

Detailed Mechanism Generation. 1. Generalized Reactive Properties as Reaction Class Substructures

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This paper, the first in a series on the automatic generation of detailed hydrocarbon mechanisms for hydrocarbons, describes how generalized reaction types, specifically the 25 types outlined by Curran et al. for heptane and isooctane combustion, can be translated into general reaction classes. Each type description from Curran et al. ranges from specific, such as differentiating among 1°, 2°, and 3° centers, to nonspecific such as specifying intermediate specific as “products”. In the latter case, additional interpretation of the reaction type must be extrapolated from other sources. The types are translated to the substructure “patterns” representing reaction classes. The success of fully translating all the rate and structural information described in these reaction types as they are defined in the literature demonstrates the power of the approach used here. A comparison of the generated reactions using these 25 types with that of a hand-produced heptane mechanism showed that, aside from well-defined exceptions, the set of reactions were almost identical. Often just the elimination of selected species (and sometimes reactions) was enough to make them identical. A notable exception was the use of lumped species in the hand-produced mechanism. The purpose of this paper is to show that an established set of reaction type descriptions can be translated to reaction classes suitable for automatic mechanism generation. A further goal of this paper is to show that these classes can be used to generate a detailed mechanism that mimics a hand produced one.

1. INTRODUCTION

Through analogies with known reactions and through extrapolation of general physical principles, specific reactions of a large detailed combustion mechanism can be generated.^{1–4} As the need for mechanisms of larger model fuels, such as decane,⁵ even hexadecane⁶ and more extensive and accurate mechanisms for smaller molecules^{7–9} increases, automatic generation is becoming a necessity rather than an option. The use of automatic generators within combustion mechanisms of larger more complex molecules is a direct response to the unwieldiness of designing a complete mechanism. In addition, there is a recognition that there is rarely enough experimental evidence available, and generalizations,^{8,10,11} the heart of automatic generation, must be used regardless whether the procedure is automated or not.

The principles and techniques used in mechanism generation are a formalization and automatization of the traditional principles and techniques used in “smaller” mechanism development.³ Reaction classes, as used here, are founded on the basic principle that reactivity of a molecule is based solely on the structural features around the reaction center, i.e., the set of bonds and atoms that change in the course of a reaction. Strong structural features, such as influences of primary, secondary, and tertiary centers or neighboring functional groups (not directly participating), are included in the structural features around the reactive center. Weaker influences, for example, the location of secondary hydrocarbons in a straight chain are not included. The specification of “weak” and “strong” is dependent on the level of

approximation. The representation of the structural features used in this work is general enough to allow straight, branched, cyclic, and aromatic features and any combination of heteroatoms and radicals.

The goal of this paper is 2-fold. The first is to show that reaction type descriptors from the literature can be translated to reaction classes which can then be used to generate detailed mechanisms. This will be demonstrated on the 25 reactive types specified by Curran et al. The second purpose is to use these derived reaction classes to generate a mechanism which mimics a mechanism which has been produced by hand. This will be demonstrated on the C_7 submechanism (just those reactions whose largest reactant or product has seven carbons) of the Curran et al. heptane mechanism.

The first part of this paper translates the reaction types of Curran et al. to reaction classes. The main thrust of the work is the determination of the reactant and product substructures of the reactive center. This involves determining which functional groups of the neighboring environment around the bond and valence changes are necessary. More often than not, more detailed descriptions of the reactive center are given. This allows for future differentiations with regard to rate constants. For the hydrocarbons dealt with in this paper, this usually takes the form of differentiating among primary, secondary, and tertiary carbons. This paper outlines the translation of an entire set of accepted combustion reaction types into reaction classes suitable for mechanism generation.

In the conclusion a comparison of the reactions generated with the derived reaction classes are compared with the corresponding reactions of the Curran et al. heptane mechanism produced by hand.

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2. MECHANISM GENERATION SYSTEM

The goal of a mechanism generation system is to simulate the procedures used for producing mechanisms by hand. It is, in essence, a formalization of the procedures used to generate and manipulate all objects associated with mechanism development. This formalization leads to the automation of the steps and allows the developer to operate at a higher level and to deal with more complex problems. The tedious details, which could be error prone if done by hand, are left to the system.

The following sections outline the components of the mechanism generation system used in this paper and how they are used in mechanism generation.

2.1. Database. The heart of the mechanism generation system is the “database” of molecules, substructures, reactions, reaction classes, submechanisms, and mechanisms. Each of these objects has its own random access binary database accessed by the system. Each object has all the essential chemical data associated with it. For example, the molecule object has its “graphical” structure, thermodynamic and transport information, and its standard name (usually following IUPAC conventions) and CHEMKIN name (a compact name with less than 16 characters, usually somewhat standard from published combustion mechanisms). The molecule is referenced (by other objects from the database or from the user interface) from the database through its standard name or a uniquely defined ID number. For the other database objects, similar concepts apply.

The source of the database information is from “accepted” literature values. Modifications of these standard values, for example through optimization, are noted as exceptions within the relevant data structures. Input of objects to the database is done through ASCII files and the JAVA GUI interface. For example, the molecule structural information is done through a standard SDF format,¹³ and the thermodynamic information is done through either the standard NASA polynomial format¹⁴ or as a list of heat capacities and standard enthalpy and entropy values. The reaction class information is given as a list of substructures, the atom–atom correspondences between the reactants and products, and the associated rate constant data. Mechanism and submechanism data is done through the JAVA GUI interface.

It should be emphasized here that the expansion of the database involves the manipulation of information that is common knowledge to a chemist. No FORTRAN, C, or C++ programming is involved, and as the software is developed, less and less dependence on software technical issues is involved.

2.2. Reaction Generation. The key to the generation process is the production of a set of reactions from a given reaction class and a set of reactants. A reaction class gives the generic description of how molecules react. In this system³ this is done by describing the “reactive center”, i.e., the set of atoms and bonds that change during a reaction. The reactive center description in a reaction class is “2D graphical”,¹⁵ i.e., a set of reactant and product substructures and the atom correspondences between them (see figures in the reaction class descriptions of this paper). The spatial arrangement of the atoms is only implied by the atomic valence and bonding. How these substructures change from the reactant side to the product side define the reaction.

Included in the reaction class description is the influence of functional groups around the reactive center. The major assumption in this description is that the influence of the structures outside the reaction class are insignificant relative to those within the reaction class.

To generate a reaction from a reaction class, first the atoms and bonds of the reactant substructures of the reaction class are matched within the reactant molecules. The product molecules are then produced by changing the atom valences and bonds of the reactant molecule in exactly the same way as in the reaction class. Often, a single reaction class can be matched more than once within the reactant. If the matched atoms are not exactly equivalent by symmetry, the result is more than one reaction. For example, in the hydrogen abstraction of heptane, there are 10 secondary hydrogens, but only three different reactions are generated. The four hydrogens on carbons 2 and 6 produce the first reaction, the four hydrogens on carbons 3 and 5 produce the second, and the two hydrogens on carbon 4 produce the third. If the reaction rate is given “per hydrogen”, then the rates of the three reactions would be multiplied by the “symmetry factors”, number of equivalent matches, four, four, and two, respectively. The symmetry factor, in general, reflects the relationship between the symmetry of the matched substructures and the rate constant. Sometimes, the factor can be a matter of definition. For example, in the abstraction of the secondary hydrogen, if the rate constant was given as per secondary carbon instead of per hydrogen, then the symmetry factors would be two, two, and one, respectively, for heptane.

A single reaction class is used to generate a single step of reactions from a given set of reactants. However, a complete mechanism consists of many such steps. For example, the products of the current step can become the reactants of the next step. One strategy to generate a mechanism is to iteratively apply a set of reaction classes to the reactants and the products they produce. However, two major problems can arise with this approach. First, a combinatorial explosion of species and reactions occur. The second, and more damaging problem, is that a larger number of “insignificant” or unphysical molecules and reactions arise. The main reason for this latter consequence is that the primary assumption of the application of reaction classes, namely that the parts of the molecule outside the reaction class substructures have no significant influence, breaks down. Although there are ways to circumvent this problem, for example through filtering, the preferred choice of this system is define specific “pathways”, a series of reactive steps where each step consists of a set of reaction classes. This, more controlled, application method reduces significantly the problems of the iterative method. The pathway method has an additional significant advantage of adding an important organizational layer to the mechanism. A pathway describes generically a specific type of reactive sequence, such as either the high or low-temperature alkane or alkene pathways or decomposition or formation of alkenes, aldehydes, or ketones or radical isomerizations. The reaction classes within the pathway itself are applied to an initial “seed molecule”, the first reactant, to form a submechanism of reactions. A mechanism would be classified as a set of submechanisms of seed molecules reacting through specified pathways.

Unwanted, or “dead ends”, molecules, which do not react further, are avoided by designing the pathways in such a

way so the product of each step either reacts in the next step of the pathway or reacts within another submechanism. In designing the “next” step in a pathway, the functionality produced by the current step, i.e., one of the product substructures, is the functionality that is reacted in the next step, i.e., one of the reactant substructures. To avoid unwanted or dead end molecules, a general “rule of thumb” in designing combustion pathways is that all generated species which do not react specifically in the next step of the pathway have only a single simple functionality, such as a radical, alkene, aldehyde, or ketone (and not a combination of these) and that they are smaller, i.e., have fewer carbons.

A complete mechanism consists of a hierarchical set of generated submechanisms produced by the chosen pathways and seed molecules and a nongenerated “base” mechanism, a validated mechanism of “smaller” molecules (usually four or less carbons). To design a complete mechanism, the first task is to choose the set of pathways that are significant for the range of temperatures and pressures to be dealt with. The set of reaction classes needed are indirectly selected by the choice of pathways. In mechanisms of larger molecules, for example, decane, sometimes two sets of pathways are used, one primary set to generate all the reactions of the initial reactant, in this case decane, and another secondary set which deal with the products of the primary and subsequent secondary submechanisms. For decane, the seed molecule for the primary set of pathways is decane itself, and the seed molecules for the secondary pathways are pentane through nonane. The base mechanism takes care of the smaller molecules.

Given a database of molecules, reaction classes, and pathways, generating a complete mechanism has just a few steps. First, the set of significant pathways and seed molecules relevant for the given conditions to be studied are chosen. Next, each submechanism is generated by applying each seed molecule to its set of pathways. Both reaction data, the rates, and molecule data, the thermodynamic data, make up the submechanism. These submechanisms are then combined into one single generated mechanism. This generated mechanism is then combined with the base mechanism. The main task in combining submechanisms is to automatically eliminate duplicate reactions and molecules (the base mechanism data takes precedence over the generated data). This total mechanism can then be used in a numerical solver for the physical conditions desired.

One purpose of this paper is to illustrate that a complete set of accepted combustion reaction types, as outlined by the Curran et al. in their heptane and isooctane papers, can be, *without exception*, translated into reaction classes suitable for mechanism generation. This work not only expands the database of reaction classes to a significant set of reaction types for hydrocarbon combustion but also illustrates a variety of issues that arise when translating literature “generalized” reaction types to fully functional reaction classes useful for automatic generation. Some of the descriptions of the reaction types, especially where the chemistry has been more exactly studied and is already generalized, can be directly translated to reaction classes in a straightforward one-to-one correspondence. However, sometimes only fairly vague reaction type descriptions are given. The most common being simply “products”, meaning intermedi-

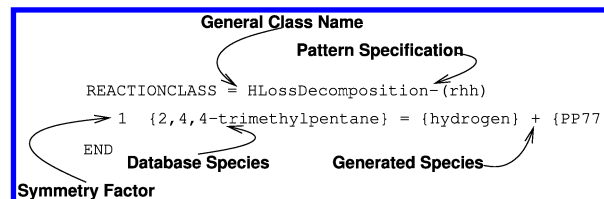


Figure 1. The set of reactions in a REACTIONCLASS block all have the same rate constant. Each class has a **general** name and a **pattern** name specifying a specific rate which is then modified by the multiplication **symmetry** factor. Species in the database have a full name, and those not in the database have a generic name of PPxx.

ate species dependent on the fuel molecule in question. In these cases, the chemistry must be extrapolated through examination of other sources, for example, “known” reactions from established mechanisms and translating and generalizing the reactive centers of these reactions.

Examples of the use of the reaction classes to generate reactions are given with the reaction type descriptions. In the conclusion a complete C_7 submechanism of heptane is examined. In the following sections, each translation is described with the techniques used to accomplish it.

3. REACTION TYPES

The heptane¹ and the isooctane² papers of Curran et al. have outlined a set of 25 reaction “types” used in hydrocarbon combustion mechanisms. This work systematically interprets and translates each of these types into concrete reaction classes for use in automatic generation. The main purpose of this work, aside from expanding the generation database, is to emphasize that the generation concept is powerful enough to describe accepted complex chemistry found in the literature and to show its potential to produce detailed mechanisms using nontrivial chemistry. In this paper, reaction types refer to those of Curran et al. and “classes” refer to those for automatic generation.

Each section represents a reaction type given in the original papers and gives the corresponding substructure descriptions of the reactive center and a representative example of the class’s application. In most cases, the reactive center description is more detailed than what is described in the papers. This allows, in future work as the chemistry becomes more defined, more exact differentiations to be made. In some of the reaction type descriptions the structural features of the products are not described explicitly (only products is given), and a more concrete interpretation has to be made (in some cases, the details will be discussed in the second paper in this series¹²).

For each reaction class description three pieces of information are given:

Reaction Class List. Associated with each type defined there can be one or more reaction classes that are dependent on species structural features.

Reaction Class Pattern. For each reaction class associated with the type, the reactive center is given in graph theoretical form (shown in a figure).

Example. For most classes, a representative example of the specific reactions generated by the classes is given in the form outputted by the program, with reaction class and multiplicity factor (Figure 1).

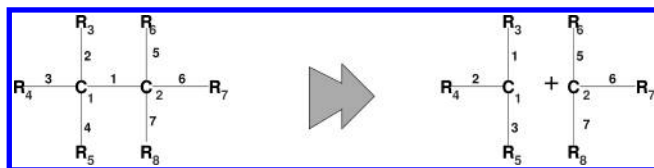


Figure 2. Type I: **Decomp**: This reaction class describes the unimolecular decomposition with loss of alkyl. The atoms R_3 through R_8 are replaced by distinguishable combinations of H and C . This results in 10 different patterns.



Figure 3. Type I: **HLossDecomposition**: Unimolecular Decomposition with loss of hydrogen has in total three different patterns for the primary, secondary, and tertiary carbons (substituting R_2 , R_3 , and R_4).

In the reaction class representations a distinction among primary, secondary, and tertiary carbons is usually made. In the representing substructures this corresponds to a specific combination of singly bonded carbons and hydrogens to the carbon atom in question. In the reaction class figures, instead of drawing all combinations, a generic R atom is used. This R atom represents either a carbon or hydrogen. For example in Figure 3, R_2 , R_3 , and R_4 can be substituted to represent the four possibilities. Substituting $R_2R_3R_4$ with HHH is methane, RHH is the primary carbon, RRH is the secondary carbon, and RRR is the tertiary carbon. This gives the four substructure patterns making up the reaction class.

In Figure 10 another meta atom is used, Q . The Q atom again represents either a carbon or a hydrogen. But, in contrast to the R atom, it does not represent a new substructure. In matching substructure with Q atoms, each Q can match with either a carbon or a hydrogen. This effectively says that the rate does not depend on this substitution.

The example reactions were chosen to have at least some species within the species database, which means their full name could be used. Those species which are not in the database, and whose information (both structural and thermodynamic) must be generated, have a generic name of PP_{xx} . The structural information for these species is known within the system and is accessible through the graphical interface when examining a mechanism. This information is also outputted in an ASCII form and can be interpreted by the interface and a knowledgeable developer. The numerical solvers being used do not need this extra information, and thus it does not appear in the files needed by the solvers.

3.1. I: Unimolecular Decomposition. Classes: Decomp, HLossDecomposition. For this reaction type, Curran et al. specifies a single rate, that of a reverse addition reaction, for two types of decomposition, loss of a hydrogen radical and loss of an alkyl radical. The reaction classes defined have been expanded to make a distinction among 1° , 2° , and 3° carbons, but the rate constants for each are the same. This allows for easy refinement as more detailed information is known.

Figure 2 shows the generalized pattern for the 10 different reaction patterns of the reaction class of **Decomp**. An

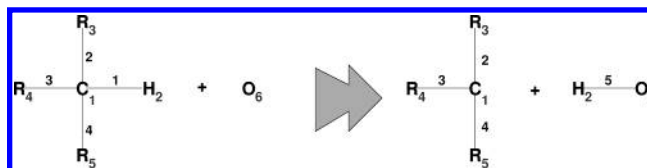


Figure 4. Type II: **H-Abstraction**: A reaction class is defined for each radical, in this case an oxygen atom. Substituting C and H for R_3 , R_4 , and R_5 results in the patterns of the reaction class.

example of the application of the reaction pattern **Decomp**-(rrh)(hhh) is

```
REACTIONCLASS = Decomp-(rrh)(hhh)
  2 pentane = methyl-radical + 1-butyl-radical
END
```

The symmetry factor of 2 refers to the two methyl groups at either end of the straight chained pentane. Figure 3 shows the generalized pattern for the four different reaction patterns of the reaction class of **HLossDecomposition**. An example of the application of **HLossDecomposition**-(rrh) is

```
REACTIONCLASS = HLossDecomposition-(rrr)
  1 2,2,4-trimethylpentane = hydrogen-radical + PP7
  1 2-methylpropane = hydrogen-radical + PP64
END
```

where PP_7 and PP_{64} are the generated tertiary radicals of 2,2,4-trimethylpentane and 2-methylpropane, respectively.

3.2. II: Hydrogen Abstraction. Classes: H-Abstraction. This reaction type describes the abstraction of a hydrogen by a radical. Each of the reaction classes differentiates among 1° , 2° , and 3° carbon radicals. This allows a one-to-one correspondence with the defined reaction classes (see Figure 4). In the isooctane paper, a distinction is made between the different primary isooctane hydrogens. Though the local environment of the primary carbon could be expanded to differentiate between the three primary types found in heptane and isooctane, for this study it was not deemed necessary.

An example application of the **H-Abstraction-Peroxyl-Radical-Secondary** reaction class is as follows

```
REACTIONCLASS = H-Abstraction-PeroxylRadical-Secondary
  2 2,2,4-trimethylpentane + peroxy-radical = PP8 + hydrogen-peroxide
  4 heptane + peroxy-radical = PP181 + hydrogen-peroxide
  2 heptane + peroxy-radical = PP183 + hydrogen-peroxide
END
```

Where PP_8 , PP_{181} , and PP_{183} represent the corresponding secondary radicals of 2,2,4-trimethylpentane and heptane. For heptane, the two different products are the two different types of secondary radicals produced. The symmetry factors here correspond to the number of secondary radicals in each reactant molecule (because the abstraction rates are given as per hydrogen).

3.3. III: Radical Decomposition. Classes: PropylRadical-ToEthene, HLoss-ethyl-radical-to-olefin. The **PropylRadical-ToEthene** and the **HLoss-ethyl-radical-to-olefin** represent the decomposition of a radical to a smaller radical and an alkene through beta-scission. The reaction type is an example where the reaction class is defined in the forward direction, a decomposition, used for generation, but the rate constants are given for the reverse direction, an addition. For both addition of hydrogen radical and addition of alkyl radical to an alkene, the only distinction is between “internal”

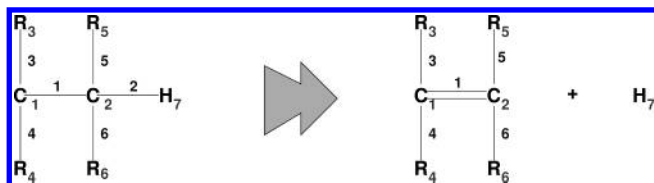


Figure 5. Type III: **HLoss-ethyl-radical-to-olefin**: Substituting the pairs R_3 , R_4 and R_5 , R_6 with all (nonequivalent) combinations carbon and hydrogen, produces nine different patterns (three each on carbons 1 and 2).

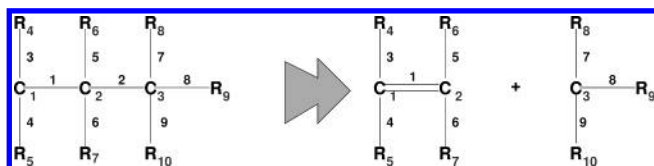


Figure 6. Type III: **PropylRadicalToEthene**: Substituting the R_4 , R_5 on carbon 1, R_6 , R_7 on carbon 2, and R_8 , R_9 , R_{10} on carbon 3 with nonequivalent combinations of hydrogen and carbon produces 36 patterns in this class.

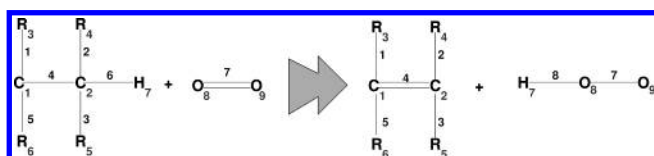


Figure 7. Type IV: **ethyl-radical-oxidation-to-olefin**: Substituting pairs R_3 , R_6 and R_4 , R_5 with carbon and hydrogens produces nine patterns in this class.

(2° and 3°) and “terminal” (1°) addition. Figures 5 and 6 show that this corresponds to differentiating between R_5 and R_6 and differentiating between R_6 and R_7 , respectively. The distinction between the other cases is left for future studies. The forward rate is either calculated by the thermodynamics or an explicit “representative” value is used.

An example of the application of the PropylRadicalToEthene-(rh)(hh)(hhh) reaction to 3 - C_8H_{17} , 3 - C_6H_{13} , and 3 - C_5H_{11} (PP8, PP165, and PP220, respectively) gives the following:

```
REACTIONCLASS = PropylRadicalToEthene-(rh)(hh)(hhh)
1 PP8 = methyl-radical + 1-hexene
1 PP165 = methyl-radical + 1-pentene
2 PP220 = methyl-radical + 1-butene
END
```

The symmetry factor of 2 for the PP220, which is 3-pentyl radical, represents the two ways the products can be formed (left and right).

3.4. IV: Alkyl Radical Oxidation to Olefin. Classes: ethyl-radical-oxidation-to-olefin. This reaction class is simply the abstraction of a hydrogen from the carbon next to the radical by an oxygen resulting in an olefin. The reactive center of the reaction class, shown in Figure 7, involves only the two carbons undergoing the valence change. Nine patterns are used to allow distinction among primary, secondary, and tertiary centers on each of the carbons (Curran et al. gives only one reaction constant for all).

3.5. V: Alkyl Radical Isomerization. Classes: Ring-chain-h-isomerization. This reaction type describes alkyl radical isomerization and is dependent on the type of reactant and product radicals and the ring strain involved. The model used by Curran et al. can be translated to a reaction class



Figure 8. Type V: **Ring-chain-h-isomerization**: This alkyl radical isomerization is shown where no additional structural information is given, thus it is free to be any connecting atom. In this particular pattern the ring size is 5. The complete class has several patterns representing the different ring sizes of the abstraction.

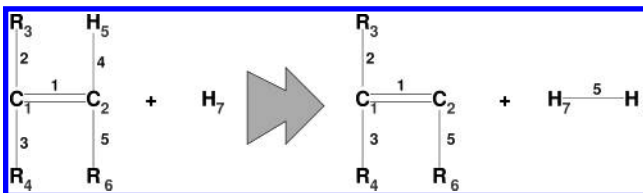


Figure 9. Type VI: **H-Alkenyl-Abs**: There is one set of patterns of this type for each of the four radicals, hydrogen, oxygen, hydroxyl, and methyl. In each of these sets there are six patterns representing the combinations of substitutions of the pair R_3 , R_4 on carbon 1 and R_6 on carbon 2.

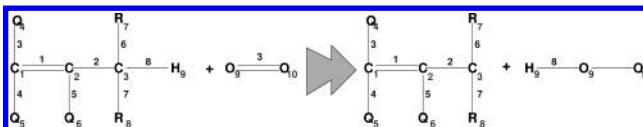


Figure 10. Type VI: **AlphaHAbstractionFromOlefin**: The patterns allow for either a hydrogen or a (single bonded) carbon to be on the Q_4 , Q_5 , and Q_6 . Whether the hydrogen is to be abstracted is primary, secondary, or tertiary is determined by R_7 and R_8 in three different patterns.

substructure description and differs (for the heptane and isooctane cases) only in the preexponential constant. The generalized rate constants were taken to be the average values.

Figure 8 show a typical representative description with a ring size of five. No distinction is made between radical carbons. A distinction could be made, as Curran et al. did, by expanding the description about the radical (and hydrogen) carbons. The other carbons within the ring structure remain unchanged. Currently, patterns exist for up to a ring size of seven.

