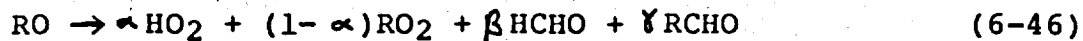


The inherent uncertainty of the decomposition, reaction with O_2 , and isomerization of the alkoxy and hydroxy-alkoxy radicals class can be presented by the generalized reaction step:



From the earlier discussions of alkoxy radical behavior, RO always gives rise to either HO_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 RO lumped 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.³¹ In this study the effects of rate constant and mechanistic uncertainties on predicted concentrations are illustrated.