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.  

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.  

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.  

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.  

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.  

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.  

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.  

Table S 8: 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.  

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.  

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.  

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.  

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.  

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 [32, 33] (red symbols).  

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

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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

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### Isoprenol+OH

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| \(\text{Isoprenol+OH}^{+}\) | \(\text{Product}^{+}\) | 5.29015 | 2.46772 | 2.11741 |

| \(\text{addC3}^{+}\) | \(\text{Saddle point}^{+}\) | 2.86957 | 1.79716 | 1.39367 |

| \(\text{addC2}^{+}\) | \(\text{Product}^{+}\) | 4.12296 | 1.81061 | 1.71938 |

| \(\text{addC}^{+}\) | \(\text{Saddle point}^{+}\) | 3.83131 | 1.671 | 1.58311 |

| \(\text{Product}^{+}\) | 3.9616 | 1.65873 | 1.46415 |

| \(\text{Product}^{+}\) | 3.51326 | 1.5042 | 1.32371 |

| \(\text{Product}^{+}\) | 7.61224 | 1.88195 | 1.55242 |

| \(\text{Product}^{+}\) | 3.10263 | 1.67878 | 1.4459 |

| \(\text{Product}^{+}\) | 3.83131 | 1.671 | 1.58311 |

| \(\text{Product}^{+}\) | 4.12296 | 1.81061 | 1.71938 |

| \(\text{Product}^{+}\) | 2.86957 | 1.79716 | 1.39367 |

| \(\text{Product}^{+}\) | 5.29015 | 2.46772 | 2.11741 |

<p>| (\text{Product}^{+}) | 2.83967 | 1.96686 | 1.40736 |</p>
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1001, 1016, 1058, 1083, 1152, 1200, 1243, 1342, 1386, 1401, 1429, 1458, 1491, 1501, 1512, 1534, 3047, 3068, 3080, 3127, 3154, 3175, 3179, 3270, 3736, 3863 | 7.26553, 1.95374, 1.64642 |
| absC4 | 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 |
| absC5 | i990, 70, 94, 143, 198, 219, 252, 343, 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, 3043, 3057, 3082, 3116, 3119, 3157, 3262, 3865 | 5.55997, 2.56175, 2.16501 |
| absO | 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 |
| addC3 | 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 |
**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.

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*These frequency were calculated at the M062X/6-311++G(2df,2pd) level of theory but without Ultrafine keyword.*
<p>| C     | H     | O     |  | C     | H     | O     |  |
|-------|-------|-------|  |-------|-------|-------|  |
| absC2_saddle point | absC2_product | absC4_saddle point | absC4_product | absC5_saddle point | absC5_product |
| C     | H     | O     |  | C     | H     | O     |  |
| -0.09875 | -1.10423 | 1.4092729 |  | -1.203032 | 0.322092 | 3.569433 |  |
| -0.04045 | -1.1059 | -0.38137 |  | -0.126089 | -2.05914 | 4.173994 |  |
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Table S 4: Optimized Cartesian coordinates (angstrom) of the stationary points on the PES of the reaction isoprenol+OH at the M062X/6-31++G(2df,2pd) level of theory

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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.

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**Table S 6:** High-pressure limit rate constants for the different pathways of the reaction prenol+OH (cm³ 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

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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.

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**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 O₂ 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 O₂ is expected to make O₂ addition even more competitive.

We ran closed batch homogeneous simulations at constant volume with ChemKin for prenol:O₂:N₂ 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 O₂ is found to be 3.5×10⁶ and 3.5×10¹⁰ times larger than that of the adduct addC2 at 650 and 2000 K, respectively. Much higher [O₂]/[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 O₂ 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 $\Gamma$ (ratio of the variational to the non-variational rate constant) as function of temperature for (a) prenol + OH, and (b) isoprenol + OH

References: