The Density of Plausible Reaction Mechanisms in Atmospheric Chemistry: An Examination of the Ethylene-OH Reaction

The aims of this (October 23, 1997) document are to:

1. demonstrate the applicability of MECHEM to atmospheric reaction mechanisms, using as a vehicle the oxidation of ethylene via initial OH addition to the double bond.
2. suggest that the density of plausible atmospheric mechanisms is higher than commonly suspected.
3. argue that to handle this density, computerized searches are called for, since one cannot reject mechanisms that one has not thought of, nor consider alternative mechanisms that might have been overlooked.

The ideal way to make these arguments would be for an expert who is knowledgeable in a specific chemistry to use MECHEM interactively to generate the simplest mechanisms that are consistent with reliable evidence and background considerations, such as similarity to analogous reactions that are considered solved. However, this ideal scenario is unlikely to happen without first demonstrating the program's relevance and utility to atmospheric chemistry, since all of the program's applications so far have been to industrial and engineering catalysis (both heterogeneous and homogeneous).

Instead, we will follow a different strategy to make the arguments, which obviates the need (but not the desirability) of close collaboration with an expert. We will target a well-established mechanism from the literature, in this case the reaction of OH, O_2, and NO with ethylene taken from the textbook Air Pollution: Physical and Chemical Fundamentals by J.H. Seinfeld (McGraw Hill, 1974):

1.	$CH_2{=}CH_2 + OH$	$\longrightarrow$	$OH\text{-}CH_2\text{-}CH_2$
2.	$O_2 + OH\text{-}CH_2\text{-}CH_2$	$\longrightarrow$	$O\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$
3.	$NO + O\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$	$\longrightarrow$	$NO_2 + OH\text{-}CH_2\text{-}CH_2\text{-}O$
4.	$O_2 + OH\text{-}CH_2\text{-}CH_2\text{-}O$	$\longrightarrow$	HO_2 + glycol aldehyde
5.	$OH\text{-}CH_2\text{-}CH_2\text{-}O$	$\longrightarrow$	$CH_2O + OH\text{-}CH_2$
6.	$NO + HO_2$	$\longrightarrow$	$OH + NO_2$
7.	$O_2 + OH\text{-}CH_2$	$\longrightarrow$	$HO_2 + CH_2O$

We will ask the following questions about this reaction:

1. What representative assumptions are needed to single out the textbook mechanism as the unique simplest? We will select these assumptions based on general criteria, not specific knowledge of this chemistry or the literature about it, because of the limited aims of this document and because study of this literature is beyond our competence.
2. What other mechanisms, that are either simpler or as simple as the textbook mechanism, make their appearance when some of these assumptions are repealed?
3. Under the same assumptions, how many mechanisms are there that are slightly more complex than textbook and that contain at least one intermediate that does not appear in the textbook mechanism? What do these mechanisms look like?

To formulate the problem for the computer program, we define the starting materials as $CH_2{=}CH_2$, O_2, OH, and NO, and the observed products or intermediates as NO_2, HO_2, CH_2O, and a glycol aldehyde ($HOCH_2CHO$). The distinction between what is a product and what is an intermediate is not made yet; that distinction is expressed in the assumptions (constraints) that are dealt with below.

It is instructive to consider first what happens when we deny the program access to any prior knowledge about the reaction beyond what are the starting materials and products/intermediates.[1] In this baseline case, the program finds 47 pathways, each having 4 steps and 1 conjectured species (= species not given as input to the program). These "mechanisms" are all undoubtedly implausible and uninteresting; we show the first of them only for illustration:

1.	2(NO)	$\longrightarrow$	NO_2 + *N*
2.	OH + NO	$\longrightarrow$	HO_2 + *N*
3.	$CH_2{=}CH_2 + O_2$	$\longrightarrow$	$2(CH_2O)$
4.	$2(CH_2O)$	$\longrightarrow$	glycol aldehyde

Here and below, asterisks are a visual aid to highlight conjectured species; they do not designate radicals. All of the 47 "pathways" can account for the formation of the products/intermediates, but are otherwise implausible. However, the program has not yet been given the right plausibility criteria for this reaction; this step is next.

