Detailed Mechanism Generation. 2. Aldehydes, Ketones, and Olefins

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Generalized reaction classes for the consumption and decomposition of aldehydes, ketones, and olefins are described. These classes are important for generating not only reactions for the consumption of the branching agents of low-temperature hydrocarbon combustion but also reactions of the oxidation of alkenes and the decomposition of cyclic ethers. These reaction classes have been extrapolated from specific reactions of existing validated mechanisms. The reaction patterns making up the class were derived by identifying the reactive center of the specific reactions and the important surrounding functional groups. The rates used currently are definitely "first guesses" based on these specific reactions. The reaction classes in this paper supplement the reaction classes derived from accepted reaction types in the previous paper in this series. The purpose of this paper is to outline a complete (with very few exceptions) set of reaction classes which describe the C_5 and C_6 products of the low-temperature and cyclic ether path in the heptane and isooctane mechanisms.

1. INTRODUCTION

In the first paper of this series[3] a set of generalized reaction types[1,2] important for high- and low-temperature hydrocarbon combustion were translated into reaction classes. The main purpose of that work was to illustrate that established chemical concepts (especially, as published in the literature) can be converted directly to a database which can be applied in the computer generation of further, analogous, mechanisms. This paper will extend the database of reaction classes with the emphasis on the consumption of aldehydes, ketones, and alkenes.

A large detailed mechanism can be thought of as blocks of reactions, each being a submechanism. At one level, submechanisms can be classified by the size of the largest species (in terms of number of carbons) in each reaction. For example, a C_7 submechanism consists of all reactions whose largest species has seven carbons. Furthermore, when producing detailed mechanisms, whether by hand or automatically, one speaks of the primary submechanism, the C_n mechanism for the consumption of the primary fuel of n carbons. For example, C_7 is the primary submechanism of heptane. The secondary submechanisms are those of smaller species. In the case of heptane, the secondary submechanisms are the C_0 through C_6 submechanisms.

A submechanism can also be defined by its purpose, for example, low-temperature oxidation or aldehyde/ketone consumption. These submechanisms represent a pathway, i.e., a sequence of reactions leading to a prescribed purpose. The prerequisite of a pathway is that the reactants of one step should be the products of the previous step. An aldehyde/ketone pathway describes the consumption aldehydes and ketones to species which can be found in other (with smaller species) submechanisms.

The products of a submechanism can be thought of as those species which are not consumed by reactions within the submechanism. In the design of a complete detailed mechanism, the products of a given submechanism must be consumed by another submechanism. For example the products of the primary submechanism should be consumed by the secondary submechanisms. When automatically generating submechanisms, the "base" submechanism is the set of detailed submechanisms which are not explicitly generated. In this paper, this is considered to be the C_0 through C_4 submechanisms.

The 25 reaction types of Curran et al.[1,2] were designed to describe the entire set of reactions of the primary C_7 submechanism of heptane. They also describe a part, but not all, of the C_4, C_5, and C_6 secondary submechanisms. However, one set of products of the primary heptane submechanism not consumed by reactions of the 25 types are the aldehyde/ketone species produced by addition of radical species to olefin (type 7), low-temperature (ending with type 24), and cyclic ether decomposition (ending with type 25). All of these products are consumed in the secondary mechanisms. For the heptane mechanism, the number of these ketyl species is small and manageable. Only five aldehydes, two aldehyde radicals (the aldehyde hydrogen removed), and five ketyl radicals are formed by the low-temperature decomposition, and only one extra ketyl radical comes from the decomposition of cyclic ethers. The aldehydes and aldehyde radicals are easily decomposed to simple alkyl radicals (with the loss of carbon monoxide) and with one decomposition reaction, the ketyl radicals produce species in submechanisms of C_4 or less (which can be considered the detailed base mechanism). Thus the number of additional reactions needed is manageable.

However, if the same principle, i.e., reaction classes, were to be used to anaologously generate a larger mechanism, such as decane, a significant portion of the products of the low-temperature and cyclic ether decomposition would not be in the base submechanisms. For some products, more than one reaction step is needed to reach species small enough to be

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in the base mechanism. Thus, as the fuel molecule gets larger, the number of these intermediate products increases, and, eventually, the number of reactions needed to consume these species becomes unmanageable. At this point automated generation techniques are needed. For this reason explicit reaction classes for their consumption must be designed.

In terms of automation,[6] the consequence of not defining how species react further is the production of "dead ends", i.e., species which do not have further reactions associated with them (aside from the reverse of the production reactions) and do not appear in the base mechanism. The result is that in a, for example, simple ignition calculation these intermediate species would accumulate as products and detract from the species leading to combustion. The end result can be, for example, slower ignition delay times.
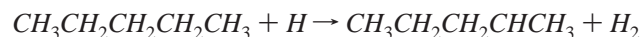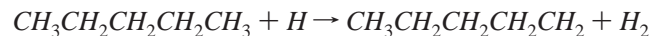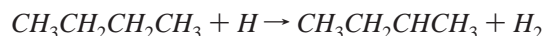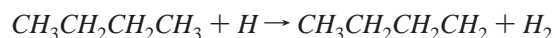
Though the products produced by these reaction classes are realistic, the corresponding rate constants involved are admittedly "first guesses" based on the smaller hydrocarbons. However, the reaction patterns are designed so as to allow more detailed rates, based in differing structures, as the information becomes available.

It is the purpose of this paper to outline the reaction classes which represent the consumption of the possible products of the low-temperature, cyclic ether decomposition and alkene oxidation pathways. The goal of the paper is to be able to generate automatically all the reactions used in the heptane and isooctane mechanisms of Curran et al. which was produced by hand.

2. SPECIFIC TO GENERAL

If a reaction type is not defined as a generalized reaction type or established physical principles are not well established, one alternative is to examine existing "accepted" examples within mechanisms from mechanisms in the literature. From the specific reactions, the reaction class is derived from the "reactive center" and the necessary functional groups around this center which could strongly effect the rates. The philosophy of the approach is to draw upon the experience of the designer of the mechanism. Since these reactions appear in "established" and validated mechanisms, it can be assumed that the specific reactions were determined "necessary" and their rate constants should be "reasonable".

The design of the structure of the reaction class involves determining the reactive center and the necessary functional groups surrounding it. The reactive center is the set of bond and valence changes that occur in going from reactants to products. Take, for example, hydrogen abstraction by a hydrogen radical from a set of alkanes:

$$CH_3CH_2CH_2CH_3 + H \rightarrow CH_3CH_2CH_2CH_2 + H_2$$

$$CH_3CH_2CH_2CH_3 + H \rightarrow CH_3CH_2CHCH_3 + H_2$$

$$CH_3CH_2CH_2CH_2CH_3 + H \rightarrow CH_3CH_2CH_2CH_2CH_2 + H_2$$

$$CH_3CH_2CH_2CH_2CH_3 + H \rightarrow CH_3CH_2CH_2CHCH_3 + H_2$$

The reactive center of all these reactions are, for the reactants, the combined structure of the *CH* bond and the hydrogen radical, *H*, and, for the products, the carbon radical, *C*, and hydrogen, H_2. The necessary functional groups surrounding

the reactive center are those determined to influence the rate constants the most. From experience, the minimal set of functional groups surrounding this particular reactive center should, at least, distinguish between primary and secondary carbons. Thus, the surrounding atoms of the carbon in the reactive center should be included, forming two "patterns" of the reaction class:

$$C(C)(H_3) + H \rightarrow C(C)(H_2) + H_2$$

$$C(C_2)(H_2) + H \rightarrow C(C_2)(H) + H_2$$
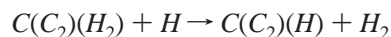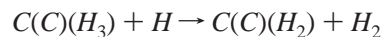
The weak point in the procedure is the derivation of the rate constants. Once again, one is tapping the mechanism developer's experience by using the same (or similar) rate constants, one for each pattern. The best candidate, since these reaction classes are to be used for larger hydrocarbons, is to take the example involving the largest hydrocarbon, i.e., the one which is most analogous to the ones to be generated. The hope is that, at least for a first guess, the rate constant used will be adequate. If the reaction in question is a "sensitive" one, i.e., the properties to be modeled are dependent on it, this procedure is not suitable and one is forced to determine more accurate rate constants. However, a large majority of reactions are indeed not sensitive and only have to have reasonable rate constants. They should, at least, have the right order of magnitude. For example, a rate constant should not be so slow as to stop the flow of reactants through it. This would form a bottleneck. These reactions, nevertheless, have to be present, because they are intermediates providing throughput from the fuel to the final product species. If consumption reactions were not present, the unconsumed species would form dead ends, as discussed previously, which would also be a form of "blocking" of throughput.

In the following sections, in the cases where the rate constants are being derived from specific reactions, a table of the specific reactions is shown with the chosen rate constant. Associated with the reaction is the "functional" group portion of the reaction pattern. As in the example above, these are distinctions between carbon types. The distinction between terminal carbons in the reaction center is noted by **(hhh)**, **(rhh)**, **(rrh)**, and **(rrr)**, where **r** denotes that a carbon of another branching chain is attached and **h** denotes that a hydrogen is attached. Carbons on nonterminal carbons are denoted with **(hh)**, **(rh)**, and **(rr)**. In the text, the correspondence to the atoms in the reaction class figures is given. Unless otherwise noted, the reaction examples were taken from the Curran et al. heptane and isooctane mechanism.

3. ALDEHYDE AND KETONES

A set of species occurring in many stages of the oxidation of alkane combustion are the aldehydes and ketones. They are the primary "branching" products of the low-temperature mechanism and occur also in the oxidation of olefins and the decomposition of cyclic ethers. These classes were derived through specific reactions of the Curran et al. heptane and isooctane mechanism.

A common strategy in the combustion aldhydes and ketones involves first a hydrogen abstraction and subsequent decomposition. The reaction pathways of decomposition depend on the where the abstraction occurred. The necessary

Table 1: Rate Constants of Hydrogen Abstraction from an Aldehyde Derived from Specific Examples

base reaction	abstractor	direction	A	n	E_a
nc5h11cho+oh = nc5h11co+h2o	OH	forward	1.000E+13	0.00	0.00
		reverse	2.000E+13	0.00	155
nc5h11cho+h = nc5h11co+h2	H	forward	4.000E+13	0.00	17.6
		reverse	1.800E+13	0.00	100
nc5h11cho+ch3 = nc5h11co+ch4	CH3	forward	1.700e+12	0.00	35.
		reverse	1.500e+13	0.00	117.
nc5h11cho+o2 = nc5h11co+ho2	O2	forward	2.000E+13	0.50	177
		reverse	1.000E+07	0.00	167
nc5h11cho+o = nc5h11co+oh	O	forward	5.000E+12	0.00	7.49
		reverse	1.000E+12	0.00	79.5
nc5h11cho+ho2 = nc5h11co+h2o2	HO2	forward	2.800E+12	0.00	56.9
		reverse	1.000E+12	0.00	42.0
nc5h11cho+ch3o = nc5h11co+ch3oh	CH3O	forward	1.150E+11	0.00	5.36
		reverse	3.000E+11	0.00	75.3
nc5h11cho+ch3o2 = nc5h11co+ch3o2h	CH3O2	forward	1.000E+12	0.00	39.8
		reverse	2.500E+10	0.00	41.9

reaction classes for these pathways, if not already described in the previous paper,[3] are described in this section. The pathways considered are as follows:

CO. If the abstraction is the hydrogen of the aldehyde (AldehydeHAbstraction), then the product decomposes to a radical and a carbon monoxide (KetoneRadicalDecomp).

Alpha. If the abstraction of hydrogen is next to the ketyl group (H-Abstraction-AlphaToKetone), then either a ketene is formed or an olefin is formed through loss of an alkyl group (AldehydeDecompToKetylAlkene-Alkyl and KetoneDecompToKetylAlkene-Alkyl).

Beta. If the abstraction of hydrogen is two carbons away (after normal alkane-like abstraction reaction classes, type II of Curran et al.), then there is a decomposition to a $^\bullet CO$ and an olefin (KetoAldCRadDecomp, AldehydeDecomp-ToAlkene-Alkyl, and KetoneDecompToAlkene-Alkenyl).

Further. If the abstraction occurs further away from the aldehyde and ketone, then the decomposition occurs such as a normal alkyl, usually through decomposition to an olefin (AldehydeDecompToAlkeneAndch2co-Alkyl, KetoneDecomp-ToAlkeneAndch2co-Alkyl, or PropylRadicalToEthene).

The source of the class of species for the above decompositions is either when the radical is formed directly by the low-temperature or cyclic ether decomposition pathways or when a hydrogen abstraction occurs from a nonradical aldehyde/ketone from these pathways. An additional functionality that can occur in the proximity of the ketyl group is an alkene group. This is oxidized by the addition of an OH radical (KetoneAdditionOH−Alpha). In section 4 the pathways through ketenes will be presented.

The following sections describe the derived reaction classes. All activation energies are given in kilojoules and the Arrhenius constants in mol-s^{-1} units.

3.1. H Abstraction from Aldehyde. Classes: Aldehyde-HAbstraction. One path for the decomposition of aldehydes begins with the abstraction of aldehyde hydrogen, AldehydeHAbstraction (Figure 1). The abstractions use the radicals $^\bullet OH$, $^\bullet H$ CH_3, O_2, O, HO_2, CH_3O, and CH_3O_2. The rate constants and the pattern for the abstractions are based on the reactions on smaller hydrocarbons. In this study, the rate constants for $C_5H_{11}CHO$ were chosen. The actual constants being used are shown in Table 1.

Although the patterns of this reaction class differentiate between different carbon radicals of the reactive center, only
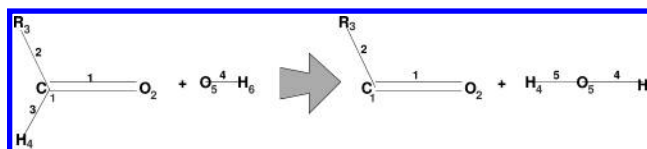

Figure 1. AldehydeHAbstractionOH: This is the abstraction of a hydrogen from an aldehyde. The aldehydes are differentiated by R_3 which can be a singly substituted carbon or hydrogen. Analogous patterns are available for abstracting with a methyl or a hydrogen radical.
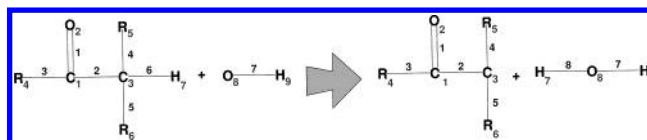

Figure 2. H-Abstraction-AlphaToKetone: The pattern abstracts a hydrogen with a hydroxyl radical and is differentiated through R_5 and R_6.

one representative rate constant is used. As more examples appear, different rate constants will be introduced.

An example of the use of this class within the butane submechanism of the abstraction with hydroxyl is the following:

```
REACTIONCLASS  = AldehydeHAbstractionOH-(rh)
    1 {1-propanal} + {hydroxyl-radical} = {1-yl-1-propanal} + {water}
    1 {ethanal} + {hydroxyl-radical} = {ethanal-1-yl} + {water}
END
```

Since there is only one hydrogen to be abstracted from the aldehyde, the symmetry factor is always one. After the abstraction of the aldehyde hydrogen, the product decomposes to an alkyl radical and carbon monoxide.

3.2. H Abstraction to 1-AlkylKetone Radical. Classes: H-Abstraction-AlphaToKetone. The H-Abstraction-AlphaToKetone (Figure 2) abstracts the hydrogen next to the carbonyl group by a hydroxyl radical. The set of rate constants based on specific reactions from the heptane and isooctane mechanisms is shown in Tables 2−4. The constants are shown using hydroxyl, peroxyl, and methylperoxyl radicals as the hyrodron abstractor.

An example of the application of this reaction class is as follows:

```
REACTIONCLASS  = H-Abstraction-AlphaToKetone-(h)(rh)
    1 {1-butanal} + {hydroxyl-radical} = {water} + {2-yl-1-butanal}
    1 {1-propanal} + {hydroxyl-radical} = {water} + {2-yl-1-propanal}
END
```

Table 2: Rate Constants for the **H-Abstraction-AlphaToKetone** Reaction Class Using Hydroxyl Radical as the Hyrodron Abstractor[a]

prototype	direction	A	n	E_a
nc5h11cho+oh = c5h10cho-5+h2o	forward	4.670E+07	1.61	0.0
(rh)(h)	reverse	3.317E+09	1.25	129.
ic3h7cho+oh = tc3h6cho+h2o	forward	1.684E+12	0.00	−3.27
(rr)(h)	reverse	1.194E+13	−0.09	125
nc4h9coch3+oh = nc4h9coch2+h2o	forward	5.100E+11	0.00	49.9
(hh)(r)	reverse	3.615E+13	−0.43	115
nc3h7coc2h5+oh = c3h6coc2h5−3+h2o	forward	8.450E+11	0.00	−0.955
(rh)(r)	reverse	3.313E+13	−0.32	120
ic3h7coch3+oh = tc3h6coch3+h2o	forward	1.684E+12	0.00	−0.33
(rr)(r)	reverse	2.420E+13	−0.18	125

[a] The *Prototype* shows both the prototype reaction used and the substitutions, R_5, R_6, and R_4 (in Figure 2), used.

Table 3: Rate Constants for the **H-Abstraction-AlphaToKetone** Reaction Class Using Peroxyl Radical as the Hyrodron Abstractor[a]

prototype	direction	A	n	E_a
ch3cho+ho2 = ch3co+h2o2	forward	3.010E+12	0.00	49.9
(hh)(h)	reverse	1.210E+13	−0.34	50.2
nc5h11cho+ho2 = c5h10cho-5+h2o2	forward	2.950E+04	2.60	58.2
(rh)(h)	reverse	1.244E+07	1.91	55.8
ic3h7cho+ho2 = tc3h6cho+h2o2	forward	2.950E+04	2.60	58.2
(rr)(h)	reverse	1.244E+07	1.91	55.8
nc4h9coch3+ho2 = nc4h9coch2+h2o2	forward	2.380E+04	2.55	611
(hh)(r)	reverse	1.001E+07	1.80	3.99
nc4h9coch3+ho2 = c4h8coch3−4+h2o2	forward	2.000E+11	0.00	36.4
(rh)(r)	reverse	2.294E+13	−0.56	25.5
ic3h7coc2h5+ho2 = tc3h6coc2h5+h2o2	forward	8.000E+10	0.00	49.9
(rr)(r)	reverse	6.993E+12	−0.51	46.7

[a] The **Prototype** shows both the prototype reaction used and the substitutions, R_5, R_6, and R_4 (in Figure 2), used.

Table 4: Rate Constants for the **H-Abstraction-AlphaToKetone** Reaction Class Using Methylperoxyl Radical as the Hyrodron Abstractor[a]

prototype	direction	A	n	E_a
ic3h7cho+ch3o2 = ic3h6cho+ch3o2h	forward	4.760E+04	2.55	69.0
(hh)(h)	reverse	2.377E+05	2.04	15.7
nc5h11cho+ch3o2 = c5h10cho-5+ch3o2h	forward	3.980E+12	0.00	71.4
(rh)(h)	reverse	6.897E+15	−0.86	65.9
ic3h7cho+ch3o2 = ic3h6cho+ch3o2h	forward	4.760E+04	2.55	69.0
(rr)(h)	reverse	2.377E+05	2.04	15.7
nc4h9coch3+ch3o2 = nc4h9coch2+ch3o2h	forward	3.010E+12	0.00	73.6
(hh)(r)	reverse	4.057E+15	−0.90	49.0
nc3h7coc2h5+ch3o2 = nc3h7coc2h4s+ch3o2h	forward	2.000E+12	0.00	69.8
(rh)(r)	reverse	1.839E+13	−0.54	27.9
ic3h7coc2h5+ch3o2 = tc3h6coc2h5+ch3o2h	forward	3.610E+03	2.55	33.6
(rr)(r)	reverse	1.297E+06	1.86	27.4

[a] The *Prototype* shows both the prototype reaction used and the substitutions, R_5, R_6, and R_4 (in Figure 2), used.
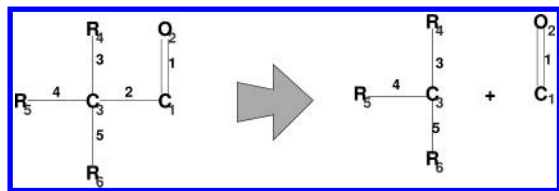
Figure 3. KetoneRadicalDecomp: A ketyl radical decomposes to carbon monoxide and a simple radical. The radical in the pattern is characterized by R_4, R_5, and R_6.

Here, the symmetry factor is always one because the rate constants were not chosen to be per hydrogen. The rate constants for the reaction pattern are exactly as shown in Tables 2−4.

3.3. Decomposition of Ketyl Radical. Classes: Ketone-RadicalDecomp. The KetoneRadicalDecomp (Figure 3) is the decomposition of a ketyl radical to a simple alkyl radical and a carbon monoxide. This is a final reaction in this pathway to decompose ketones and aldehydes since it produces a small species, carbon monoxide, and a simple radical.

Currently the rates in the patterns are based on the two reactions:

prototype	direction	A	n	E_a
nc5h11co = c5h11-1+co	forward	1.000E+11	0.00	40.
(rhh)	reverse	1.000E+11	0.00	0.00
ic3h7co = ic3h7+co	forward	1.426E+13	−0.04	45.
(rrh)	reverse	1.500E+11	0.00	20.

The distinctions in the types refer to the groups on C_3 in Figure 3, namely, $(R_4R_5R_6)$. A simple application of this class on species in the butane mechanism is

```
REACTIONCLASS = KetoneRadicalDecomp-RHH
    1 {1-yl-1-butanal} = {carbonmonoxide} + {1-propyl-radical}
    1 {1-yl-1-propanal} = {carbonmonoxide} + {ethyl-radical}
END
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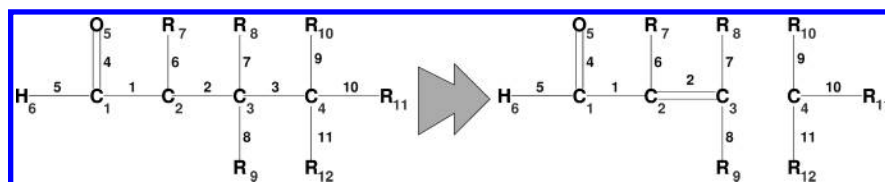
Figure 4. AldehydeDecompToKetylAlkene-Alkyl: An aldehyde with a radical on the alpha carbon decomposes, through loss of an alkyl radical, to a ketylalkene.
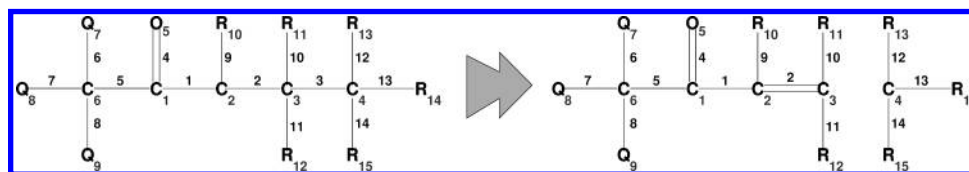

Figure 5. KetoneDecompToKetylAlkene-Alkyl: A ketone with a radical on the alpha carbon decomposes, through loss of an alkyl radical, to a ketylalkene.

Once again, since this is a simple (asymmetric) decomposition, the symmetry values are one.

3.4. Decomposition of Alpha Aldehyde/Ketone Radical. Classes: KetoneDecompToKetylAlkene-Alkyl, AldehydeDecompToKetylAlkene-Alkyl. One class of decomposition reactions of an aldehyde/ketone with a radical one carbon away from the ketyl group, a product of the low-temperature decompositions (type XXIV of Curran et al.), results in the loss of an alkyl radical three carbons away to form an $RCOCRCR_2$ (aldehyde/ketone with a neighboring alkene group) species. These are described by the reaction classes **AldehydeDecompToKetylAlkene-Alkyl** (Figure 4), for the aldehyde species, and **KetoneDecompToKetylAlkene-Alkyl** (Figure 5), for the ketyl species. The rate constants for these reactions classes are very generic. Basically, one representing the "specific" case (where all the substitutions of the reaction patterns are hydrogens) and another constant for the rest.

The rate constants for **AldehydeDecompToKetylAlkene-Alkyl** are

prototype	direction	A	n	E_a
c3h6cho-3 = c2h3cho+ch3	forward	3.174E+14	−0.39	124.
(specific)	reverse	1.230E+11	0.00	33.
c5h10cho-5 = c2h3cho+nc3h7	forward	1.564E+19	−1.53	139.
(all others)	reverse	1.000E+11	0.00	33.

and the constants for **KetoneDecompToKetylAlkene-Alkyl** are

prototype	direction	A	n	E_a
c3h6coch3-3 = c2h3coch3+ ch3	forward	9.615E+15	−0.75	136.
(specific)	reverse	1.000E+11	0.00	33.
c3h6coc2h5-3 = c2h5coc2h3+ch3	forward	2.915E+15	−0.68	135.
(all others)	reverse	1.000E+11	0.00	33.

These are fairly specific reactions, and only a few examples are used in the heptane and isooctane mechanisms. These reaction classes are very similar (in functionality) to the Curran et al. reaction type VII, "Alkyl Radical Decomposition". This reaction pattern is created to allow the influence of the ketyl group to this decomposition. However, it can be seen that the rate constants are similar but not exactly the same.

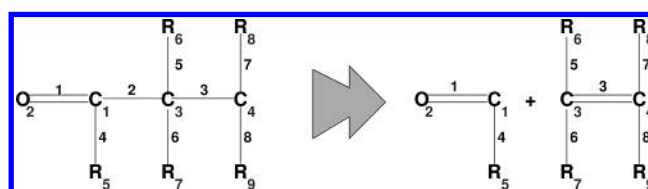**3.5. H Abstraction to 2-AlkylKetone Radical. Classes: KetoAldCRadDecomp.** The KetoAldCRadDecomp pattern,

Figure 6. KetoAldCRadDecomp: A ketone radical decomposes to a ketyl radical and an olefin. The different patterns are differentiated through the R_5 through R_9.

as shown in Figure 6, describes the decomposition of a ketone radical, where the radical is two carbons away, to produce a ketyl radical and an olefin. This reaction is similar to the PropylRadicalToEthene where a ketyl radical is lost instead of a alkyl radical. The rate constants in the patterns are based on the following reactions from the Curran et al. heptane mechanism:

prototype	direction	A	n	E_a
ch2ch2cho = c2h4+hco	forward	1.000E+14	0.00	96.
(hh)(qq)(h)	reverse	1.000E+11	0.00	0.00
pc2h4coc2h3 = c2h3co+c2h4	forward	2.016E+15	0.35	110.
(hh)(qq)(r)	reverse	8.000E+10	0.00	47.
c4h8cho-3 = c4h8-1+hco	forward	1.637E+08	0.89	70.
(rh)(qq)(h)	reverse	1.000E+11	0.00	32.6
c4h8coch3-3 = c4h8-1+ch3co	forward	5.851E+11	0.01	86.
(rh)(qq)(r), (rr)(qq)(r)	reverse	1.000E+11	0.00	41.

Distinctions were made in rate constants depending on the substitutions on the radical carbon and the carbonyl group. The distinctions shown in the table refer to (R_8R_9)-$(R_6R_7)(R_5)$ in Figure 6. The terms (qq) allows both a hydrogen or a carbon to be substituted. This is done to limit the number of patterns.

An example of two simple applications of this reaction pattern is

```
REACTIONCLASS  = KetoAldCRadDecomp-H-HH-HH
    1 {3-yl-1-propanal} = {formyl-radical} + {ethene}
END
REACTIONCLASS  = KetoAldCRadDecomp-R-HH-HH
    1 {4-yl-2-butanal} = {ethanal-1-yl} + {ethene}
END
```

In both cases the symmetry value is one since it is a nonsymmetric unimolecular decomposition.

3.6. Decomposition of Alkenyl Ketone Radical. Classes: KetoneDecompToAlkene-Alkenyl, Aldehyde-
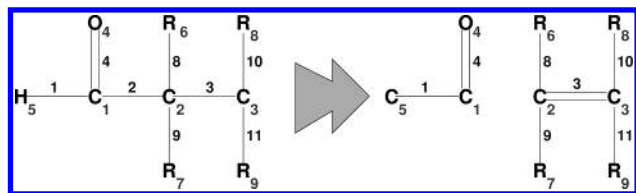
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Figure 7. AldehydeDecompToAlkene-Alkyl: This is the decomposition of an aldehyde radical with the radical on beta to the carbonyl to an alkene.
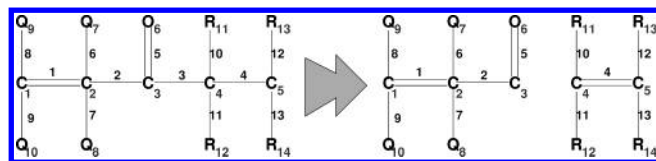

Figure 8. KetoneDecompToAlkene-Alkenyl.

DecompToAlkene-Alkyl. A class of products from the cyclic ether decomposition (Curran et al. type XXV[1,3]) is a ketone with a alkenyl group on one side an an alkyl on the other. If the alkyl group undergoes a hydrogen absraction from the beta carbon from the ketyl group, then the resulting group can undergo, as defined by the reaction classes **Aldehyde-DecompToAlkene-Alkyl** (see Figure 7) and **Ketone-DecompToAlkene-Alkenyl** (see Figure 8), a decomposition to an alkene and a ketyl radical. This reaction class, which is dependent on several functional groups, is the result of products of the cyclic ether decomposition which itself has two functional groups, an ketyl and an alkene group. The importance of such a complex reaction class in detailed mechanisms is providing pathways of complex products.

The reaction constants for this class are basically those of the specific rate, i.e., where all the Q and R groups are substituted with hydrogens, and a generic rate based on a slightly more complex species:

prototype	direction	A	n	E_a
pc2h4coc2h3 = c2h3co+c2h4	forward	2.016E+15	0.35	89.8
specific	reverse	8.000E+10	0.00	47.3
ic3h6coc2h3 = c3h6+c2h3co	forward	4.287E+17	−1.27	107.
all others	reverse	7.800E+03	0.00	44.4

3.7. KetoneDecompToAlkeneAndch2co-Alkyl. Classes: KetoneDecompToAlkeneAndch2co-Alkyl, Aldehyde-DecompToAlkeneAndch2co-Alkyl. One of the products of the low-temperature pathway can be an aldehyde/ketone with a radical on the alkyl portion. Such a radical is also formed after the first hydrogen abstraction from and aldehyde/ketone. In the previous sections, if these were on either of the first two carbons from the ketyl group, then specialized classes were needed because of the proximity of the radical and the aldehyde/ketone group. When the radical is further away from the ketyl group, its influence is dimished, and further decomposition can occur as if it were a normal alkyl radical. A typical example is with the type III reaction type of Curran et al. represented by the **PropylRadicalToEthene**[1] reaction class[3]). However, if this type of decomposition occurs "toward" the ketyl group from a radical three carbons away from the ketyl group (see Figures 9 and 10), then with the loss of the alkene a radical next to the ketyl group is formed. For this reason another pair of specialized reaction classes, **AldehydeDecompToAlkeneAndch2co-Alkyl** and **Ketone-DecompToAlkeneAndch2co-Alkyl**, is needed.
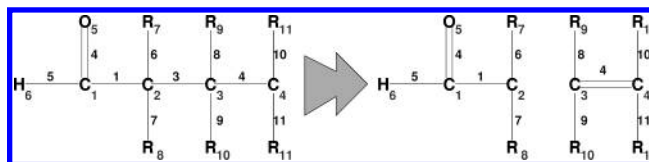

Figure 9. AldehydeDecompToAlkeneAndch2co-Alkyl.

Once again, the rate constants are generalized from specific examples and are similar to those of the corresponding type III reactions of Curran et al. For the **AldehydeDecompTo-AlkeneAndch2co-Alkyl** reaction class the following constants are used:

prototype	direction	A	n	E_a
c3h6cho-3 = c2h3cho+ch3	forward	3.174E+14	−0.39	125.
specific	reverse	1.230E+11	0.00	33.
c5h10cho-3 = c4h8-1+ch2cho	forward	2.140E+10	0.18	76.7
all others	reverse	1.000E+11	0.00	33.

For the **KetoneDecompToAlkeneAndch2co-Alkyl** reaction class the following constants are used:

prototype	direction	A	n	E_a
c3h6coc2h5-1 = c2h4+c2h5coch2	forward	1.426E+18	−1.53	102.
specific	reverse	2.500E+11	0.00	33.
c4h8coch3-2 = c3h6+ch3coch2	forward	3.175E+15	−0.79	110.
all others	reverse	1.000E+11	0.00	35.

3.8. Addition of Hydroxyl. Classes: KetoneAdditionOH−Alpha. The addition of hydroxyl radical to the double bond has been (nonspecifically) defined by Curran et al. and generalized into a set of reaction classes by Blurock. One class of the products of the cyclic ether decomposition consists of species with both an aldehyde/ketone and an olefin group. If the olefin is in the proximity of aldehyde/ketone, additional reaction classes are needed.

Two reaction classes are defined relative to whether the hydroxyl is added toward the ketyl group or away. The **KetoneAdditionOH−Alpha** (see Figure 11) reaction class adds the hydroxyl across the double bond leading to the scission forming an aldehyde radical and a normal aldehyde/ketone. The **KetoneAdditionOH−Beta** (see Figure 12) reaction class adds the hydroxyl across the double bond leading to scission forming an aldehyde/ketone and a radical aldehyde/ketone (the radical being on the carbon next to the ketyl group).

3.9. