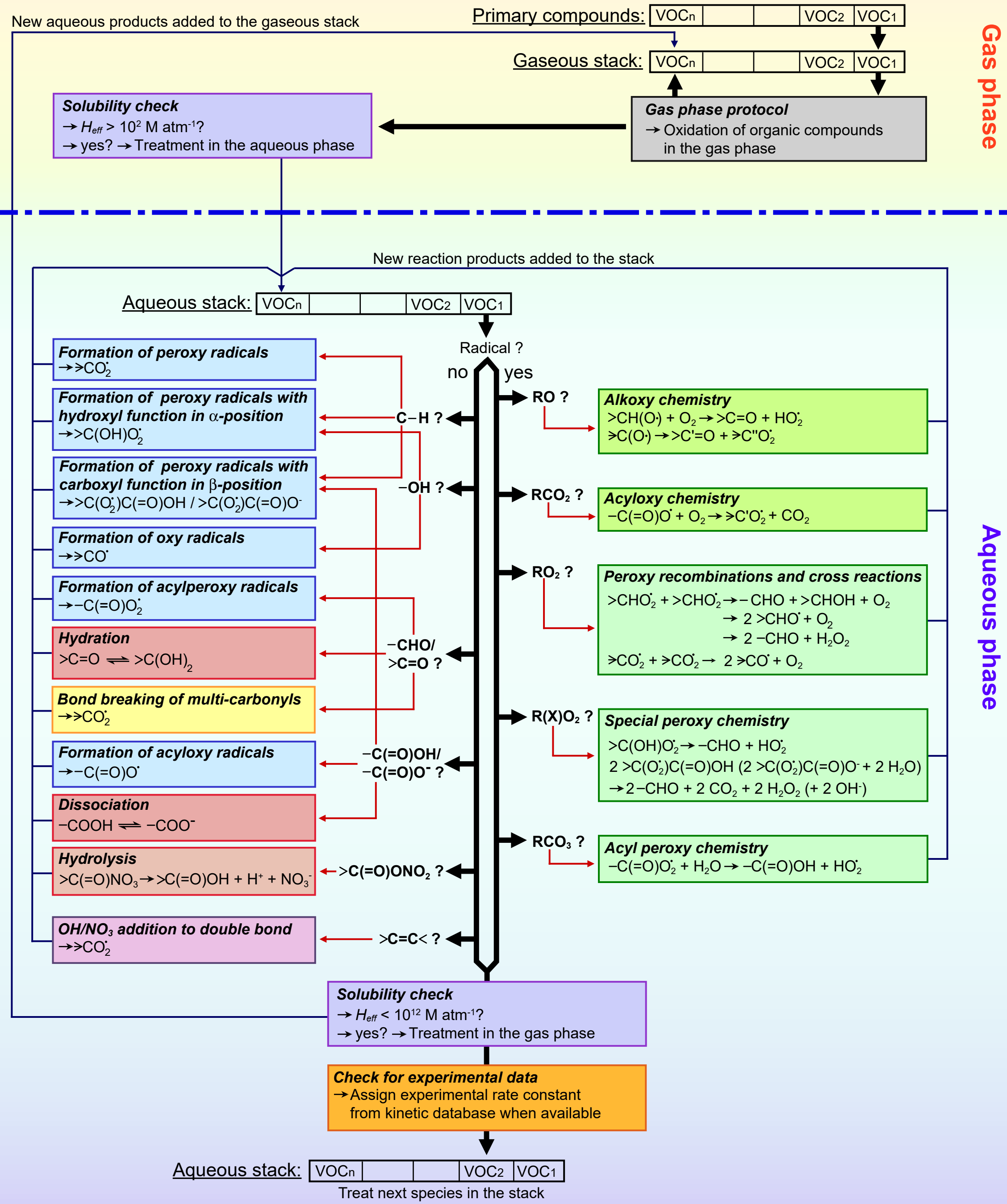
Gas phase
Aqueous phase
New aqueous products added to the gaseous stack
Primary compounds: VOCn VOC2 VOC1
Gaseous stack: VOCn VOC2 VOC1
Gas phase protocol
→ Oxidation of organic compounds in the gas phase
Solubility check
→ H_{eff} > 10^2 M atm^{-1}?
→ yes? → Treatment in the aqueous phase
New reaction products added to the stack
Aqueous stack: VOCn VOC2 VOC1
Radical ?
no
yes
Formation of peroxy radicals
→ >$CO_2^{\bullet}$
Formation of peroxy radicals with hydroxyl function in α-position
→ >C(OH)$O_2^{\bullet}$
Formation of peroxy radicals with carboxyl function in β-position
→ >C($O_2^{\bullet}$)C(=O)OH / >C($O_2^{\bullet}$)C(=O)O^-
Formation of oxy radicals
→ >$CO^{\bullet}$
Formation of acylperoxy radicals
→ −C(=O)$O_2^{\bullet}$
Hydration
>C=O ⇌ >C$(OH)_2$
Bond breaking of multi-carbonyls
→ >$CO_2^{\bullet}$
Formation of acyloxy radicals
→ −C(=O)$O^{\bullet}$
Dissociation
−COOH ⇌ −COO^-
Hydrolysis
>C(=O)NO_3 → >C(=O)OH + H^+ + NO_3^-
OH/NO_3 addition to double bond
→ >$CO_2^{\bullet}$
C−H ?
−OH ?
−CHO/ >C=O ?
−C(=O)OH/ −C(=O)O^- ?
>C(=O)ONO_2 ?
>C=C< ?
RO ?
RCO_2 ?
RO_2 ?
R(X)O_2 ?
RCO_3 ?
Alkoxy chemistry
>CH(O·) + O_2 → >C=O + $HO_2^{\bullet}$
>C(O·) → >C'=O + >C''$O_2^{\bullet}$
Acyloxy chemistry
−C(=O)$O^{\bullet}$ + O_2 → >C'$O_2^{\bullet}$ + CO_2
Peroxy recombinations and cross reactions
>C$HO_2^{\bullet}$ + >C$HO_2^{\bullet}$ → − CHO + >CHOH + O_2
→ 2 >$CHO^{\bullet}$ + O_2
→ 2 −CHO + H_2O_2
>$CO_2^{\bullet}$ + >$CO_2^{\bullet}$ → 2 >$CO^{\bullet}$ + O_2
Special peroxy chemistry
>C(OH)$O_2^{\bullet}$ → −CHO + $HO_2^{\bullet}$
2 >C($O_2^{\bullet}$)C(=O)OH (2 >C($O_2^{\bullet}$)C(=O)O^- + 2 H_2O)
→ 2 −CHO + 2 CO_2 + 2 H_2O_2 (+ 2 OH^-)
Acyl peroxy chemistry
−C(=O)$O_2^{\bullet}$ + H_2O → −C(=O)OH + $HO_2^{\bullet}$
Solubility check
→ H_{eff} < 10^{12} M atm^{-1}?
→ yes? → Treatment in the gas phase
Check for experimental data
→ Assign experimental rate constant from kinetic database when available
Aqueous stack: VOCn VOC2 VOC1
Treat next species in the stack