We now articulate some representative (but not necessarily accurate or realistic) prior knowledge or assumptions in the form of constraints, run the program, inspect the results, articulate new constraints, and so on, until we are able to arrive at the textbook mechanism as the unique simplest mechanism. Since the program is designed to search the space of mechanisms comprehensively, this implies that no other mechanism exists which is simpler than or as simple as textbook. Our two main criteria of simplicity are the number S of conjectured species and the number R of elementary steps. We will sometimes refer to *classes* of mechanisms of equal simplicity using two numbers, e.g., the textbook mechanism above is in class 4S,7R because it contains 4 conjectured species and 7 steps.

Table 1 shows the constraints set we came up with. This set is not unique and is not even minimal (as we show below). Some of the constraints could no doubt be criticized as speculative or plain wrong. However, this would detract little from our central arguments, which concern the surprising density of plausible mechanisms and the utility of MECHEM for dealing with this density. In any case, the constraints could be adjusted and the program re-run, with predictably similar results, based on our experience with industrial catalytic reactions.

Constraint #21 on overall stoichiometry calls for clarification. The cited source derives this net stoichiometry from the textbook mechanism itself, whereas we are using it as an independent constraint as if it had been measured experimentally. Thus, we are requiring that every satisfactory mechanism be able to account for this net stoichiometry, which is itself a rather stringent constraint. The requirement is met in each case by exhibiting a set of stoichiometric numbers (in the sense of Horiuti) for each elementary step, such that multiplying the steps by their stoichiometric numbers

[1]All program parameters are set at their default values, i.e., prohibit isomerization steps, prohibit isomers, and prohibit any step that involves more than 3 changes to molecular topologies, but as a special case allowing "exchange" steps of the form AB + CD $\longrightarrow$ AC + BD, which incur 4 changes to topology.

1.	Every conjectured species has at most two C atoms
2.	Every conjectured species has at most two N atoms
3.	Every conjectured species has at most three O atoms
4.	Reject formula H
5.	Reject formula O
6.	Reject any formula containing both C and N atoms
7.	All conjectured species must be radicals
8.	Every conjectured species has at least one C atom
9.	The link between N and O in NO is unbreakable
10.	Reject all cyclic structures
11.	Element C must be at valence 3 or greater
12.	At most 1 atoms or sites can be at incomplete valence
13.	CH_2O cannot appear on left-hand side of a step
14.	Glycol aldehyde cannot appear on left-hand side of a step
15.	Every reactant pair must include a radical
16.	Every co-reactant with OH must contain C
17.	HO_2 can react only with NO
18.	Reactants involve jointly at most two C atoms
19.	NO is a necessary precursor of CH_2O
20.	The only net products are: NO_2 CH_2O glycol aldehyde
21.	Overall stoichiometry is: $CH_2{=}CH_2$ (2 O_2) (2 NO) $\longrightarrow$ (2 NO_2) (1.44 CH_2O) (0.28 glycol aldehyde)
22.	CH_2OH cannot react with itself
23.	Reject species *O-CH_3*
24.	Reject species *O-O-CH_2-OH*
25.	Reject the step: $CH_2{=}CH_2$ + OH $\longrightarrow$ *O-CH_2-CH_3*
26.	Reject the step: $CH_2{=}CH_2$ + OH $\longrightarrow$ *OH-CH-CH_3*

Table 1: Representative Constraints to Identify Ethylene-OH Mechanism as Unique Simplest

and cancelling like species on opposite sides leads exactly to the stoichiometric constraint #21. These stoichiometric numbers, which are not to be confused with kinetic constants, are shown embedded in the steps' arrows.

