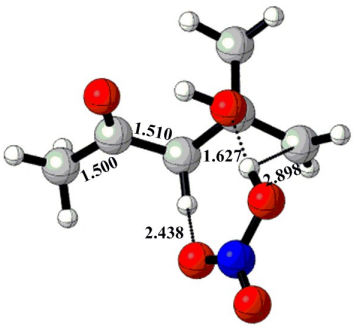

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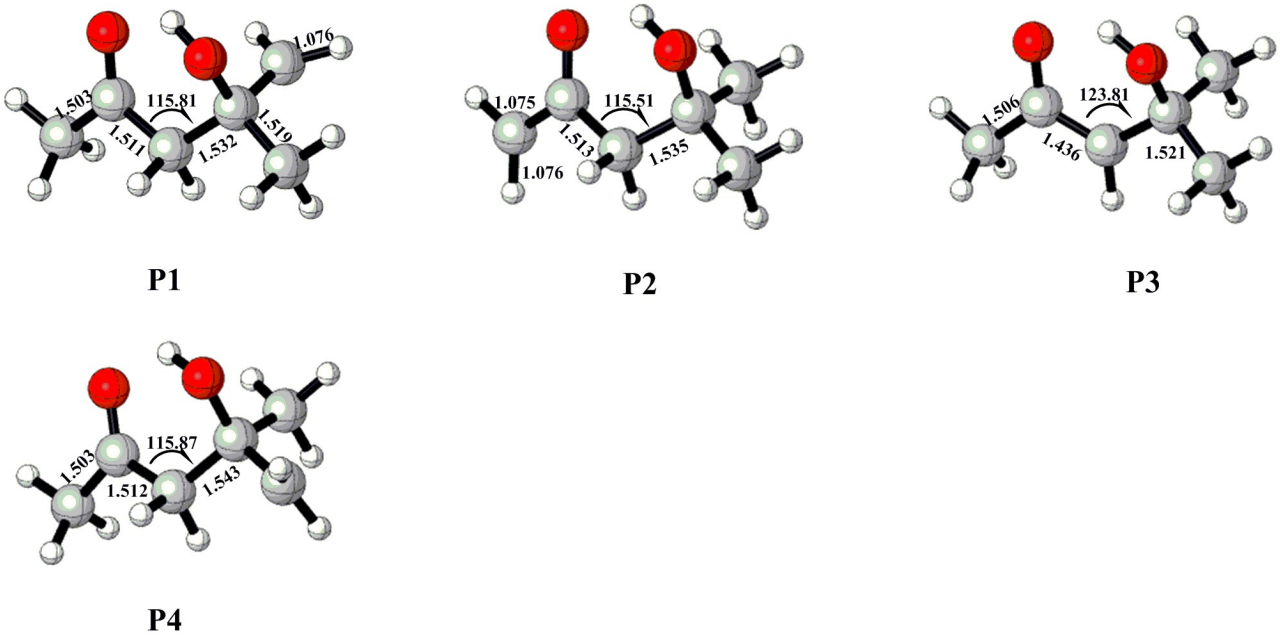
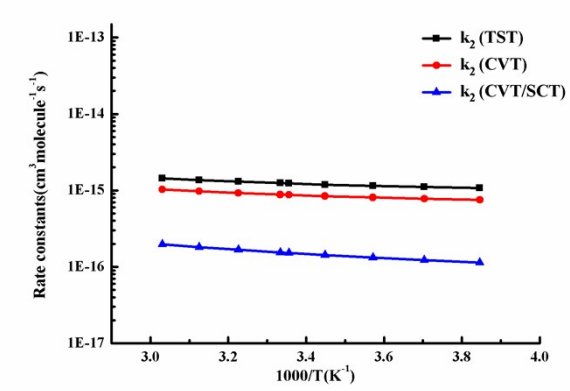


Fig. S1 Optimized geometries of all reactants (R)，reaction complexes (ER/EP), transition states (TS), and products (P) at the BH&HLYP/6-311++G(d,p) level for the reaction of 4-hydroxy-4-methyl-2-pentanone (4H4M2P) with NO_3 radical. Bond lengths are in angstroms, and angles are in degrees.

(a)



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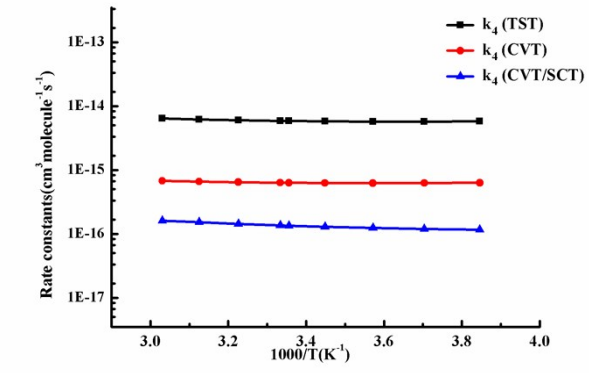


(c)

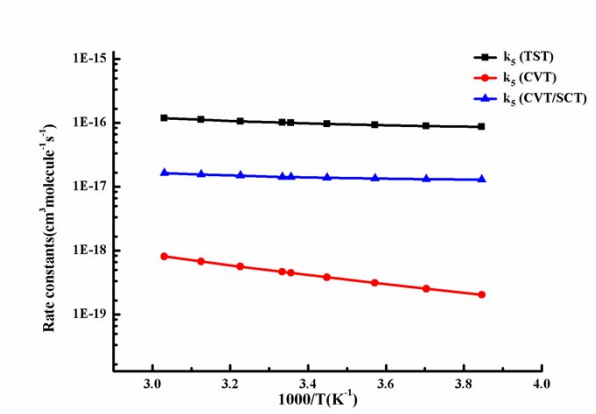
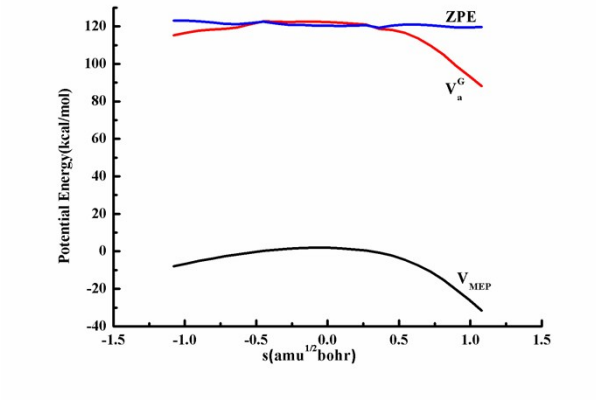
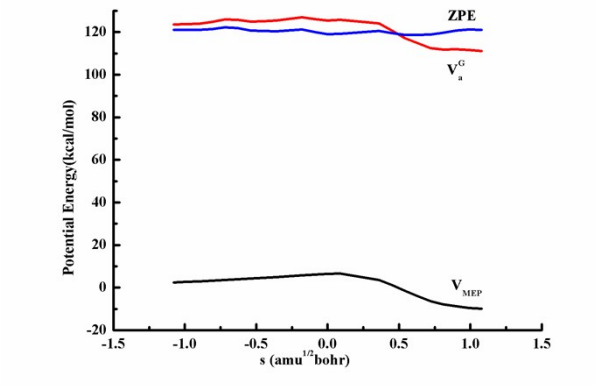


Fig. S2 Calculated TST, CVT, and CVT/SCT rate constants as a function of $10^3/T$ for title reactions in the temperature range of 260-330 K. (a) For reaction path2, (b) For reaction path4. (c) For reaction path5.

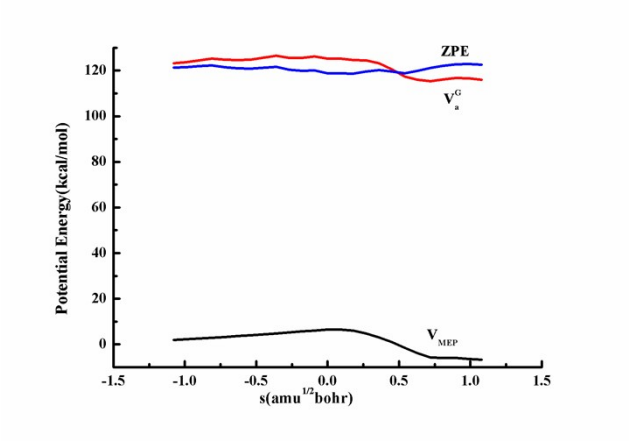
(d)



(e)



(f)



(g)

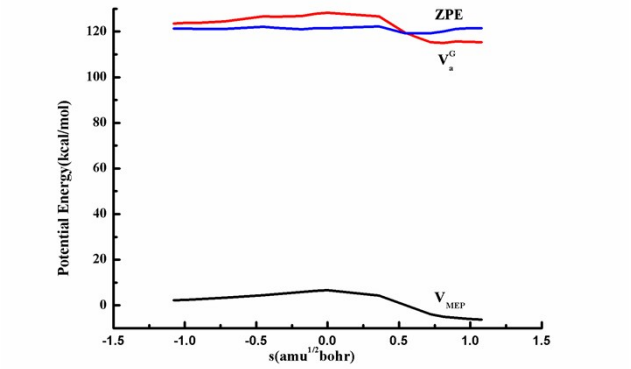
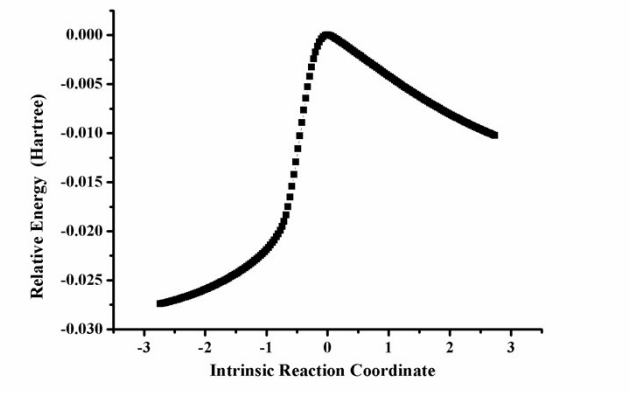
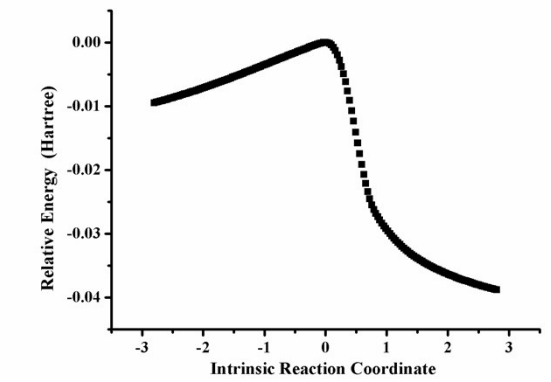
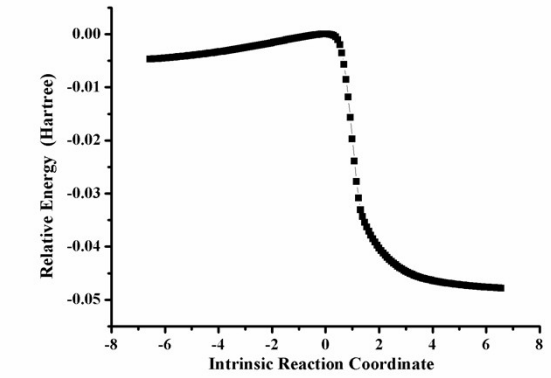


Fig. S3 Classical potential energy curve (V_{MEP}), ground-state vibrational adiabatic energy curve (V_a^G), and zero-point energy curve (ZPE) as functions of s (amu)$^{1/2}$ bohr at the CCSD(T)//BH&HLYP/6-311++G(d,p) level for the reactions. (d) For reaction path1, (e) For reaction path2. (f) For reaction path4. (g) For reaction path5.




Relative Energy (Hartree)
0.00
-0.01
-0.02
-0.03
-0.04
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate


Relative Energy (Hartree)
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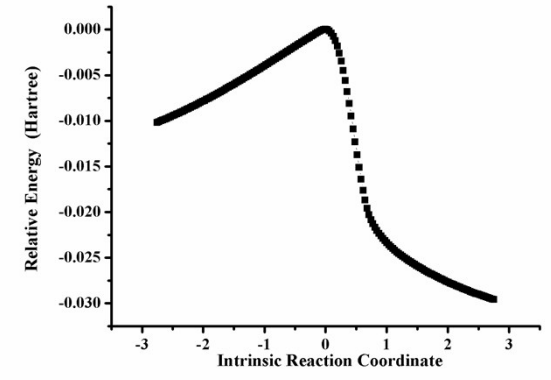
-0.02
-0.03
-0.04
-0.05
-8
-6
-4
-2
0
2
4
6
8
Intrinsic Reaction Coordinate


Relative Energy (Hartree)
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-0.010
-0.015
-0.020
-0.025
-0.030
-3
-2
-1
0
1
2
3
Intrinsic Reaction Coordinate

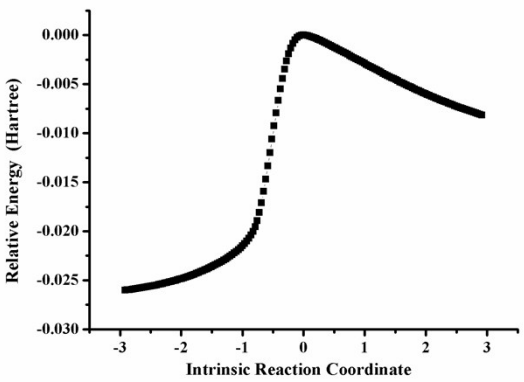

Fig. S4 IRC plots of transition states (TS1-TS5) of title reaction obtained at the BH&HLYP/6-311++G(d,p) level of theory.

Table S1 Calculated frequencies (in cm^{-1}) and $<s^2>$ values for the reactants, products, transition states, and reaction complexes for the title reactions at the BH&HLYP/6–311++G(d,p) level.

Species	BH&HLYP/6-311++G(d, p)	$<s^2>$
$CH_3CH_2C(O)CH(OH)C_2H_5$	27, 87, 100, 182, 213, 237, 239, 260, 323, 326, 436, 533, 565, 664, 786, 810, 845, 923, 1033, 1039, 1084, 1103, 1126, 1175, 1187, 1213, 1275, 1323, 1339, 1371, 1437, 1438, 1462, 1473, 1481, 1499, 1536, 1545, 1550, 1553, 1562, 1878, 3085, 3103, 3118, 3123, 3126, 3147, 3156, 3181, 3186, 3192, 3199, 4023	0.0
NO_3	445, 703, 831, 963, 1445, 1756	0.756
HNO_3	491, 641, 731, 837, 1016, 1409, 1459, 1862, 3899	0.0
TS1	1300*i*, 21, 29, 41, 57, 87, 94, 148, 169, 222, 234, 239, 264, 337, 356, 415, 438, 489, 500, 563, 695, 715, 791, 808, 820, 837, 877, 926, 1018, 1031, 1037, 1080, 1107, 1140, 1166, 1199, 1208, 1248, 1263, 1288, 1339, 1371, 1413, 1441, 1443, 1446, 1464, 1472, 1487, 1503, 1536, 1551, 1562, 1763, 1887, 3067, 3091, 3104, 3127, 3157, 3169, 3182, 3192, 3195, 3252, 4026	0.765
TS2	1279*i*, 30, 51, 54, 67, 91, 103, 139, 178, 193, 211, 238, 249, 277, 321, 342, 450, 469, 525, 597, 687, 716, 784, 809, 816, 840, 882, 922, 1012, 1037, 1055, 1084, 1112, 1125, 1168, 1189, 1204, 1223, 1270, 1341, 1355, 1373, 1420, 1441, 1451, 1464, 1467, 1484, 1533, 1534, 1541, 1552, 1563, 1763, 1865, 3052, 3102, 3116, 3147, 3153, 3179, 3182, 3184, 3197, 3216, 4023	0.775
TS3	273*i*, 25, 28, 35, 68, 80, 97, 107, 142, 169, 207, 237, 273, 325, 338, 343, 444, 497, 568, 593, 684, 706, 788, 808, 836, 859, 921, 992, 1032, 1047, 1065, 1091, 1129, 1157, 1177, 1212, 1225, 1326, 1329, 1355, 1372, 1408, 1431, 1455, 1474, 1477, 1502, 1526, 1544, 1550, 1552, 1565, 1732, 1854, 1885, 3103, 3112, 3122, 3128, 3151, 3166, 3195, 3196, 3202, 3208, 3992	0.771
TS4	1322*i*, 17, 30, 51, 64, 87, 100, 128, 170, 205, 214, 231, 258, 278, 321, 343, 367, 467, 536, 586, 685, 713, 778, 799, 837, 853, 871, 936, 1020, 1034, 1078, 1095, 1107, 1132, 1162, 1184, 1209, 1226, 1257, 1326, 1350, 1387, 1434, 1441, 1451, 1459, 1474, 1482, 1502, 1543, 1545, 1553, 1761, 1887, 3105, 3115, 3119, 3127, 3149, 3163, 3176, 3194, 3197, 3202, 4021	0.774
TS5	953*i*, 20, 35, 45, 72, 95, 97, 121, 169, 180, 217, 260, 324, 342, 429, 443, 490, 502, 568, 573, 678, 729, 786, 807, 837, 859, 890, 924, 1017, 1033, 1042, 1063, 1106, 1133, 1158, 1195, 1218, 1273, 1281, 1333, 1344, 1376, 1419, 1427, 1440, 1459, 1472, 1478, 1498, 1510, 1522, 1545, 1552, 1762, 1879, 3074, 3088, 3121, 3127, 3148, 3161, 3193, 3194, 3200, 3237, 3991	0.764

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ER2	12, 44, 55, 58, 63, 82, 100, 111, 168, 193, 228, 250, 270, 310, 325, 342, 440, 486, 498, 573, 659, 692, 790, 807, 832, 864, 923, 954, 1032, 1041, 1075, 1101, 1129, 1170, 1200, 1208, 1266, 1323, 1340, 1373, 1423, 1437, 1443, 1465, 1476, 1485, 1513, 1538, 1545, 1552, 1555, 1563, 1754, 1884, 3035, 3073, 3091, 3109, 3139, 3150, 3171, 3176, 3186, 3198, 3205, 4003	0.757
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EP5	17, 24, 32, 64, 79, 84, 96, 107, 144, 191, 216, 252, 279, 322, 339, 400, 429, 511, 564, 661, 667, 679, 719, 741, 781, 815, 844, 862, 995, 1036, 1042, 1109, 1124, 1153, 1183, 1216, 1265, 1281, 1333, 1371, 1415, 1438, 1440, 1463, 1470, 1476, 1496, 1508, 1516, 1545, 1552, 1846, 1878, 3044, 3093, 3122, 3126, 3146, 3147, 3191, 3193, 3199, 3203, 3306, 3585, 4003	0.755
$CH_2CH_2C(O)CH(OH)C_2H_5$	26, 93, 101, 156, 188, 234, 236, 263, 323, 342, 427, 458, 534, 563, 665, 781, 812, 899, 944, 1034, 1041, 1101, 1122, 1154, 1169, 1211, 1225, 1285, 1338, 1370, 1436, 1438, 1461, 1469, 1482, 1499, 1536, 1550, 1562, 1882, 3079, 3087, 3088, 3104, 3119, 3156, 3182, 3186, 3242, 3358, 4024	0.755
$CH_3CHC(O)CH(OH)C_2H_5$	42, 98, 108, 133, 204, 233, 244, 261, 328, 347, 440, 548, 595, 684, 763, 806, 846, 926, 1036, 1037, 1077, 1108, 1147, 1170, 1195, 1227, 1290, 1338, 1371, 1439, 1448, 1458, 1473, 1491, 1531, 1536, 1541, 1550, 1562, 1639, 3087, 3091, 3102, 3119, 3131, 3154, 3180, 3184, 3219, 3302, 4024	0.780
$CH_3CH_2C(O)C(OH)C_2H_5$	35, 56, 98, 177, 216, 224, 239, 325, 341, 361, 416, 540, 581, 629, 778, 818, 827, 929, 1024, 1055, 1102, 1119, 1128, 1148, 1231, 1319, 1327, 1371, 1419, 1430, 1468, 1471, 1516, 1529, 1544, 1549, 1550, 1553, 1569, 1675, 3076, 3109, 3115, 3124, 3140, 3169, 3190, 3194, 3199, 3210, 3998	0.776
$C_2H_5C(O)CH(OH)CH_2CH_3$	20, 79, 85, 122, 182, 211, 217, 247, 305, 319, 428, 487, 541, 640, 652, 784, 840, 917, 1020, 1034, 1062, 1103, 1118, 1163, 1180, 1221, 1262, 1318, 1340, 1398, 1436, 1450, 1473, 1477, 1500, 1530, 1542, 1545, 1553, 1882, 3013, 3030, 3124, 3126, 3130, 3149, 3189, 3192, 3200, 3278, 4022	0.756
$C_2H_5C(O)CH(OH)CH_2CH_2$	26, 88, 117, 151, 185, 220, 246, 313, 326, 343, 429, 521, 547, 574, 674, 786, 848, 870, 919, 1035, 1084, 1101, 1110, 1162, 1174, 1197, 1271, 1291, 1325, 1356, 1430, 1436, 1470, 1477, 1498, 1511, 1523, 1546, 1553, 1877, 3079, 3084, 3123, 3126, 3146, 3147, 3192, 3199, 3217, 3326, 3989	0.755

Table S2 The relative energy (Δ*E*), enthalpy (Δ*H*), and Gibbs free energy (Δ*G*) of the H-abstraction reaction of 4H4M2P with the NO_3 radical calculated at CCSD(T)//BH&HLYP/6–311++G(d,p) levels (kcal/mol).

Pathways	stationary points	Δ*E*	Δ*H*	Δ*G*
	4H4M2P+NO_3	0	0	0
Path1	ER1	-1.06	-1.26	10.29
	TS1	5.97	6.03	15.72
	EP1	-7.49	-6.85	1.93
	P1	-1.47	-1.18	-1.86
Path2	ER2	-0.63	-1.04	9.87
	TS2	8.34	8.22	18.94
	EP2	-17.09	-16.84	-7.31
	P2	-6.91	-7.08	-6.77
Path3	ER3	-1.25	-1.50	7.68
	TS3	4.72	4.79	15.68
	EP3	-20.23	-19.76	-10.75
	P3	-9.57	-9.39	-10.52
Path4	ER4	-0.58	-0.87	10.03
	TS4	7.63	7.74	17.42
	EP4	-15.24	-14.71	-5.30
	P4	-1.03	-0.65	-1.65

Table S3 Calculated CVT/SCT rate constant values (in cm^3 $molecule^{-1}$ s^{-1}) for the H atom abstraction reaction of 4H4M2P with the NO_3 radical at BH&HLYP/6-311++G(d,p) level of theory.

Temperature(*K*)	k_{path1} ($\times10^{-17}$)	k_{path2} ($\times10^{-18}$)	k_{path3} ($\times10^{-16}$)	k_{path4} ($\times10^{-18}$)	k_{total} ($\times10^{-16}$)
260	0.79	1.33	3.03	0.67	3.13
270	1.46	1.88	3.42	1.18	3.60
280	2.60	2.60	3.88	2.02	4.19
290	4.47	3.55	4.41	3.38	4.93
298	6.76	4.51	4.89	5.02	5.66
300	7.48	4.78	5.02	5.53	5.87
310	12.20	6.35	5.72	8.87	7.09
320	19.30	8.34	6.52	14.00	8.67
330	29.90	10.80	7.43	21.60	10.74

Table S4 The T1 diagnostic and $<s^2>$ values of the main species for the reaction of $CH_3CH_2C(O)C(OO•)(OH)CH_2CH_3$ with NO radical on the singlet surface at the CCSD(T)//BH&HLYP/6-311++G(d,p) level of theory.

Species	A	NO	IM1	IM2	IM3	Propionic acid
T1	0.020	0.022	0.017	0.017	0.016	0.014
$<s^2>$	0.758	0.755	0	0	0	0
Species	TS6	TS7	TS8	TS9	NO_2	Propionyl
T1	0.015	0.022	0.040	0.028	0.024	0.018
$<s^2>$	0	0	0	0	0.757	0.750