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.

The inherent uncertainty of the decomposition, reaction with O_2, and isomerization of the alkoxyl and hydroxy-alkoxyl radicals class can be presented by the generalized reaction step:

$$RO \longrightarrow \alpha HO_2 + (1 - \alpha)RO_2 + \beta HCHO + \gamma RCHO. \qquad (74)$$

From the earlier discussions of alkoxyl radical behavior, RO always gives rise to either HO_2 or RO_2 in any of the decomposition, isomerization, or O_2 reaction pathways. Hence, the stoichiometric coefficients representing the fraction of HO_2 and RO_2 found in the lumped RO reaction should sum to one. Since the lumped RO species represents a large class of different-sized radicals and because splits between reaction paths for even specific radicals are not known, α can have a value in the range of 0 to 1. Many RO reaction routes produce aldehydes. Thus, $0 \leq \beta \leq 1$ and $0 \leq \gamma \leq 1$. Since the composition of the RO radical pool is continually changing during the course of a photooxidation, the actual values of α, β, and γ are functions of time. Thus, the selection of constant values of these coefficients introduces uncertainty.

A comprehensive sensitivity/uncertainty analysis of photochemical smog mechanisms has been carried out by Falls et al. (1979). In this study the effects of rate constant and mechanistic uncertainties on predicted concentrations are illustrated.