in alkane-OH reactions, but after the formation of alkoxyl radicals through the conversion of NO to NO_2, the reaction mechanism becomes uncertain. Alkoxyl radicals can decompose, react with O_2, isomerize, or react with NO or NO_2, with the importance and rate of each reaction path depending on the nature of the alkoxyl group. Even for the most studied of the alkane-hydroxyl radical reactions, the relative rates between decomposition, isomerization, and reaction with O_2, NO, and NO_2 for alkoxyl radicals have not been measured, but must be estimated.[6]

Less well understood than alkane reaction mechanisms are olefin oxidation processes, primarily by HO. Olefin-hydroxyl radical reactions may proceed by addition or abstraction. For smaller olefins, the addition path predominates. However, the abstraction fraction increases with the size of the olefin. Along the addition path for terminally bonded olefins, there is uncertainty as to the ratio of internal to external addition. Similar to alkyl radicals, the hydroxy-alkyl radicals formed in the initial HO addition to olefins are thought to immediately add O_2 to form hydroxy-peroxyalkyl radicals and thereafter react with NO to give NO_2 and hydroxy-alkoxyl species. The fate of the hydroxy-alkoxyl radicals is subject to speculation, although the analogous alkoxyl reaction paths of decomposition, isomerization, and reaction with NO, NO_2 and O_2 are most likely possibilities.