Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The Effect of Hydrogen Bonding on the Reactivity of OH Radicals with Prenol and Isoprenol: A Shock Tube and Multi-Structural Torsional Variational Transition State Theory Study

Samah Y. Mohamed, M. Monge-Palacios, Binod Raj Giri , Fethi Khaled, Dapeng Liu, Aamir Farooq, and S. Mani Sarathy

Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia

Table S 1: Calculated energies (a.u) for the stationary points and pre-reaction complexes (PRC) of the potential energy surfaces (PESs) of the reactions prenol+OH and isoprenol+OH using the M062X/6-311++G(2df,2pd) and UCCSD(T)/jun-cc-pVQZ//M062X/6-311++G(2df,2pd) levels of theory along with their corresponding T1 diagnostic values**.**

Reaction	**Species**	**M062X/6-311++G(2df,2pd)**	**UCCSD(T)/jun-cc-pVQZ**	**T1 diagnostic**
Prenol+OH				
Prenol		-271.7187535	-271.3747831	0.010
OH		-75.72958500	-75.66350420	0.009
HO_2		-76.42570860	-76.36172840	0.009
absC1	Saddle point	-347.4502679	-347.0386091	0.018
	Product	-271.0824904	-270.7336089	0.022
absC2	Saddle point	-347.4460364	-347.0337637	0.021
	Product	-271.0380038	-270.6897704	0.023
absC4	Saddle point	-347.4462428	-347.0349292	0.019
	Product	-271.0688847	-270.7225500	0.022
absC5	Saddle point	-347.4502498	-347.0387938	0.021
	Product	-271.0681214	-270.7219532	0.022
absO	Saddle point	-347.4469929	-347.0325756	0.022
	Product	-271.0422650	-270.6939594	0.016
addC2	Saddle point	-347.4571225	-347.0457696	0.025
	Product	-347.5102924	-347.0948437	0.012
	PRC	-347.4581516		
addC3	Saddle point	-347.4631760	-347.0517423	0.027
	Product	-347.5078864	-347.0931887	0.012
Isoprenol+OH				
Isoprenol		-271.7202105	-271.3759987	0.010
absC1	Saddle point	-347.4526623	-347.0410270	0.018
	Product	-271.0624732	-270.7145798	0.014
absC2	Saddle point	-347.4517126	-347.0396230	0.019
	Product	-271.0689475	-270.7227054	0.022
absC4	Saddle point	-347.4458897	-347.0326293	0.022
	Product	-271.0356558	-270.6866663	0.024
absC5	Saddle point	-347.4518405	-347.0395286	0.020
	Product	-271.0689768	-270.7230394	0.021
absO	Saddle point	-347.4483183	-347.0334049	0.023
	Product	-271.0415735	-270.6940688	0.015
addC3	Saddle point	-347.4607744	-347.0487234	0.026
	Product	-347.5039858	-347.0898306	0.011
	PRC	-347.4614147		
addC4	Saddle point	-347.4623087	-347.0495599	0.026
	Product	-347.5069706	-347.0915122	0.012
	PRC	-347.4627878		

Table S 2: Frequencies and rotational constants of the stationary points on the PESs of the reactions prenol+OH and isoprenol+OH at the M062X/6-311++G(2df,2pd) level of theory

Reaction	Species	Frequencies (cm^{-1})	A	B	C
Prenol+OH					
Prenol		60, 129, 152, 214, 285, 330, 375, 435, 506, 522, 793, 883, 962, 970, 1017, 1061, 1081, 1108, 1147, 1196, 1251, 1339, 1380, 1414, 1423, 1427, 1476, 1487, 1496, 1500, 1522, 1766, 3050, 3057, 3070, 3101, 3104, 3105, 3149, 3161, 3172, 3891	6.83287	1.88486	1.61842
absC1	Saddle point	i752, 23, 98, 110, 130, 159, 208, 229, 281, 372, 404, 439, 493, 509, 690, 792, 865, 945, 970, 1008, 1013, 1057, 1110, 1117, 1172, 1237, 1267, 1368, 1395, 1415, 1426, 1430, 1476, 1488, 1497, 1503, 1759, 1908, 3052, 3058, 3092, 3103, 3106, 3143, 3152, 3189, 3789, 3873	3.3737	1.45523	1.07512
	Product *(HO_2)*	88, 145, 187, 193, 225, 344, 403, 414, 450, 537, 752, 842, 892, 979, 996, 1045, 1065, 1102, 1196, 1256, 1318, 1362, 1409, 1416, 1454, 1476, 1486, 1499, 1516, 1539, 3025, 3029, 3064, 3071, 3134, 3137, 3139, 3244, 3876 *(1627, 3885, 3988)*	7.76608 (*831.8577*)	1.88036 (*432.7341*)	1.54247 (*284.6557*)
absC2	Saddle point	i1089, 79, 90, 115, 146, 155, 209, 252, 304, 360, 419, 438, 460, 521, 576, 831, 875, 934, 969, 985, 993, 1072, 1085, 1106, 1160, 1211, 1253, 1349, 1405, 1410, 1421, 1477, 1483, 1491, 1496, 1503, 1523, 1770, 3053, 3054, 3061, 3108, 3110, 3113, 3158, 3166, 3769, 3879	2.97295	1.66554	1.13588
	Product	57, 136, 158, 207, 218, 277, 344, 419, 486, 544, 786, 950, 959, 973, 1013, 1085, 1098, 1168, 1201, 1229, 1327, 1396, 1408, 1419, 1476, 1482, 1489, 1494, 1500, 1787, 2974, 3053, 3057, 3097, 3108, 3111, 3158, 3160, 3894	6.98437	1.8536	1.60805
absC4	Saddle point	i809, 40, 60, 81, 126, 152, 165, 274, 305, 329, 375, 436, 509, 516, 740, 799, 869, 931, 975, 992, 1059, 1072, 1086, 1146, 1196, 1250, 1340, 1344, 1381, 1390, 1420, 1426, 1466, 1489, 1496, 1517, 1562, 1759, 3060, 3070, 3086, 3103, 3111, 3159, 3168, 3178, 3796, 3890	4.57624	1.02322	0.98648
	Product	88, 131, 170, 233, 284, 390, 435, 479, 578, 593, 742, 817, 851, 933, 998, 1023, 1046, 1063, 1127, 1210, 1251, 1350, 1388, 1412, 1424, 1433, 1491, 1506, 1520, 1539, 3057, 3068, 3098, 3130, 3158, 3170, 3186, 3267, 3886	6.55862	2.27536	1.91433
absC5	Saddle point	i1067, 53, 78, 139, 180, 210, 276, 316, 330, 379, 418, 489, 563, 604, 796, 850, 886, 966, 968, 989, 1022, 1046, 1081, 1104, 1140, 1198, 1265, 1336, 1367, 1387, 1411, 1422, 1477, 1486, 1498, 1528, 1552, 1731, 3056, 3072, 3108, 3111, 3125, 3151, 3175, 3177, 3681, 3877	2.6428	1.94772	1.31326
	Product	26, 61, 146, 230, 324, 373, 454, 487, 522, 583, 708, 839, 881, 927, 999, 1049, 1063, 1092, 1138, 1199, 1260, 1294, 1366, 1400, 1415, 1482, 1491, 1499, 1500, 1558, 3043, 3069, 3073, 3130, 3153, 3174, 3185, 3275, 3888	7.7973	1.86134	1.57231

absO	Saddle point	i1306, 54, 78, 125, 153, 169, 215, 229, 320, 377, 419, 450, 502, 541, 788, 839, 884, 905, 965, 1000, 1014, 1066, 1074, 1108, 1141, 1231, 1282, 1349, 1402, 1415, 1424, 1470, 1474, 1490, 1495, 1504, 1617, 1756, 3041, 3052, 3058, 3102, 3105, 3107, 3151, 3167, 3180, 3790	3.51326	1.5042	1.32371
	Product*	42, 111, 175, 199, 252, 348, 453, 462, 492, 513, 847, 857, 964, 1009, 1037, 1085, 1106, 1133, 1140, 1218, 1320, 1363, 1394, 1417, 1422, 1477, 1487, 1497, 1499, 1770, 2934, 2961, 3034, 3038, 3087, 3089, 3140, 3141, 3158	7.61224	1.88195	1.55242
addC2	Saddle point	i191, 58, 89, 115, 121, 148, 196, 234, 292, 334, 383, 427, 475, 546, 654, 790, 893, 961, 970, 998, 1062, 1082, 1093, 1147, 1184, 1266, 1341, 1373, 1406, 1413, 1421, 1473, 1478, 1494, 1496, 1528, 1679, 3050, 3061, 3089, 3103, 3113, 3146, 3147, 3172, 3176, 3823, 3892	3.10263	1.67878	1.4459
	Product	57, 110, 132, 142, 174, 263, 293, 309, 328, 421, 434, 503, 557, 824, 896, 944, 977, 1004, 1021, 1059, 1102, 1129, 1196, 1247, 1285, 1320, 1340, 1390, 1395, 1412, 1419, 1432, 1472, 1479, 1487, 1502, 1504, 2993, 2997, 3020, 3034, 3075, 3075, 3118, 3125, 3143, 3867, 3890	3.9616	1.65873	1.46415
addC3	Saddle point	i191, 82, 141, 177, 185, 216, 241, 319, 335, 368, 392, 501, 524, 649, 716, 782, 879, 958, 971, 1000, 1068, 1083, 1098, 1141, 1211, 1266, 1348, 1384, 1413, 1423, 1454, 1470, 1482, 1490, 1502, 1526, 1648, 3058, 3063, 3069, 3100, 3120, 3135, 3151, 3167, 3186, 3765, 3824	3.83131	1.671	1.58311
	Product	41, 144, 234, 239, 275, 281, 316, 342, 378, 418, 451, 517, 548, 629, 762, 899, 936, 977, 997, 1007, 1013, 1098, 1132, 1188, 1213, 1273, 1349, 1364, 1387, 1402, 1414, 1419, 1478, 1486, 1500, 1502, 1510, 3056, 3062, 3067, 3102, 3130, 3139, 3147, 3150, 3204, 3826, 3875	4.12296	1.81061	1.71938
Isoprenol+OH					
isoprenol		67, 143, 193, 246, 369, 394, 423, 447, 575, 740, 785, 895, 944, 958, 1002, 1012, 1071, 1092, 1123, 1213, 1224, 1307, 1359, 1379, 1414, 1430, 1449, 1479, 1488, 1501, 1523, 1736, 3026, 3055, 3063, 3108, 3116, 3121, 3151, 3160, 3244, 3847	5.29015	2.46772	2.11741
absC1	Saddle point	i695, 48, 104, 114, 146, 199, 241, 250, 398, 420, 448, 467, 573, 675, 752, 783, 906, 934, 958, 998, 1008, 1036, 1075, 1091, 1174, 1221, 1287, 1309, 1363, 1415, 1418, 1443, 1451, 1477, 1491, 1504, 1733, 1874, 3057, 3064, 3114, 3117, 3118, 3153, 3160, 3244, 3787, 3804	2.86957	1.79716	1.39367
	Product	66, 131, 185, 234, 391, 414, 438, 459, 552, 647, 751, 838, 918, 958, 971, 1005, 1044, 1074, 1183, 1201, 1298, 1318, 1362, 1410, 1442, 1446, 1469, 1482, 1498, 1735, 2993, 3055, 3097, 3110, 3152, 3160, 3225, 3244, 3804	5.29518	2.5232	2.25589
absC2	Saddle point	i955, 73, 82, 169, 171, 200, 270, 326, 360, 419, 449, 503, 540, 698, 770, 826, 890, 950, 958, 1001, 1015, 1049, 1065, 1122, 1156, 1211, 1252, 1281, 1365, 1385,	2.83967	1.96686	1.40736

		1414, 1426, 1452, 1484, 1499, 1516, 1584, 1724, 3038, 3057, 3083, 3114, 3128, 3156, 3165, 3246, 3736, 3863			
	Product	47, 143, 174, 250, 313, 379, 471, 495, 517, 581, 751, 831, 853, 924, 1001, 1016, 1058, 1083, 1152, 1200, 1243, 1342, 1386, 1401, 1429, 1458, 1491, 1501, 1512, 1534, 3047, 3068, 3080, 3127, 3154, 3171, 3179, 3270, 3886	7.26553	1.95374	1.64642
absC4	Saddle point	i1503, 104, 119, 152, 176, 206, 230, 357, 380, 401, 447, 532, 563, 632, 750, 789, 877, 889, 945, 974, 1007, 1052, 1080, 1109, 1125, 1203, 1230, 1286, 1361, 1391, 1406, 1416, 1421, 1482, 1486, 1497, 1515, 1723, 3041, 3055, 3073, 3111, 3126, 3133, 3156, 3205, 3728, 3851	2.73219	2.02356	1.38195
	Product	64, 171, 188, 254, 335, 370, 403, 432, 541, 711, 775, 870, 888, 973, 999, 1020, 1095, 1128, 1186, 1219, 1254, 1379, 1392, 1403, 1429, 1460, 1486, 1487, 1512, 1711, 3033, 3043, 3057, 3082, 3116, 3119, 3157, 3262, 3865	6.97823	2.23952	1.91239
absC5	Saddle point	i990, 70, 94, 143, 198, 219, 252, 343, 403, 426, 439, 566, 568, 710, 785, 831, 893, 952, 967, 997, 1003, 1021, 1077, 1121, 1156, 1178, 1273, 1302, 1331, 1343, 1379, 1414, 1437, 1455, 1472, 1490, 1529, 1724, 3048, 3061, 3089, 3093, 3119, 3165, 3172, 3250, 3676, 3880	2.51966	2.15185	1.50305
	Product	60, 143, 230, 373, 396, 433, 446, 538, 583, 630, 801, 807, 841, 890, 975, 986, 1038, 1056, 1118, 1186, 1218, 1312, 1337, 1384, 1400, 1428, 1480, 1489, 1516, 1542, 3026, 3075, 3118, 3125, 3165, 3175, 3267, 3269, 3857	5.55997	2.56175	2.16501
absO	Saddle point	i1374, 81, 96, 135, 171, 187, 274, 349, 404, 423, 437, 450, 567, 733, 775, 823, 895, 942, 957, 993, 1014, 1045, 1077, 1110, 1112, 1237, 1277, 1310, 1369, 1401, 1415, 1447, 1466, 1475, 1493, 1499, 1542, 1733, 3037, 3053, 3058, 3081, 3115, 3120, 3148, 3160, 3244, 3771	2.87169	1.96264	1.62227
	Product	17, 96, 180, 200, 338, 399, 461, 532, 580, 729, 848, 869, 958, 992, 1014, 1033, 1071, 1092, 1142, 1249, 1300, 1318, 1360, 1381, 1415, 1452, 1482, 1492, 1501, 1742, 2940, 2991, 3054, 3066, 3106, 3123, 3150, 3164, 3248	7.19227	1.9485	1.68139
addC3	Saddle point	i198, 90, 168, 182, 205, 227, 276, 286, 347, 392, 436, 554, 561, 671, 691, 784, 877, 942, 964, 1000, 1016, 1043, 1097, 1156, 1242, 1258, 1296, 1377, 1403, 1417, 1441, 1454, 1476, 1482, 1496, 1541, 1629, 3017, 3049, 3063, 3075, 3093, 3130, 3159, 3167, 3264, 3709, 3824	3.60013	1.9147	1.6512
	Product	47, 148, 200, 249, 266, 305, 340, 360, 408, 428, 460, 494, 508, 580, 751, 879, 916, 925, 973, 985, 1053, 1123, 1132, 1179, 1200, 1264, 1294, 1340, 1380, 1394, 1406, 1450, 1456, 1466, 1496, 1499, 1520, 3018, 3058,	4.20945	1.78556	1.71671

		3062, 3104, 3110, 3132, 3150, 3171, 3282, 3853, 3873			
addC4	Saddle point	i188, 45, 113, 128, 158, 214, 240, 297, 395, 424, 437, 566, 614, 706, 763, 792, 886, 952, 959, 1001, 1012, 1055, 1084, 1130, 1218, 1241, 1315, 1346, 1402, 1412, 1438, 1470, 1478, 1485, 1500, 1515, 1654, 3024, 3056, 3062, 3109, 3111, 3125, 3163, 3168, 3261, 3629, 3810	2.86216	2.17606	1.62456
	Product	50, 95, 101, 175, 189, 259, 323, 371, 416, 484, 561, 594, 747, 868, 921, 980, 995, 1004, 1023, 1048, 1115, 1187, 1205, 1228, 1236, 1304, 1350, 1354, 1402, 1408, 1438, 1447, 1472, 1481, 1491, 1516, 1518, 3013, 3020, 3030, 3046, 3080, 3083, 3097, 3108, 3126, 3776, 3880	3.05245	2.26024	1.60474

*These frequency were calculated at the M062X/6-311++G(2df,2pd) level of theory but without Ultrafine keyword.

Table S 3: Optimized Cartesian coordinates (angstrom) of the stationary points on the PES of the reaction prenol+OH at the M062X/6-311++G(2df,2pd) level of theory

Prenol

C	-1.559705	0.207458	-0.476209
C	-0.276057	-0.542571	-0.305640
C	0.932642	-0.046795	-0.043165
C	2.120966	-0.954578	0.109823
C	1.258724	1.412174	0.110420
O	-2.543370	-0.220796	0.455542
H	-1.986570	-0.001996	-1.457765
H	-1.412039	1.286791	-0.410411
H	-0.379507	-1.620485	-0.390851
H	2.575935	-0.825974	1.094405
H	2.889096	-0.705757	-0.625895
H	1.849544	-2.000635	-0.013951
H	0.386813	2.058543	0.088572
H	1.786181	1.577377	1.052066
H	1.936015	1.729019	-0.685762
H	-2.157938	-0.184634	1.333881

abs1_saddle point

C	-0.10807	-0.01618	0.130624
C	0.023952	-0.28311	1.593188
C	1.069738	-0.04674	2.384126
C	1.016645	-0.39936	3.843754
C	2.375264	0.547884	1.940932
O	-1.3165	0.61868	-0.2016
H	-1.46955	1.325333	0.431959
H	-0.06308	-0.9274	-0.46761
H	-0.86707	-0.72756	2.030441
H	1.182621	0.490207	4.454912
H	0.062629	-0.84142	4.122498

absC1_product

C	1.460499	0.302874	-0.000002
C	0.345369	-0.502018	0.000001
C	-0.964534	-0.054019	0.000000
C	-2.114620	-1.007195	-0.000001
C	-1.267369	1.413054	0.000001
O	2.736530	-0.157536	0.000000
H	1.419157	1.381217	-0.000007
H	0.512687	-1.577047	0.000004
H	-2.753156	-0.855454	-0.875721
H	-2.753177	-0.855430	0.875699
H	-1.781403	-2.043796	0.000017

H	1.812777	-1.10423	4.092729	H	-0.843533	1.909513	-0.878049
H	3.168724	-0.19588	2.044877	H	-2.340738	1.594429	-0.000052
H	2.37129	0.905915	0.916702	H	-0.843625	1.909491	0.878109
H	2.641676	1.37989	2.595583	H	2.735475	-1.118804	0.000007
H	0.762163	0.630701	-0.24103				
O	1.334037	1.760322	-1.07054				
H	0.510712	1.867214	-1.57316				
absC2_ saddle point				absC2_product			
C	-0.09875	-0.03724	0.081553	C	-1.613893	0.149007	-0.505221
C	-0.04045	-0.01321	1.570348	C	-0.282862	-0.451539	-0.308979
C	0.961366	0.00212	2.434595	C	0.943318	-0.062910	-0.049814
C	0.711967	-0.01881	3.91686	C	2.077024	-1.047972	0.067261
C	2.412346	0.063478	2.035232	C	1.330485	1.385483	0.144313
O	-0.91428	-1.1059	-0.38137	O	-2.563614	-0.259935	0.461550
H	0.902877	-0.09546	-0.35315	H	-2.024030	-0.142439	-1.472487
H	-0.5727	0.869319	-0.29468	H	-1.519473	1.245356	-0.513669
H	-1.14611	-0.05778	2.024745	H	2.541841	-0.973344	1.052471
H	1.119431	0.881389	4.381381	H	2.849528	-0.822596	-0.670771
H	1.221607	-0.87063	4.371438	H	1.733994	-2.068238	-0.083615
H	-0.34976	-0.08236	4.142663	H	0.476969	2.056479	0.089672
H	2.562892	0.017541	0.960361	H	1.813736	1.514607	1.114466
H	2.857495	0.989919	2.40301	H	2.053773	1.682751	-0.617398
H	2.958863	-0.75878	2.500532	H	-2.141856	-0.245514	1.323567
H	-0.54336	-1.93052	-0.05625				
O	-2.43186	-0.3513	2.153309				
H	-2.53037	-0.76301	1.278713				
abs4_ saddle point				absC4_product			
C	-0.06043	-0.29277	0.022397	C	1.496940	-0.334070	0.522242
C	0.059756	-0.28746	1.514118	C	0.136709	-0.883515	0.240768
C	1.117608	0.063517	2.25133	C	-0.987596	-0.079620	0.033479
C	1.048128	0.005249	3.736452	C	-2.198763	-0.641566	-0.278818
C	2.456042	0.487785	1.717036	C	-0.857727	1.418082	0.168628
O	-1.16863	0.48024	-0.41204	O	2.083731	0.300277	-0.614256
H	1.756714	-0.83108	4.101364	H	2.154236	-1.122899	0.894803
O	2.574238	-2.05914	4.173994	H	1.451951	0.445184	1.284642
H	1.455565	0.896366	4.21574	H	0.022165	-1.957659	0.158580
H	0.05809	-0.22462	4.121589	H	-2.306283	-1.713605	-0.370206
H	-0.26307	-1.30498	-0.33073	H	-3.076828	-0.033747	-0.441458
H	0.858694	0.042714	-0.46053	H	-0.039151	1.793254	-0.443639
H	-0.84995	-0.5817	2.030005	H	-1.778636	1.915682	-0.126089
H	3.222092	-0.20487	2.071733	H	-0.642627	1.691330	1.203032
H	2.500163	0.525702	0.63327	H	2.007940	-0.295622	-1.363406
H	2.717499	1.472503	2.10908				
H	-1.0782	1.365948	-0.05308				
H	2.017629	-2.57484	3.569433				
absC5_ saddle point				absC5_product			

C	0.011483	0.095071	0.028096	C	-1.502992	0.356637	0.295710
C	0.003219	0.020282	1.527059	C	-0.249101	-0.442953	0.192898
C	1.105442	0.002638	2.283121	C	1.039502	0.060555	0.002800
C	1.033534	0.040909	3.781356	C	2.174655	-0.937753	-0.035759
C	2.471827	0.010587	1.700105	C	1.315017	1.398181	-0.125872
O	0.357325	1.398	-0.4554	O	-2.621538	-0.338706	-0.228049
H	2.769582	1.120493	1.474693	H	-1.391341	1.329855	-0.189764
O	2.832181	2.366582	0.802989	H	-1.748795	0.548839	1.343768
H	3.235416	-0.34132	2.391	H	-0.376120	-1.512783	0.318018
H	2.558318	-0.49704	0.743172	H	2.322318	-1.388326	0.946028
H	0.757156	-0.57207	-0.40104	H	3.107012	-0.463327	-0.333811
H	-0.95993	-0.19733	-0.3744	H	1.959410	-1.743228	-0.737290
H	-0.96373	0.037144	2.018196	H	2.329382	1.739280	-0.272613
H	1.566273	0.916777	4.157297	H	0.545387	2.153907	-0.085379
H	0.005895	0.079531	4.135983	H	-2.437442	-0.562581	-1.143221
H	1.520771	-0.83658	4.210239				
H	-0.24943	2.033135	-0.06544				
H	2.088316	2.15788	0.206331				
absO_ saddle point				absO_product			
C	0.001897	0.046851	-0.04318	C	1.571493	0.328473	0.003317
C	0.020611	-0.03042	1.453743	C	0.328662	-0.519970	0.003487
C	1.094435	-0.01463	2.244364	C	-0.920354	-0.067175	0.000262
C	0.951314	-0.09686	3.738628	C	-2.098642	-0.997065	-0.001092
C	2.515841	0.091876	1.767261	C	-1.266411	1.395339	-0.001591
O	-0.48888	-1.13656	-0.63115	O	2.744206	-0.365187	-0.006531
H	0.973662	0.311126	-0.45999	H	1.612946	1.001428	0.878968
H	-0.7093	0.818549	-0.35643	H	1.598709	1.029354	-0.849300
H	-0.95781	-0.1303	1.913234	H	0.519542	-1.587747	0.006421
H	1.395058	0.783023	4.209658	H	-2.724353	-0.821985	-0.879088
H	-0.09067	-0.16394	4.043455	H	-2.727437	-0.821043	0.874498
H	1.487522	-0.96431	4.129288	H	-1.787888	-2.039543	-0.000030
H	2.94678	1.04489	2.081786	H	-0.392198	2.042217	0.001079
H	2.620297	-0.00063	0.690927	H	-1.868324	1.640424	-0.879369
H	3.119098	-0.69132	2.231077	H	-1.873130	1.640781	0.872774
H	0.266968	-1.88673	-0.61316				
O	1.196029	-2.55382	-0.03472				
H	1.00339	-2.44312	0.909582				
addC2_ saddle point				addC2_product			
C	0.005063	0.00351	-0.00127	C	-1.154912	-0.562887	0.624560
C	0.005312	-0.0003	1.497268	C	-0.292224	-0.001172	-0.502465
C	1.08996	-0.00756	2.304353	C	1.159977	0.015417	-0.153840
C	0.939667	0.077416	3.79243	C	1.981187	-1.192113	-0.447330
C	2.49899	-0.15604	1.823014	C	1.651983	0.974990	0.875958
O	-0.20793	1.309425	-0.51778	O	-2.515420	-0.593409	0.268926
O	0.196565	-2.21193	1.603738	O	-0.820951	1.302186	-0.737220
H	1.383668	-0.80274	4.263255	H	-0.992806	0.046892	1.520972

H	-0.10339	0.149665	4.093988	H	-0.852210	-1.587008	0.841947
H	0.920122	-0.43836	-0.3969	H	1.002560	1.845055	0.954524
H	-0.82426	-0.60162	-0.35864	H	2.664756	1.313080	0.645934
H	3.130738	0.612198	2.273013	H	1.702583	0.503761	1.866722
H	2.886134	-1.12441	2.14599	H	1.958574	-1.908223	0.385531
H	2.594678	-0.09794	0.743228	H	1.628638	-1.718295	-1.334665
H	-0.96591	0.150696	1.957741	H	3.030196	-0.928147	-0.595638
H	1.475582	0.946054	4.181201	H	-0.452695	-0.628568	-1.387397
H	-0.37133	-2.29819	2.382469	H	-0.338179	1.706768	-1.461708
H	0.474553	1.889305	-0.17253	H	-2.736509	0.279056	-0.071169
addC3_ saddle point				addC3_product			
C	0.002726	0.001248	0.003074	C	-1.707387	-0.750735	-0.184254
C	0.005043	-0.0058	1.49939	C	-0.349357	-0.634075	-0.768699
C	1.097679	-0.00618	2.313652	C	0.768789	0.005313	0.006819
C	0.932553	-0.01819	3.803777	C	1.173654	1.331367	-0.649990
C	2.499033	0.228861	1.839533	C	1.969960	-0.934452	0.073713
O	-0.42762	-1.24928	-0.4917	O	-2.233174	0.531781	0.196852
O	1.076859	-2.0971	1.794428	O	0.384694	0.235250	1.353438
H	3.184839	-0.38121	2.424743	H	-1.681577	-1.316349	0.749254
H	2.766935	1.27682	1.992675	H	-2.391555	-1.255181	-0.868024
H	2.633746	-0.0184	0.791834	H	1.484618	1.178148	-1.683667
H	-0.97061	-0.1256	1.960543	H	1.997709	1.776721	-0.092696
H	0.983802	0.268057	-0.39496	H	0.332619	2.026161	-0.642866
H	-0.71067	0.743367	-0.35867	H	1.686940	-1.864562	0.564033
H	1.249911	0.941095	4.21892	H	2.338042	-1.158870	-0.926889
H	-0.09953	-0.19719	4.099305	H	2.767507	-0.464556	0.648592
H	1.569892	-0.78724	4.240064	H	-0.149348	-0.976352	-1.775238
H	0.078924	-1.91104	-0.00053	H	-2.292393	1.076505	-0.592593
H	0.355743	-2.39583	2.365754	H	-0.438673	0.737581	1.352227
addC2_PRC							
C	-1.5957	0.204876	0.107828				
C	-0.29271	0.011639	-0.60256				
C	0.85704	-0.45438	-0.09481				
C	2.079161	-0.58371	-0.95673				
C	1.065926	-0.87213	1.330487				
O	-2.62167	-0.59891	-0.45792				
H	-2.33096	-1.51347	-0.44224				
H	-1.50098	0.025389	1.179468				
H	-1.93035	1.234643	-0.01511				
H	-0.3202	0.254858	-1.66195				
H	2.883677	0.035744	-0.55419				
H	1.886311	-0.28332	-1.98483				
H	2.440726	-1.61414	-0.95603				
H	1.460372	-1.88977	1.361967				
H	1.81002	-0.22081	1.791446				
H	0.162839	-0.83065	1.930871				

O	0.802199	2.042106	0.587567
H	0.855518	2.379136	-0.31979

Table S 4: Optimized Cartesian coordinates (angstrom) of the stationary points on the PES of the reaction isoprenol+OH at the M062X/6-311++G(2df,2pd) level of theory

Isoprenol			
C	1.480114	-0.62277	0.003368
C	0.302453	-0.38266	0.951718
C	-0.90497	0.113301	0.201684
C	-1.20021	1.408325	0.140725
C	-1.71706	-0.93001	-0.51072
O	1.912679	0.567122	-0.61477
H	1.140542	1.018538	-0.97069
H	2.331105	-1.00484	0.565121
H	0.610058	0.348273	1.699833
H	0.068675	-1.31894	1.464413
H	-0.61353	2.142809	0.678088
H	-2.04633	1.768809	-0.42996
H	-2.51754	-0.48475	-1.09745
H	-2.15773	-1.62041	0.211467
H	-1.09164	-1.5279	-1.17656
H	1.213018	-1.37567	-0.7468

absC1_ saddle point			
C	-0.22377	-0.24549	0.298596
C	-0.09212	-0.0837	1.810851
C	1.351517	0.03223	2.225408
C	1.906772	1.221269	2.443477
C	2.120282	-1.25331	2.318949
O	0.342606	0.804071	-0.42346
H	1.158302	1.068823	0.019567
H	-1.26417	-0.33906	-0.0092
H	-0.56163	-0.94292	2.293313
H	-0.64256	0.81345	2.100635
H	2.952067	1.314854	2.707583
H	1.324907	2.133148	2.388641
H	3.163536	-1.07461	2.570097
H	1.682801	-1.89406	3.087439
H	2.074695	-1.80277	1.376959
H	0.278509	-1.23071	-0.00854
O	1.173792	-2.07271	-0.91428
H	1.229524	-1.36135	-1.57236

absC1_product			
C	-1.519395	-0.514653	0.122746
C	-0.345216	-0.262241	1.013809
C	0.878817	0.081371	0.196717
C	1.308938	1.334823	0.092245
C	1.518171	-1.062571	-0.533236
O	-1.861924	0.452233	-0.768328
H	-1.082187	0.986250	-0.965851
H	-2.366154	-1.094252	0.458002
H	-0.162717	-1.157776	1.610455
H	-0.556948	0.560879	1.709393
H	0.834178	2.139068	0.640711
H	2.161208	1.589898	-0.524135
H	2.336746	-0.729052	-1.167103
H	0.778771	-1.579203	-1.148153
H	1.904600	-1.794041	0.179621

absC2_ saddle point			
C	-0.065	0.126235	0.156501
C	0.034815	-0.13659	1.642992
C	1.400698	-0.11746	2.251899

absC2_product			
C	-1.451404	0.280418	0.408654
C	-0.240614	-0.572781	0.253955
C	1.056067	-0.122480	0.019311

C	2.519406	-0.14351	1.530499	C	2.092915	-1.019905	-0.089553
C	1.415493	-0.0567	3.751164	C	1.341081	1.356302	-0.110315
O	0.345023	1.443148	-0.17488	O	-2.545036	-0.200559	-0.360083
H	-1.10262	0.048089	-0.16219	H	-2.250093	-0.310353	-1.267220
H	0.511101	-0.61355	-0.40928	H	-1.233598	1.323249	0.163746
H	-0.56481	0.730192	2.155134	H	-1.804443	0.259379	1.443060
H	-0.51929	-1.03013	1.941415	H	-0.406441	-1.640412	0.347365
H	3.488924	-0.1354	2.009809	H	3.105476	-0.691484	-0.271834
H	2.514448	-0.20663	0.44933	H	1.918396	-2.082430	0.005534
H	0.915345	0.852715	4.088757	H	0.762457	1.800877	-0.920468
H	0.86277	-0.89956	4.17114	H	1.085094	1.890291	0.804788
H	2.429294	-0.07397	4.144282	H	2.395174	1.526033	-0.316614
H	1.243026	1.570703	0.145839				
O	-1.0549	2.048805	2.336602				
H	-0.76276	2.366948	1.463944				
absC4_ saddle point				absC4_product			
C	0.061713	0.00756	0.032968	C	-1.565041	-0.419996	-0.416165
C	-0.00813	-0.03856	1.561348	C	-0.165794	-0.932922	-0.117732
C	1.371916	0.006721	2.166651	C	0.904781	0.133399	-0.092977
C	2.059659	-1.09694	2.400063	C	0.667799	1.389281	-0.374516
C	1.940876	1.374469	2.4387	C	2.288077	-0.347602	0.281577
O	0.754278	-1.10548	-0.50226	O	-2.068076	0.415401	0.604362
H	1.675495	-1.04502	-0.22957	H	-1.495978	1.186010	0.666045
H	-0.94355	-0.03326	-0.38191	H	-1.570145	0.097306	-1.381567
H	0.525035	0.940556	-0.3029	H	-2.254607	-1.260147	-0.483555
H	-0.59919	0.810648	1.910309	H	0.115182	-1.682434	-0.864436
H	-0.51653	-0.95516	1.858752	H	-0.169457	-1.444891	0.848941
H	3.068793	-1.17187	2.785515	H	1.241562	2.299452	-0.436866
H	2.972914	1.325107	2.777599	H	2.271346	-0.784847	1.281206
H	1.898079	1.99148	1.538486	H	2.611931	-1.126553	-0.410934
H	1.345041	1.878921	3.201341	H	3.015851	0.459935	0.265151
H	1.533122	-2.18145	2.181209				
O	0.924746	-3.16766	1.661771				
H	0.68969	-2.75813	0.810675				
absC5_ saddle point				absC5_product			
C	0.000302	-0.00335	0.000792	C	-1.468668	-0.593626	-0.068565
C	0.000751	0.004128	1.525986	C	-0.269513	-0.540879	0.877906
C	1.388686	-0.00026	2.111828	C	0.958463	-0.009957	0.173711
C	1.805375	0.974747	2.916324	C	1.239114	1.339213	0.224464
C	2.27531	-1.12656	1.723845	C	1.742072	-0.885619	-0.561973
O	0.793523	1.039037	-0.54742	O	-1.848279	0.683684	-0.530112
H	0.68272	1.837551	-0.02488	H	-1.089086	1.091680	-0.957166
H	0.429997	-0.93044	-0.37955	H	-1.242180	-1.259816	-0.908663
H	-1.02536	0.068989	-0.36836	H	-2.334960	-0.996055	0.454587
H	-0.54823	0.877123	1.887185	H	-0.077568	-1.545769	1.257191
H	-0.54697	-0.88059	1.863516	H	-0.521841	0.096737	1.725447

H	2.802903	0.97097	3.335117	H	2.087244	1.750442	-0.305162
H	1.15682	1.797682	3.188294	H	0.634330	2.014485	0.812523
H	3.166049	-1.20183	2.341744	H	1.521122	-1.942801	-0.595381
H	1.756973	-2.08368	1.665325	H	2.600355	-0.533167	-1.115740
H	2.688163	-0.96389	0.63925				
O	3.117795	-0.62718	-0.66588				
H	2.514213	0.13339	-0.76922				
absO_ saddle point				absO_product			
C	0.030979	0.079345	0.011677	C	-1.397556	0.111798	-0.417474
C	-0.00218	-0.04734	1.535729	C	-0.352150	-0.348286	0.602453
C	1.360158	-0.03636	2.176379	C	1.052916	-0.128588	0.110569
C	1.773841	0.993416	2.909396	C	1.836829	-1.143807	-0.231226
C	2.219269	-1.24435	1.933895	C	1.508375	1.300318	0.015193
O	0.467478	1.339571	-0.41668	O	-2.688520	-0.030696	-0.004871
H	0.627143	-0.71304	-0.44814	H	-1.294464	1.193957	-0.617342
H	-0.99015	-0.01913	-0.37057	H	-1.244779	-0.370087	-1.394530
H	-0.60611	0.770724	1.928427	H	-0.518287	-1.405763	0.806729
H	-0.50732	-0.98609	1.782142	H	-0.522483	0.200538	1.531728
H	1.141575	1.856147	3.073704	H	2.843115	-0.982002	-0.594937
H	2.749275	0.994197	3.380162	H	1.497686	-2.168457	-0.151605
H	3.167791	-1.17005	2.461872	H	0.901827	1.864996	-0.696090
H	1.706572	-2.14959	2.265067	H	1.408833	1.798448	0.981759
H	2.431527	-1.36013	0.86958	H	2.546226	1.365325	-0.303836
H	1.513335	1.341942	-0.62944				
O	2.734734	1.149076	-0.33403				
H	2.782328	1.33575	0.617641				
addC3_ saddle point				addC3_product			
C	-0.18039	-0.10397	0.024776	C	-0.00418	-0.00644	0.005164
C	-0.05735	0.103951	1.525895	C	0.003515	0.008515	1.528895
C	1.336948	0.042929	2.091604	C	1.40331	0.004927	2.168055
C	2.403031	-0.37555	1.366838	C	2.170063	-1.22823	1.822617
C	1.435899	0.26497	3.569517	C	1.277648	0.146737	3.684028
O	0.443107	0.900473	-0.73904	O	0.364063	1.229297	-0.56441
H	1.009081	1.434745	-0.16278	H	1.158214	1.530148	-0.11133
H	-1.24049	-0.12461	-0.23659	H	-1.01503	-0.21489	-0.34473
H	0.231159	-1.08481	-0.24233	H	0.637865	-0.81587	-0.36302
H	-0.48916	1.069092	1.802348	H	-0.52993	0.898105	1.873122
H	-0.65282	-0.65857	2.038117	H	-0.53251	-0.86718	1.900763
H	3.372751	-0.48811	1.834119	H	2.730275	-1.27424	0.900892
H	2.32696	-0.57888	0.308103	H	2.04234	-2.12982	2.40301
H	0.915149	-0.53676	4.097644	H	0.744471	1.064958	3.925144
H	2.470564	0.287658	3.904917	H	0.734905	-0.69923	4.105638
H	0.957457	1.205883	3.836502	H	2.26519	0.181131	4.14682
O	1.892662	2.02853	1.391913	O	2.077236	1.15351	1.634987
H	2.858649	2.075606	1.417302	H	2.981273	1.15817	1.961618
addC4_ saddle point				addC4_product			

C	-0.08933	-0.24789	0.058594	C	-0.16731	0.023403	0.10837
C	-0.01981	0.216352	1.526377	C	-0.12334	0.017555	1.646896
C	1.355291	0.07441	2.099741	C	1.268005	0.044599	2.184554
C	2.223738	1.106094	2.11867	C	2.005959	1.331588	2.26945
C	1.756392	-1.2861	2.567045	C	2.068384	-1.21299	2.203428
O	0.610357	0.604707	-0.80035	O	0.310511	1.226505	-0.44105
H	1.557434	0.505689	-0.60774	H	1.234793	1.343808	-0.18533
H	-1.13293	-0.23815	-0.25481	H	-1.20061	-0.08013	-0.22226
H	0.270232	-1.28032	-0.02057	H	0.392489	-0.83762	-0.27526
H	-0.72047	-0.38526	2.111034	H	-0.68686	0.886328	1.995019
H	-0.34436	1.256086	1.559507	H	-0.63847	-0.88184	1.995842
H	1.919742	2.088513	1.781603	H	2.705849	1.31435	3.110884
H	3.195991	1.005667	2.580029	H	1.311792	2.165427	2.399381
H	1.108487	-1.61373	3.382646	H	1.455963	-2.07061	2.484507
H	1.637668	-2.00605	1.754358	H	2.495798	-1.42981	1.216722
H	2.792032	-1.31081	2.895439	H	2.907849	-1.13935	2.896246
O	3.153648	0.184851	0.23009	O	2.754886	1.510969	1.049153
H	3.687951	0.990289	0.168469	H	3.256527	2.328484	1.101821
addC3_PRC				addC4_PRC			
C	1.662573	-0.82262	0.12849	C	-1.60788	-0.6601	-0.34348
C	0.269819	-1.12608	-0.39687	C	-0.51809	-1.20308	0.590627
C	-0.87248	-0.42722	0.292629	C	0.823234	-0.56451	0.370088
C	-0.71173	0.36517	1.360967	C	1.320398	0.335342	1.227322
C	-2.22526	-0.70929	-0.28642	C	1.57418	-0.98803	-0.85543
O	2.084852	0.500646	-0.11378	O	-1.93546	0.67462	-0.06305
H	1.326621	1.044059	-0.36249	H	-1.17964	1.225296	-0.30752
H	2.374531	-1.49375	-0.35593	H	-2.51559	-1.24491	-0.19633
H	1.702154	-1.03572	1.20317	H	-1.30376	-0.78329	-1.38904
H	0.223149	-0.88319	-1.46351	H	-0.42989	-2.28057	0.423075
H	0.091663	-2.20406	-0.32708	H	-0.84812	-1.04381	1.617234
H	-1.56914	0.814142	1.846443	H	0.773025	0.618063	2.11761
H	0.263769	0.570013	1.781436	H	2.301604	0.76806	1.079093
H	-2.43341	-1.78083	-0.25765	H	1.768828	-2.062	-0.82477
H	-3.01304	-0.18556	0.25094	H	0.984497	-0.79119	-1.75232
H	-2.25089	-0.40094	-1.33257	H	2.518315	-0.45712	-0.94937
O	-0.43021	1.768736	-0.79176	O	0.583305	1.857097	-0.70672
H	-0.75175	2.437969	-0.16843	H	0.803049	2.509119	-0.02302

Table S 5: Adopted schemes (NS:SC) for the different stationary points involved in prenol+OH and isoprenol+OH reactions, where NS and SC refer to nearly separable and strongly coupled, respectively

Reaction pathway	**absC1**	**absC2**	**absC4**	**absC5**	**absO**	**addC2**	**addC3**	**addC4**
Prenol+OH	2:5	1:6	1:6	1:6	1:6	2:4	1:5	N/A
Isoprenol+OH	1:6	1:6	1:6	1:6	2:5	N/A	2:4	2:4

Table S 6: High-pressure limit rate constants for the different pathways of the reaction prenol+OH (cm^3 $molecule^{-1}$ s^{-1}) at the UCCSD(T)/jun-cc-pVQZ//M062X/6-311++G(2df,2pd) level of theory with and without the effect of the complex (PRC) for the addition channels

	UCCSD(T)/jun-cc-pVQZ							UCCSD(T)/jun-cc-pVQZ (PRC)	
T(K)	**absC1**	**absC2**	**absC4**	**absC5**	**absO**	**addC2**	**addC3**	**addC2**	**addC3**
250	3.33E-12	2.33E-15	2.21E-14	2.30E-15	1.58E-14	1.14E-11	4.81E-10	1.12E-11	2.90E-10
298	2.68E-12	3.55E-15	3.43E-14	3.83E-15	1.92E-14	4.21E-12	7.13E-11	4.19E-12	6.67E-11
350	2.34E-12	5.59E-15	5.26E-14	6.06E-15	2.51E-14	2.03E-12	1.98E-11	2.03E-12	1.97E-11
400	2.20E-12	8.45E-15	7.64E-14	8.76E-15	3.32E-14	1.26E-12	9.37E-12	1.26E-12	9.43E-12
450	2.16E-12	1.25E-14	1.07E-13	1.21E-14	4.23E-14	8.91E-13	5.90E-12	8.92E-13	5.95E-12
500	2.18E-12	1.78E-14	1.46E-13	1.63E-14	5.64E-14	6.97E-13	4.19E-12	6.98E-13	4.23E-12
550	2.25E-12	2.49E-14	1.94E-13	2.14E-14	7.46E-14	5.83E-13	3.48E-12	5.84E-13	3.52E-12
600	2.35E-12	3.38E-14	2.52E-13	2.76E-14	9.74E-14	5.14E-13	3.10E-12	5.15E-13	3.15E-12
650	2.49E-12	4.50E-14	3.21E-13	3.50E-14	1.26E-13	4.69E-13	2.90E-12	4.70E-13	2.94E-12
700	2.65E-12	5.86E-14	4.02E-13	4.39E-14	1.60E-13	4.41E-13	2.81E-12	4.42E-13	2.85E-12
750	2.83E-12	7.49E-14	4.97E-13	5.44E-14	2.02E-13	4.24E-13	2.78E-12	4.25E-13	2.82E-12
800	3.04E-12	9.43E-14	6.05E-13	6.68E-14	2.51E-13	4.14E-13	2.80E-12	4.15E-13	2.84E-12
850	3.27E-12	1.17E-13	7.29E-13	8.14E-14	3.09E-13	4.10E-13	2.67E-12	4.11E-13	2.71E-12
900	3.52E-12	1.43E-13	8.68E-13	9.82E-14	3.76E-13	4.10E-13	2.74E-12	4.11E-13	2.79E-12
950	3.80E-12	1.73E-13	1.02E-12	1.18E-13	4.53E-13	4.13E-13	2.84E-12	4.14E-13	2.88E-12
1000	4.10E-12	2.07E-13	1.20E-12	1.40E-13	5.41E-13	4.19E-13	2.95E-12	4.20E-13	3.00E-12
1100	4.76E-12	2.87E-13	1.59E-12	1.95E-13	7.53E-13	4.38E-13	3.22E-12	4.39E-13	3.28E-12
1200	5.51E-12	3.86E-13	2.07E-12	2.58E-13	1.02E-12	4.64E-13	3.55E-12	4.65E-13	3.61E-12
1300	6.36E-12	5.05E-13	2.62E-12	3.44E-13	1.34E-12	4.95E-13	3.93E-12	4.97E-13	4.00E-12
1400	7.30E-12	5.80E-13	3.26E-12	4.51E-13	1.72E-12	5.32E-13	4.35E-12	5.33E-13	4.43E-12
1500	8.33E-12	7.21E-13	3.98E-12	5.81E-13	2.16E-12	5.72E-13	4.82E-12	5.74E-13	4.91E-12
1600	9.46E-12	8.80E-13	4.78E-12	7.39E-13	2.68E-12	6.17E-13	5.33E-12	6.18E-13	5.43E-12
1700	1.07E-11	1.06E-12	5.68E-12	9.27E-13	3.27E-12	6.65E-13	5.89E-12	6.67E-13	5.99E-12
1800	1.20E-11	1.26E-12	6.65E-12	1.15E-12	3.93E-12	7.17E-13	6.49E-12	7.19E-13	6.60E-12
1900	1.34E-11	1.48E-12	7.72E-12	1.41E-12	4.68E-12	7.73E-13	7.13E-12	7.74E-13	7.25E-12
2000	1.50E-11	1.71E-12	8.88E-12	1.71E-12	5.50E-12	8.32E-13	7.82E-12	8.33E-13	7.95E-12

Table S 7: High-pressure limit rate constants for the different pathways of the reaction isoprenol+OH (cm^3 $molecule^{-1}$ s^{-1}) at the UCCSD(T)/jun-cc-pVQZ//M062X/6-311++G(2df,2pd) level of theory with and without the effect of the complex (PRC) for the addition channels

	UCCSD(T)/jun-cc-pVQZ							UCCSD(T)/jun-cc-pVQZ ((PRC)	
T(K)	**absC1**	**absC2**	**absC4**	**absC5**	**absO**	**addC3**	**addC4**	**addC3**	**addC4**
250	2.93E-13	1.32E-14	3.53E-16	1.10E-14	1.01E-14	1.01E-10	1.40E-11	8.87E-11	1.37E-11
298	2.65E-13	1.96E-14	4.82E-16	1.46E-14	1.27E-14	6.11E-11	9.91E-12	5.76E-11	9.78E-12
350	2.58E-13	2.78E-14	7.34E-16	2.02E-14	1.74E-14	4.02E-11	7.39E-12	4.00E-11	7.34E-12
400	2.66E-13	3.00E-14	1.13E-15	2.16E-14	2.38E-14	2.98E-11	5.97E-12	3.09E-11	5.95E-12
450	2.83E-13	3.89E-14	1.75E-15	3.06E-14	3.21E-14	1.86E-11	5.10E-12	1.98E-11	5.10E-12
500	3.09E-13	4.93E-14	2.63E-15	4.27E-14	4.22E-14	1.57E-11	4.55E-12	1.71E-11	4.56E-12
550	3.40E-13	6.14E-14	3.84E-15	5.84E-14	5.44E-14	1.38E-11	4.20E-12	1.55E-11	4.22E-12
600	3.77E-13	7.53E-14	5.47E-15	7.82E-14	6.88E-14	1.26E-11	3.98E-12	1.45E-11	4.02E-12
650	4.19E-13	9.11E-14	7.57E-15	1.03E-13	8.54E-14	1.18E-11	3.85E-12	1.39E-11	3.90E-12
700	4.66E-13	1.09E-13	9.98E-15	1.32E-13	1.04E-13	1.13E-11	3.79E-12	1.36E-11	3.85E-12
750	5.18E-13	1.29E-13	1.32E-14	1.66E-13	1.26E-13	1.10E-11	3.78E-12	1.35E-11	3.85E-12
800	5.75E-13	1.51E-13	1.70E-14	2.06E-13	1.50E-13	1.08E-11	3.81E-12	1.33E-11	3.89E-12
850	6.36E-13	1.76E-13	2.16E-14	2.53E-13	1.78E-13	1.07E-11	3.87E-12	1.35E-11	3.96E-12
900	7.02E-13	2.03E-13	2.70E-14	3.05E-13	2.07E-13	1.08E-11	3.95E-12	1.37E-11	4.06E-12
950	7.73E-13	2.32E-13	3.32E-14	3.64E-13	2.40E-13	1.09E-11	4.06E-12	1.40E-11	4.19E-12
1000	8.49E-13	2.65E-13	4.04E-14	4.30E-13	2.76E-13	1.11E-11	4.20E-12	1.44E-11	4.33E-12
1100	9.37E-13	3.37E-13	5.79E-14	5.83E-13	3.58E-13	1.16E-11	4.42E-12	1.52E-11	4.58E-12
1200	1.11E-12	4.20E-13	7.98E-14	7.59E-13	4.52E-13	1.23E-11	4.80E-12	1.63E-11	4.99E-12
1300	1.31E-12	5.15E-13	1.07E-13	9.52E-13	5.61E-13	1.31E-11	5.23E-12	1.74E-11	5.45E-12
1400	1.52E-12	6.22E-13	1.39E-13	1.19E-12	6.83E-13	1.40E-11	5.70E-12	1.86E-11	5.95E-12
1500	1.76E-12	7.41E-13	1.77E-13	1.42E-12	8.03E-13	1.44E-11	6.24E-12	1.90E-11	6.53E-12
1600	2.02E-12	8.73E-13	2.21E-13	1.46E-12	9.47E-13	1.51E-11	6.84E-12	1.97E-11	7.17E-12
1700	2.30E-12	1.02E-12	2.71E-13	1.77E-12	1.10E-12	1.61E-11	7.50E-12	2.10E-11	7.87E-12
1800	2.59E-12	1.17E-12	3.27E-13	2.12E-12	1.27E-12	1.69E-11	8.21E-12	2.18E-11	8.63E-12
1900	2.91E-12	1.35E-12	3.91E-13	2.52E-12	1.46E-12	1.81E-11	8.98E-12	2.33E-11	9.45E-12
2000	3.25E-12	1.53E-12	4.61E-13	2.95E-12	1.66E-12	1.94E-11	9.81E-12	2.47E-11	1.03E-11

Table S8: High-pressure limit rate constants for the different pathways of the reaction prenol+OH (cm^3 $molecule^{-1}$ s^{-1}) at the UCCSD(T)/CBS//M062X/6-311++G(2df,2pd) level of theory with and without the effect of the complex (PRC) for the addition channels

	UCCSD(T)/CBS							UCCSD(T)/CBS (PRC)	
T(K)	**absC1**	**absC2**	**absC4**	**absC5**	**absO**	**addC2**	**addC3**	**addC2**	**addC3**
250	1.99E-12	1.80E-15	1.75E-14	4.73E-15	1.26E-14	4.11E-12	1.58E-10	4.09E-12	1.30E-10
298	1.74E-12	2.77E-15	2.75E-14	7.04E-15	1.52E-14	1.79E-12	2.80E-11	1.79E-12	2.73E-11
350	1.62E-12	4.42E-15	4.31E-14	9.96E-15	1.98E-14	9.83E-13	8.94E-12	9.83E-13	8.92E-12
400	1.60E-12	6.79E-15	6.36E-14	1.33E-14	2.63E-14	6.65E-13	4.67E-12	6.65E-13	4.69E-12
450	1.62E-12	1.01E-14	9.05E-14	1.73E-14	3.53E-14	5.06E-13	3.18E-12	5.07E-13	3.19E-12
500	1.69E-12	1.47E-14	1.25E-13	2.22E-14	4.72E-14	4.19E-13	2.40E-12	4.19E-13	2.41E-12
550	1.78E-12	2.08E-14	1.68E-13	2.80E-14	6.27E-14	3.67E-13	2.10E-12	3.68E-13	2.11E-12
600	1.90E-12	2.85E-14	2.20E-13	3.49E-14	8.23E-14	3.36E-13	1.95E-12	3.37E-13	1.97E-12
650	2.04E-12	3.83E-14	2.83E-13	4.32E-14	1.07E-13	3.17E-13	1.89E-12	3.18E-13	1.91E-12
700	2.20E-12	5.04E-14	3.58E-13	5.30E-14	1.37E-13	3.07E-13	1.89E-12	3.07E-13	1.90E-12
750	2.39E-12	6.49E-14	4.45E-13	6.45E-14	1.73E-13	3.02E-13	1.92E-12	3.02E-13	1.94E-12
800	2.59E-12	8.23E-14	5.45E-13	7.80E-14	2.16E-13	3.01E-13	1.85E-12	3.02E-13	1.87E-12
850	2.82E-12	1.03E-13	6.60E-13	9.36E-14	2.67E-13	3.04E-13	1.92E-12	3.04E-13	1.94E-12
900	3.06E-12	1.26E-13	7.90E-13	1.12E-13	3.27E-13	3.09E-13	2.01E-12	3.09E-13	2.04E-12
950	3.32E-12	1.54E-13	9.36E-13	1.32E-13	3.95E-13	3.16E-13	2.12E-12	3.17E-13	2.14E-12
1000	3.61E-12	1.85E-13	1.10E-12	1.56E-13	4.74E-13	3.25E-13	2.23E-12	3.26E-13	2.26E-12
1100	4.24E-12	2.59E-13	1.48E-12	2.14E-13	6.64E-13	3.48E-13	2.50E-12	3.48E-13	2.54E-12
1200	4.96E-12	3.51E-13	1.93E-12	2.88E-13	9.02E-13	3.75E-13	2.82E-12	3.76E-13	2.85E-12
1300	5.77E-12	4.61E-13	2.45E-12	3.80E-13	1.19E-12	4.07E-13	3.17E-12	4.08E-13	3.22E-12
1400	6.66E-12	5.92E-13	3.06E-12	4.93E-13	1.54E-12	4.43E-13	3.57E-12	4.44E-13	3.62E-12
1500	7.65E-12	7.45E-13	3.75E-12	6.32E-13	1.95E-12	4.83E-13	4.00E-12	4.84E-13	4.06E-12
1600	8.73E-12	9.20E-13	4.53E-12	7.99E-13	2.43E-12	5.26E-13	4.48E-12	5.27E-13	4.55E-12
1700	9.91E-12	9.90E-13	5.39E-12	9.98E-13	2.98E-12	5.73E-13	5.00E-12	5.74E-13	5.07E-12
1800	1.12E-11	1.18E-12	6.34E-12	1.23E-12	3.60E-12	6.23E-13	5.56E-12	6.24E-13	5.64E-12
1900	1.26E-11	1.39E-12	7.37E-12	1.51E-12	4.29E-12	6.76E-13	6.16E-12	6.77E-13	6.25E-12
2000	1.40E-11	1.62E-12	8.49E-12	1.82E-12	5.07E-12	7.02E-13	6.80E-12	7.03E-13	6.90E-12

Table S 9: High-pressure limit rate constants for the different pathways of the reaction isoprenol+OH (cm^3 $molecule^{-1}$ s^{-1}) at the UCCSD(T)/CBS//M062X/6-311++G(2df,2pd) level of theory with and without the effect of the complex (PRC) for the addition channels

	UCCSD(T)/CBS							UCCSD(T)/CBS (PRC)	
T(K)	**absC1**	**absC2**	**absC4**	**absC5**	**absO**	**addC3**	**addC4**	**addC3**	**addC4**
250	3.79E-14	1.32E-14	2.92E-16	2.01E-14	8.43E-15	3.89E-11	5.41E-12	3.69E-11	5.37E-12
298	4.68E-14	1.96E-14	3.96E-16	2.32E-14	1.06E-14	2.74E-11	4.47E-12	2.66E-11	4.45E-12
350	5.83E-14	2.78E-14	6.04E-16	2.94E-14	1.45E-14	2.03E-11	3.76E-12	2.02E-11	3.74E-12
400	7.20E-14	3.00E-14	9.37E-16	3.85E-14	1.98E-14	1.29E-11	3.30E-12	1.31E-11	3.30E-12
450	8.85E-14	3.89E-14	1.45E-15	5.12E-14	2.68E-14	1.09E-11	3.01E-12	1.13E-11	3.01E-12
500	1.08E-13	4.93E-14	2.20E-15	6.81E-14	3.53E-14	9.69E-12	2.83E-12	1.02E-11	2.84E-12
550	1.31E-13	6.14E-14	3.24E-15	8.34E-14	4.57E-14	8.92E-12	2.73E-12	9.60E-12	2.74E-12
600	1.57E-13	7.53E-14	4.65E-15	1.08E-13	5.80E-14	8.45E-12	2.68E-12	9.26E-12	2.70E-12
650	1.87E-13	9.11E-14	6.48E-15	1.37E-13	7.24E-14	8.18E-12	2.67E-12	9.12E-12	2.70E-12
700	2.20E-13	1.09E-13	8.82E-15	1.60E-13	8.90E-14	7.95E-12	2.70E-12	9.00E-12	2.73E-12
750	2.57E-13	1.29E-13	1.17E-14	1.97E-13	1.08E-13	7.92E-12	2.75E-12	9.11E-12	2.79E-12
800	2.98E-13	1.51E-13	1.53E-14	2.40E-13	1.29E-13	7.98E-12	2.83E-12	9.30E-12	2.88E-12
850	3.43E-13	1.76E-13	1.89E-14	2.90E-13	1.53E-13	8.10E-12	2.92E-12	9.56E-12	2.98E-12
900	3.92E-13	2.03E-13	2.38E-14	3.24E-13	1.80E-13	8.27E-12	3.04E-12	9.87E-12	3.10E-12
950	4.45E-13	2.32E-13	2.94E-14	3.39E-13	2.09E-13	8.48E-12	3.11E-12	1.02E-11	3.18E-12
1000	5.02E-13	2.65E-13	3.60E-14	3.99E-13	2.41E-13	8.74E-12	3.25E-12	1.06E-11	3.33E-12
1100	6.31E-13	3.37E-13	5.20E-14	5.39E-13	3.15E-13	9.34E-12	3.57E-12	1.16E-11	3.67E-12
1200	7.77E-13	4.20E-13	7.22E-14	7.08E-13	4.01E-13	1.01E-11	3.94E-12	1.26E-11	4.06E-12
1300	9.41E-13	5.15E-13	9.70E-14	9.10E-13	5.00E-13	1.09E-11	4.34E-12	1.37E-11	4.49E-12
1400	1.12E-12	6.22E-13	1.27E-13	1.15E-12	6.12E-13	1.13E-11	4.81E-12	1.42E-11	4.99E-12
1500	1.33E-12	7.41E-13	1.62E-13	1.42E-12	7.38E-13	1.20E-11	5.33E-12	1.50E-11	5.54E-12
1600	1.55E-12	8.73E-13	2.04E-13	1.73E-12	8.78E-13	1.30E-11	5.90E-12	1.62E-11	6.14E-12
1700	1.79E-12	1.02E-12	2.51E-13	2.08E-12	1.03E-12	1.37E-11	6.52E-12	1.71E-11	6.80E-12
1800	2.05E-12	1.17E-12	3.04E-13	2.48E-12	1.16E-12	1.48E-11	7.20E-12	1.84E-11	7.52E-12
1900	2.33E-12	1.35E-12	3.64E-13	2.91E-12	1.34E-12	1.60E-11	7.92E-12	1.98E-11	8.29E-12
2000	2.44E-12	1.53E-12	4.31E-13	3.39E-12	1.52E-12	1.69E-11	8.71E-12	2.08E-11	9.11E-12

Table S 10: SCT transmission coefficient values for the different pathways of the reaction of prenol+OH and isoprenol+OH at the UCCSD(T)/jun-cc-pVQZ//M062X/6-311++G(2df,2pd) level of theory

	Prenol+OH							Isoprenol+OH						
T(K)	**abs1**	**abs2**	**abs4**	**abs5**	**absO**	**add2**	**add3**	**abs1**	**abs2**	**abs4**	**abs5**	**absO**	**add3**	**add4**
250	1.00	5.48	3.10	1.40	8.29	1.00	1.00	1.00	1.45	30.47	1.31	14.75	1.00	1.00
298	1.00	3.41	2.24	1.27	5.02	1.00	1.00	1.00	1.30	12.42	1.21	7.86	1.00	1.00
350	1.00	2.47	1.80	1.19	3.47	1.00	1.00	1.00	1.21	6.64	1.15	4.94	1.00	1.00
400	1.00	2.02	1.57	1.14	2.71	1.00	1.00	1.00	1.16	4.42	1.12	3.60	1.00	1.00
450	1.00	1.75	1.43	1.11	2.26	1.00	1.00	1.00	1.12	3.31	1.09	2.86	1.00	1.00
500	1.00	1.58	1.34	1.09	1.97	1.00	1.00	1.00	1.10	2.68	1.07	2.40	1.00	1.00
550	1.00	1.46	1.27	1.07	1.77	1.00	1.00	1.00	1.08	2.28	1.06	2.09	1.00	1.00
600	1.00	1.38	1.23	1.06	1.63	1.00	1.00	1.00	1.07	2.01	1.05	1.88	1.00	1.00
650	1.00	1.31	1.19	1.05	1.52	1.00	1.00	1.00	1.06	1.82	1.04	1.73	1.00	1.00
700	1.00	1.27	1.16	1.04	1.44	1.00	1.00	1.00	1.05	1.68	1.04	1.61	1.00	1.00
750	1.00	1.23	1.14	1.04	1.38	1.00	1.00	1.00	1.04	1.58	1.03	1.52	1.00	1.00
800	1.00	1.20	1.12	1.03	1.33	1.00	1.00	1.00	1.04	1.50	1.03	1.45	1.00	1.00
850	1.00	1.17	1.11	1.03	1.29	1.00	1.00	1.00	1.03	1.43	1.03	1.39	1.00	1.00
900	1.00	1.15	1.10	1.03	1.26	1.00	1.00	1.00	1.03	1.38	1.02	1.35	1.00	1.00
950	1.00	1.14	1.09	1.02	1.23	1.00	1.00	1.00	1.03	1.33	1.02	1.31	1.00	1.00
1000	1.00	1.12	1.08	1.02	1.20	1.00	1.00	1.00	1.02	1.30	1.02	1.28	1.00	1.00
1100	1.00	1.10	1.06	1.02	1.17	1.00	1.00	1.00	1.02	1.24	1.02	1.22	1.00	1.00
1200	1.00	1.08	1.05	1.01	1.14	1.00	1.00	1.00	1.02	1.20	1.01	1.19	1.00	1.00
1300	1.00	1.07	1.04	1.01	1.12	1.00	1.00	1.00	1.01	1.17	1.01	1.16	1.00	1.00
1400	1.00	1.06	1.04	1.01	1.10	1.00	1.00	1.00	1.01	1.14	1.01	1.14	1.00	1.00
1500	1.00	1.05	1.03	1.01	1.09	1.00	1.00	1.00	1.01	1.12	1.01	1.12	1.00	1.00
1600	1.00	1.05	1.03	1.01	1.08	1.00	1.00	1.00	1.01	1.11	1.01	1.10	1.00	1.00
1700	1.00	1.04	1.03	1.01	1.07	1.00	1.00	1.00	1.01	1.10	1.01	1.09	1.00	1.00
1800	1.00	1.04	1.02	1.01	1.06	1.00	1.00	1.00	1.01	1.09	1.01	1.08	1.00	1.00
1900	1.00	1.03	1.02	1.01	1.05	1.00	1.00	1.00	1.01	1.08	1.01	1.07	1.00	1.00
2000	1.00	1.03	1.02	1.01	1.05	1.00	1.00	1.00	1.01	1.07	1.00	1.06	1.00	1.00

Table S 11: Measured rate constants for the reactions of OH radicals with prenol and isoprenol at the specified experimental conditions. Argon was used as bath gas.

Prenol + OH			Isoprenol + OH		
P_5 (atm)	T_5 (K)	k (10^{-11} $cm^3molecule^{-1}s^{-1}$)	P_5 (atm)	T_5 (K)	k (10^{-11} $cm^3molecule^{-1}s^{-1}$)
Prenol mixture 1: 200 ppm prenol, 20 ppm TBHP			Isoprenol mixture 1: 200 ppm isoprenol, 20 ppm TBHP		
0.94	984	1.75	1.00	1017	1.61
0.95	895	1.90	1.05	868	1.47
1.07	848	1.64	1.13	926	1.51
1.16	1264	1.68	1.23	1032	1.65
1.24	1038	1.58	1.28	1096	1.83
1.25	958	1.68	1.39	1034	1.66
1.50	1218	1.57	2.16	938	1.89
1.56	1188	1.58	2.45	1144	2.13
1.57	1218	1.53	2.76	972	1.95
2.24	900	1.81	2.88	914	1.98
2.33	886	1.50	5.21	1019	1.76
2.41	1162	1.87	5.25	962	2.34
2.50	955	1.53	5.61	937	2.24
2.54	1106	1.75	5.68	921	2.00
2.55	1007	1.72	Isoprenol mixture 2: 300 ppm isoprenol, 60 ppm TBHP		
2.57	1011	1.61	0.96	1055	1.83
2.63	991	1.83	1.25	1082	1.94
2.88	1035	1.67	1.25	1157	2.17
4.64	1109	1.69	1.31	983	1.53
5.18	1104	1.92	1.31	966	1.93
5.56	1008	1.51	1.32	915	1.59
5.87	1068	1.72	1.37	875	1.66
Prenol mixture 2: 200 ppm prenol, 10 ppm TBHP			1.66	1173	2.22
1.30	1065	1.81			
1.52	1230	1.72			
1.59	1094	1.69			
Prenol mixture 3: 300 ppm prenol, 20 ppm TBHP					
1.35	1290	1.56			
1.41	1021	1.54			
1.42	1247	1.85			
1.43	925	1.51			
1.46	1198	1.77			
1.53	1169	1.62			
1.60	1074	1.64			
1.65	1036	1.55			
1.66	1230	1.60			

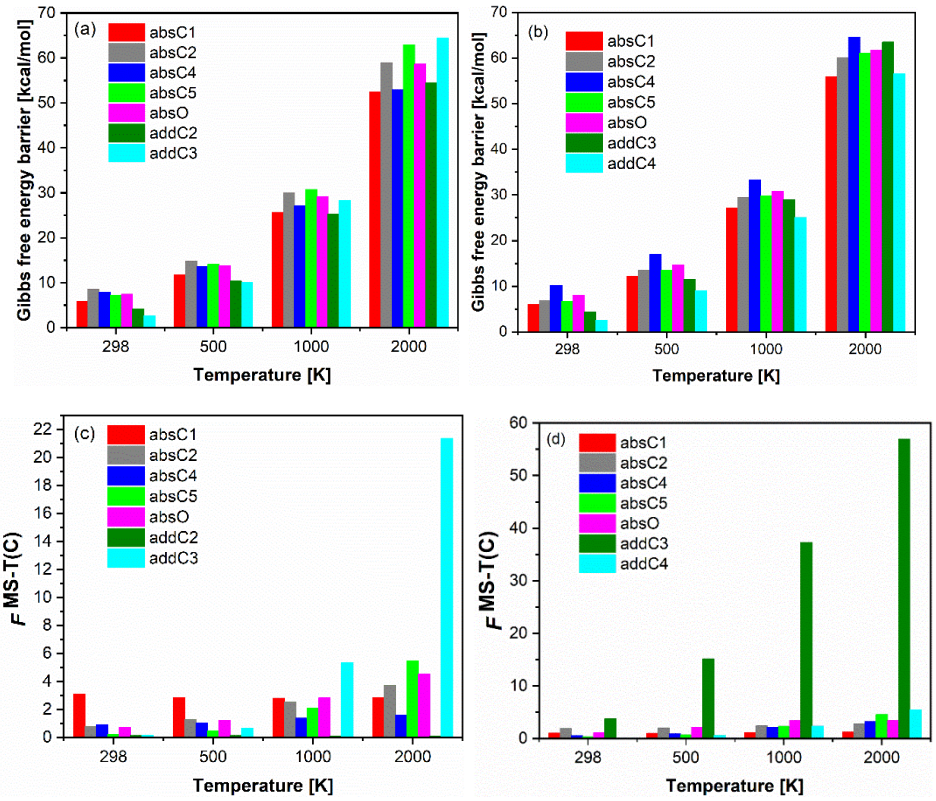

Figure S 1: Gibbs free energy barriers calculated with the harmonic approach (upper) and Multi-structural torsional anharmonicity factors (lower) for the different reaction pathways at different temperatures for prenol + OH ((a) and (c)), and isoprenol + OH ((b) and (d)).

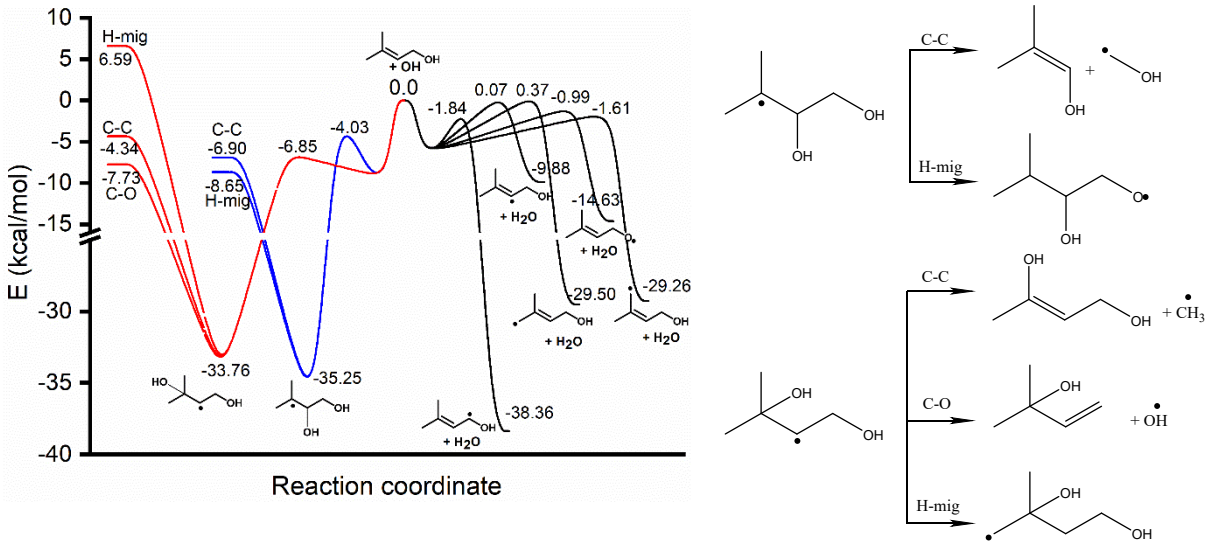

Figure S 2: Vibrationally adiabatic ground-state potential energy profile of prenol + OH (left panel), calculated at the M06-2X/6-311++G(2df,2pd) level of theory. Black lines: hydrogen abstraction channels by OH. Blue and red lines: reactions involving the addC2 and addC3 adducts, respectively, showing the energy profiles for the OH addition reaction into the double bond of prenol (adduct formation), as well as the C-C and C-O bond scission and intramolecular hydrogen transfer ("H-mig") reactions of both adducts. The stationary points labeled as "H-mig", "C-C", and "C-O" correspond to the saddle points of the reactions shown in the right panel.

As observed in Figure S2, the unimolecular decomposition reactions of addC2 and addC3 adducts are not expected to be competitive with the barrierless O_2 addition in conventional combustion/oxidation environments, especially at low temperatures and lean conditions. Low temperatures are expected to hinder those unimolecular dissociation reactions with large barrier heights, while an excess of O_2 is expected to make O_2 addition even more competitive.

We ran closed batch homogeneous simulations at constant volume with ChemKin for prenol:O_2:N_2 mixtures at stoichiometric conditions (0.0291:0.2039:0.7670), 15 bar and 650 - 2000 K, using the kinetic model developed by Lokachari et al. [1] updated with our calculated rate constants. At 20% fuel consumption, the concentration of O_2 is found to be 3.5×10^{6} and 3.5×10^{10} times larger than that of the adduct addC2 at 650 and 2000 K, respectively. Much higher [O_2]/[addC2] concentration ratios were observed at other fuel consumption stages of the simulations, and even larger ratios can be expected at lean conditions. The flux analysis obtained by Lokachari et al. [1] for prenol/air mixtures at phi = 2.0 (0.0566:0.1981:0.7453), 30 atm, and 615 and 915 K also seems to indicate that addC2 and addC3 adducts are mostly consumed by O_2 addition even at rich conditions.

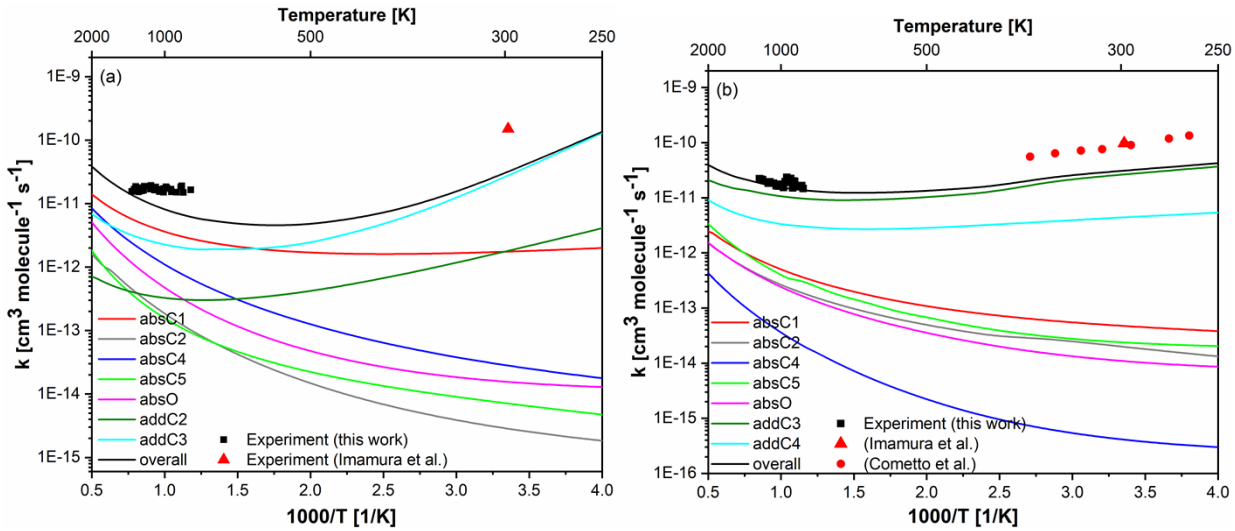

Figure S 3: Calculated rate constants (lines) for (a) prenol + OH and (b) isoprenol + OH at the UCCSD(T)/CBS//M06-2X/6-311++G(2df,2pd) level of theory, compared to the measured rate constants in this work (black symbols) and those from literature [2, 3] (red symbols).

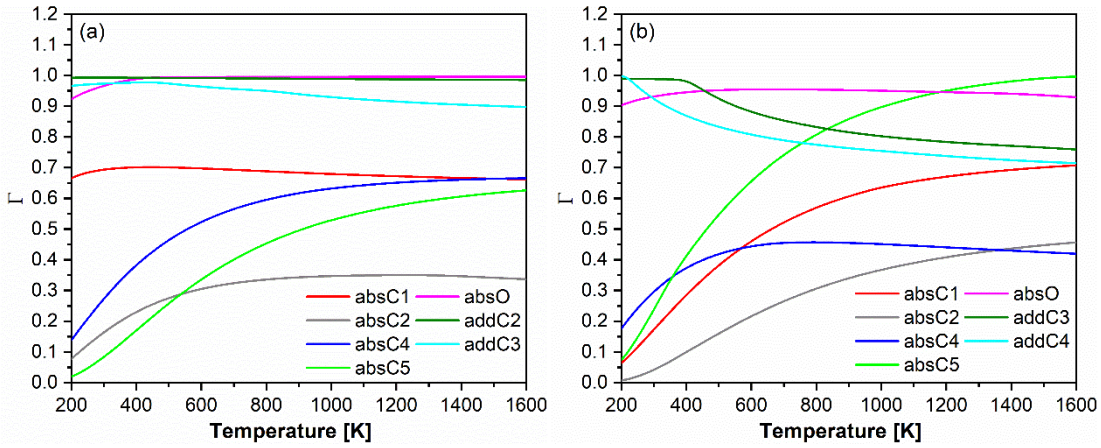

Figure S 4: Re-crossing transmission coefficient Γ (ratio of the variational to the non-variational rate constant) as function of temperature for (a) prenol + OH, and (b) isoprenol + OH

References:

[1] N. Lokachari, S.W. Wagnon, G. Kukkadapu, W.J. Pitz, H.J. Curran, Experimental and Kinetic Modeling Study of 3-Methyl-2-butenol (Prenol) Oxidation, Energy & Fuels 35 (2021) 13999-14009.
[2] T. Imamura, Y. Iida, K. Obi, I. Nagatani, K. Nakagawa, I. Patroescu-Klotz, S. Hatakeyama, Rate coefficients for the gas-phase reactions of OH radicals with methylbutenols at 298 K, Int J Chem Kinet 36 (2004) 379-385.
[3] P.M. Cometto, P.R. Dalmasso, R.A. Taccone, S.I. Lane, F. Oussar, V. Daële, A. Mellouki, G.L. Bras, Rate Coefficients for the Reaction of OH with a Series of Unsaturated Alcohols between 263 and 371 K, J. Phys. Chem. A 112 (2008) 4444-4450.