3.6. VI: Abstraction from Olefin. Classes: H-Alkenyl-Abs, AlphaHFromOlefin, AlphaHAbstractionFromOlefin, BetaOlefinDecomp. This reaction class describes the abstraction of a hydrogen from an olefin. Where the reaction paths are not fully described these generalizations have to be to be extrapolated from specific examples. Here, the abstraction of hydrogen was interpreted in two ways. First, a vinyl was formed by abstraction of one of the double bond hydrogens (Figure 9). The second is the abstraction from the alkyl part of the alkene (as suggested Curran et al.). This is done either with abstraction by an oxygen (Figure 10), or by simple decomposition by loss of hydrogen (Figure 11), or by loss of an alkyl radical (Figure 12).

If the abstraction takes place far enough from the alkene group, then the abstraction can be considered to be a type II hydrogen abstraction (see section 3.2), and no influence of the alkene is considered. The patterns shown in section 3.1 would be applied to the beta hydrogens from the alkene group. For the alpha hydrogens, forming the resonant allyl, another pattern would be needed. Currently, these resonant allyl structures are formed by decomposition (see the BetaOlefinDecomp shown in Figure 12).

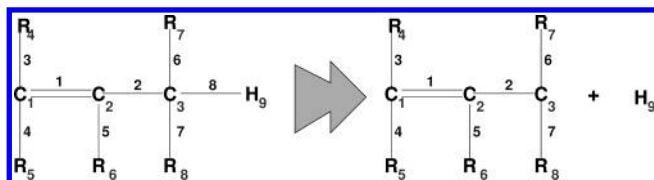


Figure 11. Type VI: **AlphaHFromOlefin**: The patterns allow for either a hydrogen or a (single bonded) carbon to be on the Q_4 , Q_5 , and Q_6 . Whether the hydrogen is to be abstracted is primary, secondary, or tertiary is determined by R_7 and R_8 in three different patterns.

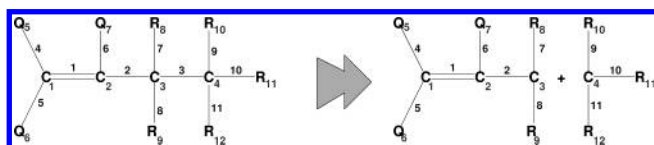


Figure 12. Type VI: **BetaOlefinDecomp**: The patterns allow for either a hydrogen or a (single bonded) carbon to be on the Q_5 , Q_6 , and Q_7 . The two radicals produced are characterized by R_8 through R_{12} in 12 different patterns.

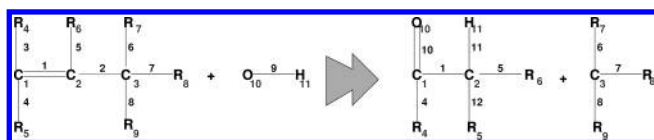


Figure 13. Type VII: **AddHydroxylToPropene**: A hydroxyl radical is added across an alkene resulting in the decomposition to an aldehyde and a simple radical. Substituting R_4 – R_{10} with C or H results in 24 different patterns.

It should be mentioned that automatic generation techniques can help with the bookkeeping involved with the “number and complexity” problems, i.e., the “combinatorial explosion”, mentioned by Curran et al. This is dependent, of course, on whether that amount of detail is desired. The second problem mentioned, namely the “fate” of the alkene products, is discussed in more detail in subsequent sections and the second paper in this series.¹²

The following are example applications of these reaction classes:

```
REACTIONCLASS = BetaOlefinDecomp(qq)(q)(hh)(rh)
1 {1-pentene} = {3-propenyl-radical} + {ethyl-radical}
END
REACTIONCLASS = AlphaHAbstractionFromOlefinOxygen-(rh)
1 {1-butene} + {oxygen} = {peroxyl-radical} + {1-buten-3-yl-radical}
END
REACTIONCLASS = AlphaHAbstractionFromOlefin-(rh)
1 {1-pentene} = {hydrogen-radical} + {PP79}
1 {2-pentene} = {hydrogen-radical} + {PP81}
END
```

3.7. VII: Addition of Radical Species to Olefin. Classes: OlefinToAldehydeDecomp, AddHydroxylToPropene, AddOxygenToPropene. The Curran et al. paper describes a simplified chemistry of this type as a single step reaction, the addition of the radical, either oxygen or hydroxyl, followed by immediate decomposition. The explicit products were not listed and had to be interpreted. The type is interpreted in several reaction classes. The classes OlefinToAldehydeDecomp and AddHydroxylToPropene (Figures 13 and 14) are where a hydroxyl is added across the double bond to produce an aldehyde or ketone and a radical. The two classes are the result of how the hydroxyl is added across the double bond with respect to the radical produced. The reaction class, AddOxygenToPropene, representing the addition of the oxygen radical (Figure 15) similarly produces

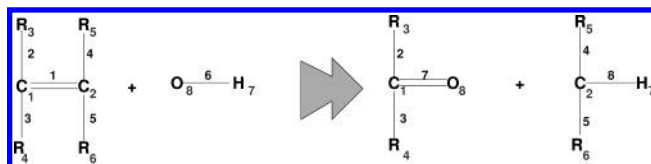


Figure 14. Type VII: **OlefinToAldehydeDecomp, OlefinToAldehydeDecompB**: Hydroxyl addition to the olefin. The class is characterized by R_3 – R_6 in nine patterns.

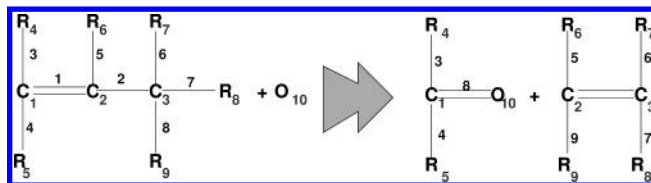


Figure 15. Type VII: **AddOxygenToPropene**: Oxygen addition to the olefin. The class is characterized by R_3 – R_9 in 24 patterns.

an aldehyde or ketone radical and an alkyl radical (in this case the addition across the double bond is symmetrical).

Examples of the addition of hydroxyl and oxygen across the double bond are

```
REACTIONCLASS = OlefinToAldehydeDecomp-(rh)(hh)
2 1-pentene + hydroxyl-radical = methyl-radical + 1-butanal
END
REACTIONCLASS = OlefinToAldehydeDecompB-(rh)(hh)
2 1-pentene + hydroxyl-radical = aldehyde + 1-butyl-radical
END
REACTIONCLASS = AddOxygenToPropene-(hh)(h)(rh)
1 1-heptene + oxygen-atom = aldehyde + 1-hexene
1 1-hexene + oxygen-atom = aldehyde + 1-pentene
1 1-pentene + oxygen-atom = aldehyde + 1-butene
END
```

The two sets of products represent the asymmetry of adding the hydroxyl radical to the double bond.

3.8. VIII: Alkenyl Radical Decomposition. Classes. In types where the product species are not specified, specific examples of what is meant, as in this case of olefin decomposition, have to be analyzed and generalized. Sometimes this could involve the use of other reaction classes or the reaction class is characterized more exactly. If the initial hydrogen abstraction occurs “away” (usually defined at least one carbon between the radical and the olefin), then decomposition follows conventional “alkyl” decomposition routes. The consumption of alkenyl radicals which are on or next to (alpha position) the olefin are through the addition of oxygen and subsequent decomposition to aldehydes, ketones, and ketenes. These reaction classes were extrapolated from explicit reactions and are explained in more detail in the second paper of this series.¹²

3.9. IX: Olefin Decomposition. Classes. For the case of alkenyl decomposition, Curran et al. gave no explicit generalizations, and thus other sources are used. Some of these decompositions are characterized more exactly by introducing generalizations of the Come⁹ propene reactions. Some of these were discussed in the type VIII reaction class.

In addition, simpler decompositions, such as type I could be used by treating the nonalkene portion as an alkane. That it would be applied to the alkene would be taken care of by specifying the decomposition directly after the alkene formation in the generation procedure. In smaller detailed mechanisms, for example, heptane, when produced by hand the product distribution can be selected such that they can react further. Those reactions producing species where further

reactions are not present are ignored. For this type, the decomposition products can split the heptene into, for example, C_3 and C_4 species which react further in the base mechanism. This will be increasingly harder as the size of the alkene increases. In automatic generation this problem is amplified because there is no reason not to generate all, as in this case, the decomposition products. As the alkene becomes larger, the chances of producing "false" combinations increases. If the species which do not react any further are identified, then those, and the reactions which produce them, can only be eliminated by filtering.

3.10. X: Addition of Alkyl Radicals to O_2 . Classes: Carbon-Radical- $(R + O_2 \rightarrow RO_2)$. For the addition of alkyl to oxygen the reaction class has a one-to-one correspondence with the reaction type. The rate is a constant dependent only on whether the carbon radical is 1° , 2° , or 3° . The reverse reaction is calculated from the species thermodynamics. However, due to the critical dependence of the negative temperature region on the reverse reaction, sometimes a "representative" value can be taken.

An example of the Carbon-Radical- $(R + O_2 \rightarrow RO_2)$ as applied within the butane mechanism is

```
REACTIONCLASS = Primary-Carbon-Radical-(R.+O2-->RO2.)
1 1-butyl-radical + oxygen = 1-butylperoxy-radical
END
REACTIONCLASS = Secondary-Carbon-Radical-(R.+O2-->RO2.)
1 2-butyl-radical + oxygen = 2-butylperoxy-radical
END
```

3.11. XI: $RO_2 + R \rightarrow RO + RO$. Classes. The description of this reaction class in terms of substructures presents no problem. However, the use of this pattern within the generation procedure adopted, a controlled application of classes,¹⁶ is not possible in its implied generality. The criteria for application is that both the RO_2 and R species have been generated in the previous step. This reaction class is usually the next step after the formation of a RO_2 species. However, that step does not, as in the case of type 10, also produce a simple alkyl radical as a product. To use this reaction class in such a context (under controlled generation), an explicit list of alkyl radical species would have to be given with this step. One, less general, way around this is to introduce specific molecules for R such as methyl, propyl, etc. radicals. The restriction to these smaller specific species most likely does not produce a significant difference due to the low relative concentration of the higher alkyl radical species.

3.12. XII: Alkyl Peroxy Radical Isomerization. Classes: Intramolecular-QOOH-Formation. This type describes the intermolecular abstraction of hydrogen by the peroxy group. The rate is dependent on the ring size of the transition state and the type of hydrogen (1° , 2° , and 3°). This type can be represented as specific substructures in a reaction class. The ring size, as shown by the example in Figure 17, is simply a chain of carbons with unspecified attachments.

The following is an example of the application of Intramolecular-QOOH-Formation class. These examples show only dependence with ring size:

```
REACTIONCLASS = Intramolecular-1-4-QOOH-Formation
2 1-butylperoxy-radical = 2-butyl-1-hydroperoxy-radical
3 2-butylperoxy-radical = 1-butyl-2-hydroperoxy-radical
2 2-butylperoxy-radical = 3-butyl-2-hydroperoxy-radical
END
```

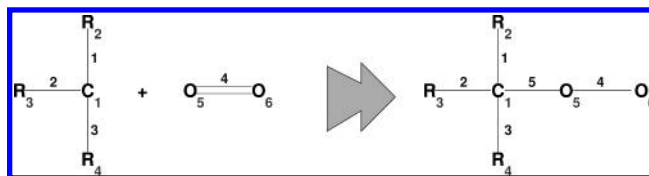


Figure 16. Type X: **Carbon-Radical- $(R + O_2 \rightarrow RO_2)$** : The addition of an oxygen to a simple radical produces a peroxy radical. By substitution of R_2 – R_4 , the distinction among 1° , 2° , and 3° patterns can be made.

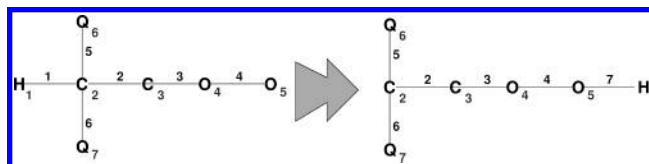


Figure 17. Type XII: **Intramolecular-QOOH-Formation**: The dependence on the type of abstracted hydrogen is accomplished through the 3 combinations of the R_6 and R_7 . Different patterns are used to represent the ring size. The ring size of 5 is shown here.

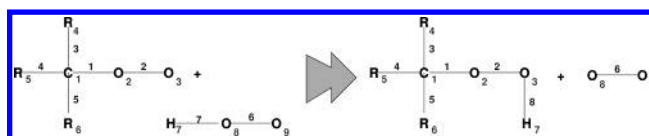


Figure 18. Type XIII: **ROOHFromPeroxy**: Through substitution of R_4 , R_5 , and R_6 in the alkyl peroxy, structural distinctions can be made. There are four patterns in this class.

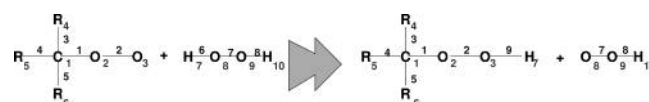


Figure 19. Type XIV: **PeroxyFromHydrogenPeroxide**: Through substitution of R_4 , R_5 , and R_6 in the alkylperoxy radical, structural distinctions can be made. There are four patterns in this class.

The rate constant is given in terms of per hydrogen so the symmetry factor reflects the number of hydrogens on the position abstracted.

3.13. XIII: $RO_2 + HO_2 = RO_2H + O_2$. Classes: ROOHFromPeroxy. A single temperature-dependent rate is used for the abstraction of hydrogen by the alkyl peroxy. With this, as with other types, the value used differs from the "experimental" value based on a smaller alkane due to the weak dependence on species size. With the simple substructure representation of reaction classes, this dependence cannot be taken account.

3.14. XIV: $RO_2 + H_2O_2 = RO_2H + HO_2$. Classes: PeroxyFromHydrogenPeroxide. This type is the abstraction of a hydrogen from hydrogen peroxide by an alkylperoxy radical. This reaction class (Figure 19) has a structure independent (with respect to the peroxy group) rate constant. In the reaction class's definition a distinction is being made among 1° , 2° , and 3° carbons on the alkylperoxy radical.

3.15. XV: $RO_2 + CH_3O_2 = RO + CH_3O + O_2$. Classes: RO2Abstraction. This reaction class is just a special case of the general reaction class shown in section 3.16, where the R groups of one of the RO_2 species are hydrogens.

3.16. XVI: $RO_2 + RO_2 = RO + RO + O_2$. Classes: RO2Abstraction. This is, in fact, the generalized version of the type XV reaction class (see section 3.15). The distinction between the two classes is easily made by the appropriate assignment of the pair, R_5 , R_6 , of the RO_2 reactant (Figure 20). By substituting R_4 , R_5 , and R_6 to hydrogen,

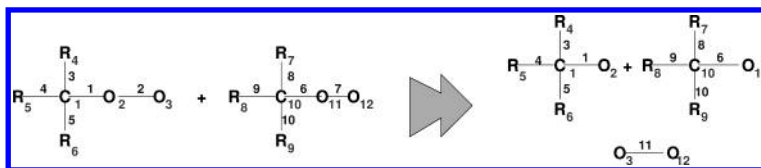


Figure 20. Type XVI: **RO2Abstraction**: A distinction among primary, secondary, and tertiary species is made through setting R_4 – R_9 to carbon or hydrogen. A total of 16 patterns are defined.

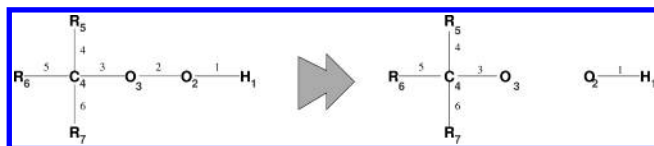


Figure 21. Type XVII: **AlkoxyFromHPeroxy**: The decomposition of an alkyl hydrogen peroxide to an alkoxy radical and a hydroxyl radical is represented by this class. By substitution of R_5 , R_6 , and R_7 with hydrogen or carbon, a total of four patterns are produced.

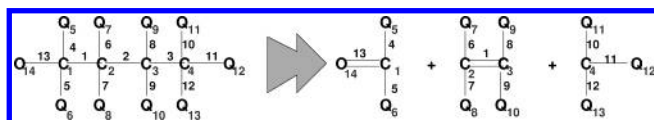


Figure 22. Type XVIII: **AlkoxyDecomp**: This general reaction class is represented by a single pattern where the Q atoms can be either hydrogen or carbon atoms. The use of the Q 's stipulates that no such substitution makes a difference in the rate. It also means that only one pattern is defined.

reaction type XV is formed. There are basically two reaction constants given, one for the type XV case and the rest.

3.17. XVII: $RO_2H = RO + OH$. Classes: AlkoxyFromHPeroxy. This decomposition of an alkyl hydrogen peroxide to an alkoxy radical and a hydroxyl radical is represented by the AlkoxyFromHPeroxy reaction class (Figure 21). The pattern has been defined to make a distinction among 1° , 2° , and 3° carbons, but at this time only one rate constant is used for all.

An example of its application within the C_4 low-temperature chemistry is shown here:

```
REACTIONCLASS = AlkoxyFromHPeroxy-RHH
2 {3-butyl-1-hydroperoxy} = {hydroxyl-radical} + {PP22}
END
REACTIONCLASS = AlkoxyFromHPeroxy-RRH
1 {4-butyl-2-hydroperoxy} = {hydroxyl-radical} + {PP24}
END
```

The species, PP22 and PP24, are the corresponding butyl-alkoxy products.

3.18. XVIII: RO Decomposition. Classes: AlkoxyDecomp. The reaction class, AlkoxyDecomp (Figure 22), the single step decomposition of an alkoxy radical to an aldehyde/ketone, an alkene, and an alkyl radical, has a single general forward rate constant with the reverse constant being zero (due to the formation of three products). The reaction class was designed to produce, in the simplest form of bond breaking and electron shifting, the desired aldehydes, ketones, olefins, and alkyl radicals. In the pattern itself, Q_6 through Q_{14} , can be either substituted with hydrogen or carbon. This was done because this is a fairly global simplified reaction. In addition, as opposed to defining a set of reaction patterns with the specific substitution, only one pattern needs to be defined. Explicit substitution in this pattern would result in 324 ($6 \times 3 \times 3 \times 6$) different patterns.

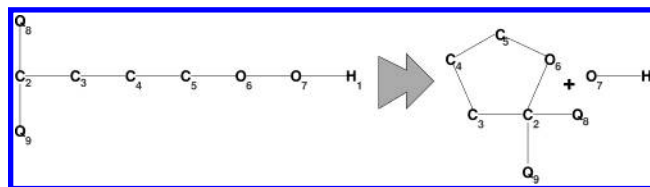


Figure 23. Type XIX: **CyclicEtherFromQOOH-Ring**: This is the case of the reaction class dealing with the five-membered cyclic ether. The other cyclic forms of this class are defined analogously with differing numbers of carbons.

An example of the use of this class is

```
REACTIONCLASS = AlkoxyDecomp
1 PP23 = aldehyde + ethene + methyl-radical
END
```

PP23 is 1-butoxyl radical, i.e., butyl with the alkoxy radical on the primary carbon. The symmetry factor for this reaction class is always one.

3.19. XIX: $QOOH = QO(cyclic) + OH$. Classes: CyclicEtherFromQOOH-Ring. The design of this reaction class (CyclicEtherFromQOOH-Ring, Figure 23), the formation of a cyclic ether through loss of a hydroxyl radical from a hydroperoxide substituted alkane, emphasizes the flexibility of the substructure description in being able to accommodate a ring structure as a product. Each of the patterns involves a different ring size. The carbons within the ring make no distinction as to what is bonded to them. The use of Q for C_2 (Figure 23) restricts the bonding to only hydrogen or singly bonded carbons. The reaction class, as defined by Curran et al., implicitly assumes that it will be used only with hydrocarbons coming from the low temperature mechanism. However, the reaction pattern here, with no specification of the carbons, can be used regardless of the functional groups attached. But, the nature of the bonding of the other carbons can be restricted by the precursor reactions in the reaction pathway where this reaction would be used. The rate constants themselves are solely dependent on the ring size.

An example in the butane mechanism is

```
REACTIONCLASS = CyclicEtherFromQOOH-3Ring
1 2-butyl-1-hydroperoxy-radical = hydroxyl-radical + PP26
1 1-butyl-2-hydroperoxy-radical = hydroxyl-radical + PP26
1 3-butyl-2-hydroperoxy-radical = hydroxyl-radical + PP27
END
REACTIONCLASS = CyclicEtherFromQOOH-4Ring
1 3-butyl-1-hydroperoxy-radical = hydroxyl-radical + PP28
1 4-butyl-2-hydroperoxy-radical = hydroxyl-radical + PP28
END
```

The PP26, PP27, and PP28 are the generated cyclic ether species. As can be seen by the reaction classes generating them, PP26 and PP27 are three-membered cyclic ethers and PP28 is a four-membered cyclic ether. The symmetry factor for this reaction is always one.

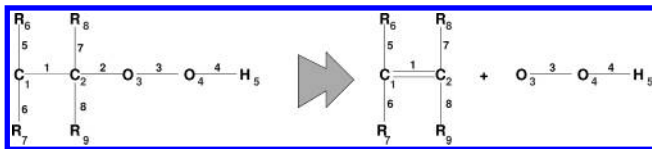


Figure 24. Type XX: **BetaHPeroxyToOlefin**: In the definition, the most important structural differentiation is with carbon 2. However, for future use a distinction is made also for carbon 1. A total of nine patterns are defined depending on the substitution of R_6 , R_7 , R_8 , and R_9 by either hydrogen or carbon.

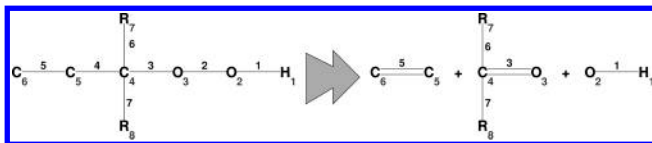


Figure 25. Type XXI: **OlefinCarbonylFromPeroxy**: The reaction class is represented by three patterns represented by the specification of the hydroperoxyl carbon through the specification of R_7 and R_8 .

3.20. XX: $QOOH = olefin + HO_2$. Classes: BetaHPeroxyToOlefin. The reaction class BetaHPeroxyToOlefin (Figure 24) is a side reaction to the intermolecular abstraction (type XII) which produced the radical next to the peroxy group (Intramolecular-1-4- $QOOH$ -Formation). Through the loss of HO_2 an olefin is formed. Once again, in this class the rate constant is specifically defined for the reverse reaction, the addition of HO_2 to an alkene, but in the generation process the forward direction is defined. In the isoctane type listed in Curran et al. a distinction in rate constants is made based on the type of carbon the hydroperoxyl group is leaving. This corresponds to C_2 in Figure 24.

An example within the butane mechanism is

```
REACTIONCLASS = BetaHPeroxyToOlefin-HHRH
1 1-butyl-2-hydroperoxyl-radical = peroxy-radical + 1-butene
END
REACTIONCLASS = BetaHPeroxyToOlefin-RHHH
1 2-butyl-1-hydroperoxyl-radical = peroxy-radical + 1-butene
END
REACTIONCLASS = BetaHPeroxyToOlefin-RHRH
1 3-butyl-2-hydroperoxyl-radical = peroxy-radical + 2-butene
END
```

In this example, the reaction classes BetaHPeroxyToOlefin-HHRH and BetaHPeroxyToOlefin-RHRH show the distinction as to where the peroxy-radical is added. The addition to two "internal" carbons, as shown by BetaHPeroxyToOlefin-RHHH and BetaHPeroxyToOlefin-RHRH, although Curran et al. gives them both the same rate constant, has been separated into two patterns depending on the structure of the olefin. This simple loss of the HO_2 always has a symmetry value of one.

3.21. XXI: $QOOH = olefin + carbonyl + OH$. Classes: OlefinCarbonylFromPeroxy. The reaction class OlefinCarbonylFromPeroxy (Figure 25) represents the beta scission products of $QOOH$ decomposition as being an aldehyde, a hydroxyl radical, and an olefin. In the patterns, a distinction among primary, secondary, and tertiary carbons is only made on the carbon with the hydroperoxyl group. The carbons which form the olefin were left general (no extra bonding specification).

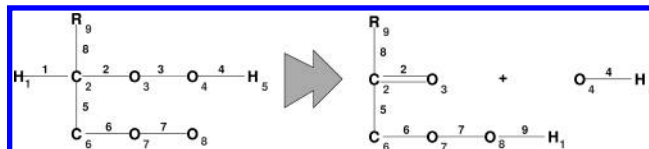


Figure 26. Type XXIII: **OOQOOH-Isomerization-Ring**: The distinction between 1° and 2° is made by appropriate substitution of R_9 in the reactant. The example shown is where the ring size is 7. Larger ring sizes are accomplished by adding carbons (with no extra attachments), and a ring size 5 is when the hydrogens to be abstracted and the peroxy group are on the same carbon.

An example of its use is

```
REACTIONCLASS = OlefinCarbonylFromPeroxy-HH
1 3-butyl-1-hydroperoxy-radical = aldehyde + propene + hydroxyl-radical
END
REACTIONCLASS = OlefinCarbonylFromPeroxy-RH
1 4-butyl-2-hydroperoxy-radical = hydroxyl-radical + ethanal + ethene
END
```

3.22. XXII: Addition of $QOOH$ to O_2 . Classes: Activated-Carbon-Radical-($R \cdot + O_2 \rightarrow RO_2 \cdot$). The substructure definition is also as in type X as shown in Figure 16. Nevertheless, the class is defined as a separate class, Activated-Carbon-Radical-($R \cdot + O_2 \rightarrow RO_2 \cdot$) in case a new set of rate constants are to be used to take into account the hydroperoxy group.

3.23. XXIII: Isomerization of O_2QOOH and Formation of Ketohydroperoxide and OH . Classes: OOQOOH-Isomerization-Ring. The OOQOOH-Isomerization-Ring (Figure 26) produces the first hydroxyl radical of the standard low-temperature chain of reactions to branching agents. In this reaction class, as with type XII, the rate constants are dependent both on the ring size of the transition state and the type of hydrogen being abstracted. The reaction class OOQOOH-Isomerization-Ring has a one-to-one correspondence with this type specification. Each reaction pattern explicitly has the proper number of carbons in the chain to form the ring of the transition-state structure. In Figure 26 the two carbons needed in the "reactant" to form the six-membered transition state are given.

An example of the application of this class is

```
REACTIONCLASS = OOQOOH-Isomerization-4Ring-Primary
2 1-hydroperoxy-2-peroxy-butane = hydroxyl-radical + 2-hydroperoxy-1-butanal
END
REACTIONCLASS = OOQOOH-Isomerization-5Ring-Primary
2 1-hydroperoxy-3-peroxy-butane = hydroxyl-radical + 3-hydroperoxy-1-butanal
END
REACTIONCLASS = OOQOOH-Isomerization-5Ring-Secondary
1 2-hydroperoxy-4-peroxy-butane = hydroxyl-radical + 4-hydroperoxy-2-butanal
END
```

The symmetry factors of two given for the primary versions of the above examples represent the choice of two hydrogens available for abstraction. This, of course, implies that the rate constants themselves are given in terms of "per-hydrogen". If this were not the case, the pattern could be defined so as to give a symmetry factor of 1.

3.24. XXIV: Decomposition of Ketohydroperoxide. Classes: KetoHydroPeroxideDecompositionR. The reaction class producing the second hydroxyl radical in the low-temperature chain to branching agents is represented by the set of reaction classes, KetoHydroPeroxideDecomposition (Figures 27–29). The generalized rate constant is given to be independent of the relative position of the keto and the hydroperoxide group. However, in the design of the reaction

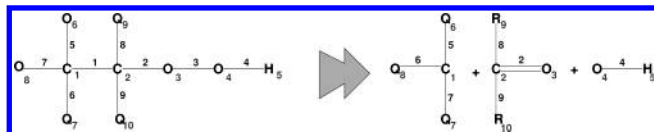


Figure 27. Type XXIV: **KetoHydroPeroxideDecomposition**: This is the decomposition of the hydroperoxide group without consideration of where on the molecule the ketyl functional group is. There is only one pattern here where the Q on the C_1 and C_2 carbons can be either single bonded carbons or hydrogens.

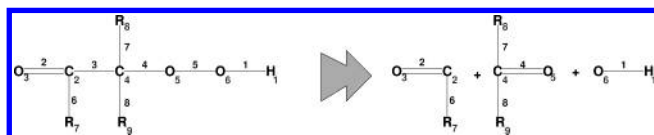


Figure 28. Type XXIV: **KetoHydroPeroxideDecompositionRRR**: This is the special case, not covered by the general KetoHydroPeroxideDecomposition case, where the ketyl and the hydroperoxide group are on adjacent carbons. A differentiation of structures is made with six patterns replacing R_7 on C_2 and the pair R_8, R_9 on C_4 with either single bonded carbon or hydrogens.

classes, distinctions have been made between whether the groups are adjacent, KetoHydroPeroxideDecompositionRRR (see Figure 28), one carbon away, KetoHydroPeroxideDecompositionRRRR (see Figure 29), or n carbons away, KetoHydroPeroxideDecompositionCn.

The use of the general class, KetoHydroPeroxideDecomposition (see Figure 27), can lead not only to the generation of the product distribution of a hydroxyl radical, an aldehyde/ketone, and an aldehyde/ketone radical but also to the product distribution of a hydroxyl radical, an alkyl radical, and dialdehyde/ketone. For example, the decomposition of 3-hydroperoxy-1-butanal can lead to hydroxyl-radical, 1,3-dipropenal, and methyl-radical. The problem with this product distribution is that the base mechanism, or a generated submechanism, may not have reactions for the dialdehyde/ketone. To avoid this, a more controlled generation was used taking into account the position of the aldehyde/ketone group relative to the hydroperoxy group and performing the scission only between the two groups. In the example above, this is shown by the KetoHydroPeroxideDecompositionC4. Naturally, if the dialdehyde/ketone is desired, the generalized class can be included. This is a good example where a controlled generation using substructures can be used to select out a desired, in this case in terms of what can react further, set of reactions.

An example of the reaction classes KetoHydroPeroxideDecompositionC4, KetoHydroPeroxideDecompositionRRR, and KetoHydroPeroxideDecompositionRRRR applied to reactions within the butane low-temperature mechanism are

```
REACTIONCLASS = KetoHydroPeroxideDecompToAldRadical-HRRH
1 2-hydroperoxy-1-butanal = hydroxyl-radical + formyl-radical + 1-propanal
END
REACTIONCLASS = KetoHydroPeroxideDecompToAldRadical-RHH
2 1-hydroperoxy-2-butanal = hydroxyl-radical + aldehyde + 1-yl-1-propanal
END
REACTIONCLASS = KetoHydroPeroxideDecompToAldRadical-RRH
1 3-hydroperoxy-2-butanal = hydroxyl-radical + 1-yl-ethanal + ethanal
END
REACTIONCLASS = KetoHydroPeroxideDecompToAldRadical-CHHHH
1 4-hydroperoxy-2-butanal = hydroxyl-radical + aldehyde + 1-yl-2-propanal
END
REACTIONCLASS = KetoHydroPeroxideDecompToAldRadical-CHHRH
1 3-hydroperoxy-1-butanal = hydroxyl-radical + ethanal + ethanoyl-radical
END
REACTIONCLASS = KetoHydroPeroxideDecompositionC4
1 4-hydroperoxy-1-butanal = hydroxyl-radical + 3-yl-1-propanal + aldehyde
END
```

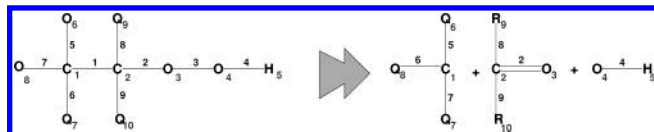


Figure 29. Type XXIV: **KetoHydroPeroxideDecompositionRRRR**: This is the second special case, not covered by the general KetoHydroPeroxideDecomposition case, where the ketyl and the hydroperoxide group are separated by exactly one carbon. A differentiation of structures is made with six patterns replacing R_7 on C_2 and the pair R_8, R_9 on C_4 with either single bonded carbon or hydrogens.

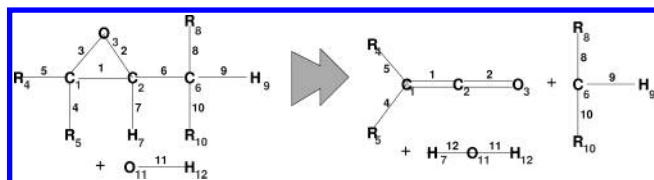


Figure 30. Type XXV: **CyclicEther-3RingDecomp**: This is an example of the decomposition of a three-membered RO ring to a ketene. The specification of the types of carbon atoms within the ring are done with the R atoms (being either carbon or hydrogens).

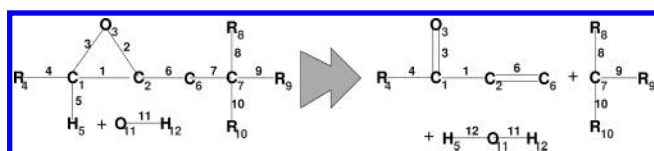


Figure 31. Type XXV: **CyclicEther-3RingDecomp2**: This is an example of the decomposition of a three-membered RO ring to a species with both an aldehyde/ketone functional group and an alkene functional group. The specification of the types of carbon atoms within the ring are done with the R atoms (being either carbon or hydrogens).

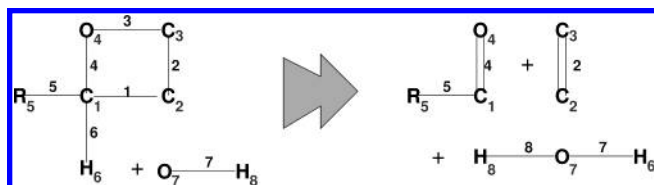


Figure 32. Type XXV: **CyclicEther-4RingDecomp**: This is an example of the decomposition of a four-membered RO ring, which is typical of all larger rings. The only difference between the ring sizes is the size of the alkyl radical aldehyde/ketone species. The specification of the types of carbon atoms within the ring are done with the R atoms (being either carbon or hydrogens).

The products of this, the last of the “standard” low-temperature mechanism, are the second hydroxyl radical and two aldehyde/ketone species, one of which is a radical.

3.25. XXV: Cyclic Ether Reactions with OH and HO_2 .
Classes: CyclicEther-RingDecomp. The reaction class CyclicEther-RingDecomp represents the decomposition of the cyclic ether in a single step. After an initial abstraction of a hydrogen, there is an immediate ring opening, producing an alkyl aldehyde or ketone and then decomposition to form an olefin. Since the types of products of this reaction class depend on the ring size, the class consists of a set of patterns for each ring size. Two types of products are produced by the cyclic ethers with a ring size of three. CyclicEther-3RingDecomp (Figure 30) produces a ketene and an alkyl radical and CyclicEther-3RingDecomp2 (Figure 31) produces an species with both an aldehyde/ketone group and an olefin group. The larger rings, as in the example shown in Figure 32, all produce an olefin and an alkyl radical aldehyde/ketone species.

An example from the pentane submechanism shows the variety of products formed and the differing products due to ring size:

```
REACTIONCLASS = CyclicEther-5Ring-(h)
1 {PP26} + {hydroxyl-radical} = {water} + {propene} + {ethanoyl-radical}
END
REACTIONCLASS = CyclicEther-5Ring-(r)
1 {PP26} + {hydroxyl-radical} = {water} + {ethene} + {ethanoyl-radical}
END
```

```
REACTIONCLASS = CyclicEther-3Ring-(rh)(h)(hhh)
1 {PP23} + {hydroxyl-radical} = {methyl-radical} + {1-butanol-1-ene} + {water}
END
REACTIONCLASS = CyclicEther-3Ring-(rh)(h)(rhh)
1 {PP23} + {hydroxyl-radical} = {water} + {1-propanal-2-ene} + {ethyl-radical}
END
```

The generated species, PP23 and PP26, are a three-membered and a five-membered cyclic ether.

4. CONCLUSION

This paper has illustrated that the entire set of 25 reaction types, as defined by Curran et al., can be directly translated to a representation suitable for reaction generation. Each of the reaction types has been translated to one or more reaction patterns making up a set of reaction classes. All the information within the literature description of the reaction type has been included. When the descriptions of the types were based on exact structural features, there was a one-to-one translation. In contrast, when the reaction types were described in terms of specific (heptane and isooctane) intermediate species (instead of generic features), then some additional interpretation were made. For example, the reaction types dealing with high temperature olefin addition and decomposition, types 6, 8, and 9, needed a higher degree of interpolation because they deal with lumped species and were not explicitly described by Curran et al. In addition, the fate of aldehydes and ketones, common products of the low-temperature pathway, cyclic ether decomposition pathway, and oxidation of alkenes were not dealt with in the reaction types of Curran. All of these types are the main topic of the second paper of this series.

In comparing the generated reactions of each type with, for example, the C_7 molecules of the published heptane mechanism, generally they correspond exactly or there are more generated reactions. For the well-defined types, where no interpretation as to the relationship between the reactants and products was necessary, the correspondence between the generated and the "by-hand" reactions is one-to-one.

Table 1 outlines the differences between the generated reactions and those produced by hand. The comparisons were made with respect to the heptane mechanism published by Curran. The emphasis in this table is on the actual reactions generated. The reaction rates used for the generation are those of the Curran paper and the rates in the actual mechanism could have been changed due to optimization.

The classifications of differences was put into five categories: A, an exact one-to-one correspondence; B, a one-to-one correspondence if reactions involving listed species were eliminated, i.e., more reactions were generated; C, like category B or A with one or two exceptions; D, the reaction classes were not explicitly described by Curran and the reaction classes were derived from specific reactions; and E, the hand generated reactions were heavily lumped, so direct comparison is difficult.

Table 1. Differences between Automatically Generation and Hand Produced Reactions^a

type	corr	notes on exceptions (see text for details)
1	A	
2	C	
3	A	
4	A	
5	C	
6	E	
7	C	
8	E	generated produced more combinations
9	E	lumped, but all abstractors are included
10	A	generated produced more combinations
11	C	extensively lumped
12	A	extensively lumped
13	A	
14	A	
15	A	
16	C	
17	A	trouble using R^{\bullet} as abstractor in pathway
18	D	
19	A	
20	A	
21	A	
22	A	
23	A	
24	A	
25	A	

^a Corr refers to the degree of correspondence (see text for explanation).

If the reaction class falls within categories A, B, or C, then the generated and hand produced reactions have exactly (with, at most, a few exceptions) a one-to-one correspondence to the heptane mechanism of Curran. These classes would be, in principle, a good basis for generated detailed mechanisms for larger hydrocarbons.

The reaction classes with errors of type D are those where, in the explanation of the type by Curran et al., a specific set of reactants are specified to react to produce a generic set of products, i.e., a definite pattern of reactivity was not specified. In these cases, the reaction classes were extrapolated from the specific reactions and reasonable bond and valence rearrangements. The usual consequence of this is that the reaction classes are more general, and a more extensive and systematic set of reactions are produced covering the explicit reactions listed in the final mechanism. This means that potentially errors of type B or C are produced.

The reaction classes with an error of type E were heavily lumped. The lumped reactions usually represented a generic reactivity and did not include the reactive complexity that was possible. A direct comparison of lumped reactions and generated reactions is not possible. In addition, the process of lumping is not unique and, especially in hand generated mechanisms, not necessarily following a single systematic well-defined procedure. Often it is a complex mixture of eliminating species, eliminating reactive paths and isomer equivalence definitions. Systematic approaches using the concept of reaction classes have been implemented within the REACTION system based on the fact that if a species is produced and consumed by the same set of reaction classes, then they have the same reactivity and hence they could be lumped. Having the same reaction classes is another way of saying that the species share a common set of the essential structural features. This will be discussed in more detail in future work.

The general conclusion of Table 1 is that the generation procedure can produce exactly a large portion of a systematically hand-produced mechanism. Aside from the comparison of lumped species, most differences can be adjusted by the elimination of individual species and reactions in the generated set.

One notable exception is the generic use of *R* and *RO2* radicals in generating reactions as found in types 2 and type 11. The problem lies not in the definition of the reaction class itself but in how the reaction class is used in the normal generation procedure. The key point in “controlled” mechanism generation is the definition of a pathway of reaction classes and that only the products of the previous step can be used in the next step. Generic radicals, such as *R* and *RO2*, are not necessarily produced by the previous step. The only way to include them in the “normal” generation procedure is to explicitly include the wanted radicals at the required step (as is done with other small species such as oxygen, hydrogen radical, etc.). However, reaction type 16 is a case where a *RO2* is used, and the reactions could be generated. In this case, a set of *RO2* species is produced by the previous step, and they all react among themselves.

It is important to note that the representation used within the generation procedure is in the form of an external database that is made available to the generation program. The expansion of the database is done through ASCII files describing the (two-dimensional, i.e., graphical) structure of the molecules and substructures (through SDF description¹³) and bonding information and rate constants of the reactions and reaction patterns. This allows for additional reaction patterns to be easily defined.

This paper has shown that a complete set of combustion reactivity can be translated to reaction classes which can be directly used to automatically generate a detailed mechanism. Furthermore, when the reaction classes are used within the reactive pathway concept, a detailed mechanism similar to one produced by hand can be generated. This elevates the

tool for automatic mechanism generation to a level where specific reactions of a mechanism are “details” managed by the generator. The mechanism developer is allowed to design a mechanism at a higher level of combining submechanisms each of which are produced via the concepts of pathways, reactive classes, and seed molecules.

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