Next, we will consider what happens when we repeal each of these 26 constraints *individually*; we thus carry out 26 separate computer experiments. Our aim in doing so is to uncover mechanisms that are not too distant from textbook (as measured by the constraints in common) and to see what they look like, as well as how numerous they might be. For simplicity of exposition, all counts that are cited will *not* include the textbook mechanism, which of course must be included in any set of mechanisms at complexity level 4S,7R.

It turns out that each of the constraints 1-5, 7, 9-13, 16-18, 20, when removed *individually*, still leads to the textbook mechanism as the unique simplest. However, by no means does this imply that all these constraints could be removed; often the effect of one of them is taken over by the remaining constraints. For example, if we remove all of these constraints, which when removed individually do not remove the uniqueness of the textbook mechanism, we get 58 simplest 3S,7R mechanisms.

When constraint 6 (Reject any formula containing both C and N atoms) is omitted, one gets ten 3S,7R mechanisms, one of which is:

1. CH_2=CH_2 + OH −(1.28)→ *OH-CH_2-CH_2*
2. OH + *OH-CH_2-CH_2* −(1)→ HO_2 + *CH_2-CH3*
3. O_2 + *OH-CH_2-CH_2* −(0.28)→ OH + glycol aldehyde
4. NO + HO_2 −(2)→ OH + NO_2
5. CH_2=CH_2 + NO_2 −(0.72)→ CH_2O + *O=N-CH_2*
6. O_2 + *CH_2-CH3* −(1)→ CH_2=CH_2 + HO_2
7. O_2 + *O=N-CH_2* −(0.72)→ NO_2 + CH_2O

When constraint 8 (Every conjectured species has at least one C atom) is omitted, one obtains a single 4S,7R mechanism, which is thus of the same complexity as the textbook mechanism:

1. O_2 + NO −(1)→ *O-O-N=O*
2. CH_2=CH_2 + OH −(1)→ *OH-CH_2-CH_2*
3. *O-O-N=O* + *OH-CH_2-CH_2* −(1)→ NO_2 + *O-CH_2-CH_2-OH*
4. O_2 + *O-CH_2-CH_2-OH* −(0.28)→ HO_2 + glycol aldehyde
5. *O-CH_2-CH_2-OH* −(0.72)→ CH_2O + *OH-CH_2*
6. NO + HO_2 −(1)→ OH + NO_2
7. O_2 + *OH-CH_2* −(0.72)→ HO_2 + CH_2O

When constraint 14 (Glycol aldehyde cannot appear on left-hand side of a step) is omitted, one obtains a single 3S,6R mechanism:

1. CH_2=CH_2 + OH −(1)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* −(1)→ *O-O-CH_2-CH_2-OH*
3. NO + *O-O-CH_2-CH_2-OH* −(1)→ NO_2 + *OH-CH_2-CH_2-O*
4. O_2 + *OH-CH_2-CH_2-O* −(1)→ HO_2 + glycol aldehyde
5. glycol aldehyde −(0.72)→ 2(CH_2O)
6. NO + HO_2 −(1)→ OH + NO_2

When constraint 15 (Every reactant pair must include a radical) is omitted, one obtains two 3S,6R mechanisms, the first of which is:

1. CH_2=CH_2 + O_2 −(1)→ HO_2 + *CH_2=CH*
2. NO + HO_2 −(1)→ OH + NO_2
3. O_2 + *CH_2=CH* −(1)→ *O=CH-CH_2-O*
4. NO + *O=CH-CH_2-O* −(1)→ NO_2 + *O=CH-CH_2*
5. OH + *O=CH-CH_2* −(0.28)→ glycol aldehyde
6. OH + *O=CH-CH_2* −(0.72)→ 2(CH_2O)

When constraint 19 (NO is a necessary precursor of CH_2O) is omitted, one obtains 26 3S,7R mechanisms, the first of which is:

1. CH_2=CH_2 + OH $-(1.28)\rightarrow$ *OH-CH_2-CH_2*
2. CH_2=CH_2 + OH $-(0.72)\rightarrow$ CH_2O + *CH3*
3. OH + *OH-CH_2-CH_2* $-(1)\rightarrow$ HO_2 + *CH_2-CH3*
4. O_2 + *OH-CH_2-CH_2* $-(0.28)\rightarrow$ OH + glycol aldehyde
5. NO + HO_2 $-(2)\rightarrow$ OH + NO_2
6. O_2 + *CH3* $-(0.72)\rightarrow$ OH + CH_2O
7. O_2 + *CH_2-CH3* $-(1)\rightarrow$ CH_2=CH_2 + HO_2

When constraint 21 (Overall stoichiometry ...) is omitted, one obtains 23 4S,7R mechanisms, the first of which is:

1. CH_2=CH_2 + OH $\longrightarrow$ *OH-CH_2-CH_2*
2. OH + *OH-CH_2-CH_2* $\longrightarrow$ 2(*OH-CH_2*)
3. O_2 + *OH-CH_2-CH_2* $\longrightarrow$ OH + glycol aldehyde
4. O_2 + *OH-CH_2* $\longrightarrow$ *OH-O-CH_2-O*
5. NO + *OH-O-CH_2-O* $\longrightarrow$ NO_2 + *OH-O-CH_2*
6. OH + *OH-O-CH_2* $\longrightarrow$ HO_2 + *OH-CH_2*
7. *OH-O-CH_2* $\longrightarrow$ OH + CH_2O

When constraint 22 (CH_2OH cannot react with itself) is omitted, one obtains the single 4S,7R mechanism:

1. CH_2=CH_2 + OH $-(1)\rightarrow$ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* $-(1.72)\rightarrow$ *O-O-CH_2-CH_2-OH*
3. NO + *O-O-CH_2-CH_2-OH* $-(1.72)\rightarrow$ NO_2 + *OH-CH_2-CH_2-O*
4. O_2 + *OH-CH_2-CH_2-O* $-(0.28)\rightarrow$ HO_2 + glycol aldehyde
5. *OH-CH_2-CH_2-O* $-(1.44)\rightarrow$ CH_2O + *OH-CH_2*
6. NO + HO_2 $-(0.28)\rightarrow$ OH + NO_2
7. 2(*OH-CH_2*) $-(0.72)\rightarrow$ OH + *OH-CH_2-CH_2*

When constraint 23 (Reject species *O-CH_3*) is omitted, one obtains the single 4S,7R mechanism:

1. CH_2=CH_2 + OH $-(1)\rightarrow$ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* $-(1)\rightarrow$ *O-O-CH_2-CH_2-OH*
3. NO + *O-O-CH_2-CH_2-OH* $-(1)\rightarrow$ NO_2 + *OH-CH_2-CH_2-O*
4. O_2 + *OH-CH_2-CH_2-O* $-(0.28)\rightarrow$ HO_2 + glycol aldehyde
5. *OH-CH_2-CH_2-O* $-(0.72)\rightarrow$ CH_2O + *O-CH3*
6. NO + HO_2 $-(1)\rightarrow$ OH + NO_2
7. O_2 + *O-CH3* $-(0.72)\rightarrow$ HO_2 + CH_2O

When constraint 24 (Reject species *O-O-CH_2-OH*) is omitted, one obtains the single 4S,7R mechanism:

1. CH_2=CH_2 + OH $-(1)\rightarrow$ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* $-(1)\rightarrow$ *O-O-CH_2-CH_2-OH*
3. NO + *O-O-CH_2-CH_2-OH* $-(1)\rightarrow$ NO_2 + *OH-CH_2-CH_2-O*
4. O_2 + *OH-CH_2-CH_2-O* $-(0.28)\rightarrow$ HO_2 + glycol aldehyde
5. O_2 + *OH-CH_2-CH_2-O* $-(0.72)\rightarrow$ CH_2O + *O-O-CH_2-OH*
6. NO + HO_2 $-(1)\rightarrow$ OH + NO_2
7. *O-O-CH_2-OH* $-(0.72)\rightarrow$ HO_2 + CH_2O

