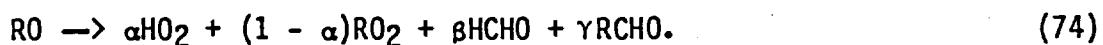


the olefin. Along the addition path for terminally bonded olefins, there is uncertainty as to the ratio of internal to external addition. Similar to alkyl radicals, the hydroxy-alkyl radicals formed in the initial HO addition to olefins are thought to immediately add O<sub>2</sub> to form hydroxy-peroxyalkyl radicals and thereafter react with NO to give NO<sub>2</sub> and hydroxy-alkoxy species. The fate of the hydroxy-alkoxy radicals is subject to speculation, although the analogous alkoxy reaction paths of decomposition, isomerization, and reaction with NO, NO<sub>2</sub> and O<sub>2</sub> are most likely possibilities.

The inherent uncertainty of the decomposition, reaction with O<sub>2</sub>, and isomerization of the alkoxy and hydroxy-alkoxy radicals class can be presented by the generalized reaction step:



From the earlier discussions of alkoxy radical behavior, RO always gives rise to either HO<sub>2</sub> or RO<sub>2</sub> in any of the decomposition, isomerization, or O<sub>2</sub> reaction pathways. Hence, the stoichiometric coefficients representing the fraction of HO<sub>2</sub> and RO<sub>2</sub> 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,  $\alpha$  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  $\alpha$ ,  $\beta$ , and  $\gamma$  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.