When constraint 25 (Reject the step: CH_2=CH_2 + OH $\longrightarrow$ *O-CH_2-CH_3*) is omitted, one obtains the single 4S,7R mechanism:

1. CH_2=CH_2 + OH −(1)→ *O-CH_2-CH3*
2. O_2 + *O-CH_2-CH3* −(1)→ *O-O-CH_2-CH_2-OH*
3. NO + *O-O-CH_2-CH_2-OH* −(1)→ NO_2 + *OH-CH_2-CH_2-O*
4. O_2 + *OH-CH_2-CH_2-O* −(0.28)→ HO_2 + glycol aldehyde
5. *OH-CH_2-CH_2-O* −(0.72)→ CH_2O + *OH-CH_2*
6. NO + HO_2 −(1)→ OH + NO_2
7. O_2 + *OH-CH_2* −(0.72)→ HO_2 + CH_2O

When constraint 26 (Reject the step: CH_2=CH_2 + OH $\longrightarrow$ *OH-CH-CH_3*) is omitted, one obtains the single 4S,7R mechanism:

1. CH_2=CH_2 + OH −(1)→ *OH-CH-CH3*
2. O_2 + *OH-CH-CH3* −(1)→ *O-O-CH_2-CH_2-OH*
3. NO + *O-O-CH_2-CH_2-OH* −(1)→ NO_2 + *OH-CH_2-CH_2-O*
4. O_2 + *OH-CH_2-CH_2-O* −(0.28)→ HO_2 + glycol aldehyde
5. *OH-CH_2-CH_2-O* −(0.72)→ CH_2O + *OH-CH_2*
6. NO + HO_2 −(1)→ OH + NO_2
7. O_2 + *OH-CH_2* −(0.72)→ HO_2 + CH_2O

To further explore the possible density of reaction mechanisms, we followed a strategy whose starting point is the same (arrive at the textbook mechanism as the unique simplest), but rather than repeal assumptions, we add an artificial assumption, as follows. MECHEM's goal is always to search for the simplest mechanisms, so to explore non-simplest mechanisms, one selects one of several "next-simplest" constraints available in the program. The one we use here is "No mechanism contains only the conjectured species from the one mechanism in 4S,7R" which serves both to avoid stopping at the accepted mechanism, as well as to ensure a degree of novelty in the new mechanisms, since they must contain species (intermediates, in this case) that were not seen in the textbook mechanism. The result is the list of 15 4S,8R mechanisms shown in the appendix.

Conclusion. Our aim has not been to argue that all of the computer-generated mechanisms are correct, or even that they are plausible, since such a judgement would require detailed expertise that is beyond our competence. Rather, our aim is to adduce detailed evidence for the proposition that the simple, *prima facie* plausible mechanisms of atmospheric chemistry that are consistent with available experimental evidence are surprisingly numerous, and comprehensive searches as enabled by computer programs like MECHEM are needed to deal with this density.

A Next Simplest 4S,8R Mechanisms beyond the Textbook 4S,7R Mechanism

mechanism 1

1. $CH_2{=}CH_2$ + OH −(1)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* −(1.28)→ *OH-O-CH_2-CH_2-O*
3. NO + *OH-O-CH_2-CH_2-O* −(1)→ NO_2 + *OH-O-CH_2-CH_2*
4. *OH-O-CH_2-CH_2-O* −(0.28)→ OH + glycol aldehyde
5. OH + *OH-O-CH_2-CH_2* −(0.28)→ HO_2 + *OH-CH_2-CH_2*
6. *OH-O-CH_2-CH_2* −(0.72)→ CH_2O + *OH-CH_2*
7. NO + HO_2 −(1)→ OH + NO_2
8. O_2 + *OH-CH_2* −(0.72)→ HO_2 + CH_2O

mechanism 2

1. $CH_2{=}CH_2$ + OH −(1)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* −(1.28)→ *OH-O-CH_2-CH_2-O*
3. NO + *OH-O-CH_2-CH_2-O* −(1)→ NO_2 + *OH-O-CH_2-CH_2*
4. *OH-O-CH_2-CH_2-O* −(0.28)→ OH + glycol aldehyde
5. OH + *OH-O-CH_2-CH_2* −(0.28)→ HO_2 + *OH-CH_2-CH_2*
6. O_2 + *OH-O-CH_2-CH_2* −(0.72)→ CH_2O + *O-CH_2-O-OH*
7. NO + HO_2 −(1)→ OH + NO_2
8. *O-CH_2-O-OH* −(0.72)→ HO_2 + CH_2O

mechanism 3

1. $CH_2{=}CH_2$ + OH −(1.28)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* −(1.28)→ *OH-O-CH_2-CH_2-O*
3. NO + *OH-O-CH_2-CH_2-O* −(1)→ NO_2 + *OH-O-CH_2-CH_2*
4. *OH-O-CH_2-CH_2-O* −(0.28)→ OH + glycol aldehyde
5. O_2 + *OH-O-CH_2-CH_2* −(0.72)→ CH_2O + *O-CH_2-O-OH*
6. *OH-O-CH_2-CH_2* −(0.28)→ $CH_2{=}CH_2$ + HO_2
7. *O-CH_2-O-OH* −(0.72)→ HO_2 + CH_2O
8. NO + HO_2 −(1)→ OH + NO_2

mechanism 4

1. $CH_2{=}CH_2$ + OH −(1.28)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* −(1.28)→ *OH-O-CH_2-CH_2-O*
3. NO + *OH-O-CH_2-CH_2-O* −(1)→ NO_2 + *OH-O-CH_2-CH_2*
4. *OH-O-CH_2-CH_2-O* −(0.28)→ OH + glycol aldehyde
5. *OH-O-CH_2-CH_2* −(0.28)→ $CH_2{=}CH_2$ + HO_2
6. *OH-O-CH_2-CH_2* −(0.72)→ CH_2O + *OH-CH_2*
7. NO + HO_2 −(1)→ OH + NO_2
8. O_2 + *OH-CH_2* −(0.72)→ HO_2 + CH_2O

mechanism 5

1. $CH_2{=}CH_2$ + OH −(1)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* −(1)→ *OH-O-CH_2-CH_2-O*
3. O_2 + *OH-CH_2-CH_2* −(0.28)→ OH + glycol aldehyde
4. NO + *OH-O-CH_2-CH_2-O* −(1)→ NO_2 + *OH-O-CH_2-CH_2*
5. OH + *OH-O-CH_2-CH_2* −(0.28)→ HO_2 + *OH-CH_2-CH_2*
6. *OH-O-CH_2-CH_2* −(0.72)→ CH_2O + *OH-CH_2*
7. NO + HO_2 −(1)→ OH + NO_2
8. O_2 + *OH-CH_2* −(0.72)→ HO_2 + CH_2O

mechanism 6

1. CH_2=CH_2 + OH –(1)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* –(1)→ *OH-O-CH_2-CH_2-O*
3. O_2 + *OH-CH_2-CH_2* –(0.28)→ OH + glycol aldehyde
4. NO + *OH-O-CH_2-CH_2-O* –(1)→ NO_2 + *OH-O-CH_2-CH_2*
5. OH + *OH-O-CH_2-CH_2* –(0.28)→ HO_2 + *OH-CH_2-CH_2*
6. O_2 + *OH-O-CH_2-CH_2* –(0.72)→ CH_2O + *O-CH_2-O-OH*
7. NO + HO_2 –(1)→ OH + NO_2
8. *O-CH_2-O-OH* –(0.72)→ HO_2 + CH_2O

mechanism 7

1. CH_2=CH_2 + OH –(1.28)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* –(1)→ *OH-O-CH_2-CH_2-O*
3. O_2 + *OH-CH_2-CH_2* –(0.28)→ OH + glycol aldehyde
4. NO + *OH-O-CH_2-CH_2-O* –(1)→ NO_2 + *OH-O-CH_2-CH_2*
5. O_2 + *OH-O-CH_2-CH_2* –(0.72)→ CH_2O + *O-CH_2-O-OH*
6. *OH-O-CH_2-CH_2* –(0.28)→ CH_2=CH_2 + HO_2
7. *O-CH_2-O-OH* –(0.72)→ HO_2 + CH_2O
8. NO + HO_2 –(1)→ OH + NO_2

mechanism 8

1. CH_2=CH_2 + OH –(1.28)→ *OH-CH_2-CH_2*
2. O_2 + *OH-CH_2-CH_2* –(1)→ *OH-O-CH_2-CH_2-O*
3. O_2 + *OH-CH_2-CH_2* –(0.28)→ OH + glycol aldehyde
4. NO + *OH-O-CH_2-CH_2-O* –(1)→ NO_2 + *OH-O-CH_2-CH_2*
5. *OH-O-CH_2-CH_2* –(0.28)→ CH_2=CH_2 + HO_2
6. *OH-O-CH_2-CH_2* –(0.72)→ CH_2O + *OH-CH_2*
7. NO + HO_2 –(1)→ OH + NO_2
8. O_2 + *OH-CH_2* –(0.72)→ HO_2 + CH_2O

mechanism 9

1. CH_2=CH_2 + OH –(1)→ *OH-CH_2-CH_2*
2. OH + *OH-CH_2-CH_2* –(1)→ 2(*OH-CH_2*)
3. O_2 + *OH-CH_2-CH_2* –(0.28)→ OH + glycol aldehyde
4. O_2 + *OH-CH_2* –(1.72)→ *OH-O-CH_2-O*
5. NO + *OH-O-CH_2-O* –(1.72)→ NO_2 + *OH-O-CH_2*
6. *OH-O-CH_2* –(1.44)→ OH + CH_2O
7. *OH-CH_2* + *OH-O-CH_2* –(0.28)→ HO_2 + *OH-CH_2-CH_2*
8. NO + HO_2 –(0.28)→ OH + NO_2

mechanism 10

1. CH_2=CH_2 + OH –(1)→ *OH-CH_2-CH_2*
2. OH + *OH-CH_2-CH_2* –(0.72)→ 2(*OH-CH_2*)
3. O_2 + *OH-CH_2-CH_2* –(0.28)→ OH + glycol aldehyde
4. O_2 + *OH-CH_2* –(1.72)→ *OH-O-CH_2-O*
5. NO + *OH-O-CH_2-O* –(1.72)→ NO_2 + *OH-O-CH_2*
6. OH + *OH-O-CH_2* –(0.28)→ HO_2 + *OH-CH_2*
7. *OH-O-CH_2* –(1.44)→ OH + CH_2O
8. NO + HO_2 –(0.28)→ OH + NO_2

mechanism 11

1. $CH_2{=}CH_2 + OH -(2)\rightarrow$ *OH-CH_2-CH_2*
2. $OH +$ *OH-CH_2-CH_2* $-(1)\rightarrow HO_2 +$ *CH_2-CH3*
3. $NO + HO_2 -(3)\rightarrow OH + NO_2$
4. $NO_2 +$ *OH-CH_2-CH_2* $-(1)\rightarrow NO +$ *O-CH_2-CH_2-OH*
5. $O_2 +$ *O-CH_2-CH_2-OH* $-(0.28)\rightarrow HO_2 +$ glycol aldehyde
6. *O-CH_2-CH_2-OH* $-(0.72)\rightarrow CH_2O +$ *OH-CH_2*
7. $O_2 +$ *CH_2-CH3* $-(1)\rightarrow CH_2{=}CH_2 + HO_2$
8. $O_2 +$ *OH-CH_2* $-(0.72)\rightarrow HO_2 + CH_2O$

mechanism 12

1. $CH_2{=}CH_2 + OH -(2)\rightarrow$ *OH-CH_2-CH_2*
2. $OH +$ *OH-CH_2-CH_2* $-(1)\rightarrow HO_2 +$ *CH_2-CH3*
3. $O_2 +$ *OH-CH_2-CH_2* $-(0.28)\rightarrow OH +$ glycol aldehyde
4. $NO + HO_2 -(2.72)\rightarrow OH + NO_2$
5. $NO_2 +$ *OH-CH_2-CH_2* $-(0.72)\rightarrow NO +$ *O-CH_2-CH_2-OH*
6. *O-CH_2-CH_2-OH* $-(0.72)\rightarrow CH_2O +$ *OH-CH_2*
7. $O_2 +$ *CH_2-CH3* $-(1)\rightarrow CH_2{=}CH_2 + HO_2$
8. $O_2 +$ *OH-CH_2* $-(0.72)\rightarrow HO_2 + CH_2O$

mechanism 13

1. $CH_2{=}CH_2 + OH -(2)\rightarrow$ *OH-CH_2-CH_2*
2. $OH +$ *OH-CH_2-CH_2* $-(1.72)\rightarrow HO_2 +$ *CH_2-CH3*
3. $O_2 +$ *OH-CH_2-CH_2* $-(0.28)\rightarrow OH +$ glycol aldehyde
4. $NO + HO_2 -(2.72)\rightarrow OH + NO_2$
5. $NO_2 +$ *CH_2-CH3* $-(0.72)\rightarrow NO +$ *O-CH_2-CH3*
6. *O-CH_2-CH3* $-(0.72)\rightarrow CH_2O +$ *CH3*
7. $O_2 +$ *CH_2-CH3* $-(1)\rightarrow CH_2{=}CH_2 + HO_2$
8. $O_2 +$ *CH3* $-(0.72)\rightarrow OH + CH_2O$

mechanism 14

1. $CH_2{=}CH_2 + OH -(2)\rightarrow$ *OH-CH_2-CH_2*
2. $OH +$ *OH-CH_2-CH_2* $-(1.72)\rightarrow HO_2 +$ *CH_2-CH3*
3. $O_2 +$ *OH-CH_2-CH_2* $-(0.28)\rightarrow OH +$ glycol aldehyde
4. $NO + HO_2 -(2.72)\rightarrow OH + NO_2$
5. $NO_2 +$ *CH_2-CH3* $-(0.72)\rightarrow NO +$ *O-CH_2-CH3*
6. $O_2 +$ *O-CH_2-CH3* $-(0.72)\rightarrow CH_2O +$ *O-O-CH3*
7. $O_2 +$ *CH_2-CH3* $-(1)\rightarrow CH_2{=}CH_2 + HO_2$
8. *O-O-CH3* $-(0.72)\rightarrow OH + CH_2O$

mechanism 15

1. $CH_2{=}CH_2 + OH -(2.72)\rightarrow$ *OH-CH_2-CH_2*
2. $OH +$ *OH-CH_2-CH_2* $-(1.72)\rightarrow HO_2 +$ *CH_2-CH3*
3. $OH +$ *OH-CH_2-CH_2* $-(0.72)\rightarrow$ 2(*OH-CH_2*)
4. $O_2 +$ *OH-CH_2-CH_2* $-(0.28)\rightarrow OH +$ glycol aldehyde
5. $NO + HO_2 -(3.44)\rightarrow OH + NO_2$
6. $NO_2 +$ *OH-CH_2* $-(1.44)\rightarrow NO +$ *O-CH_2-OH*
7. *O-CH_2-OH* $-(1.44)\rightarrow OH + CH_2O$
8. $O_2 +$ *CH_2-CH3* $-(1.72)\rightarrow CH_2{=}CH_2 + HO_2$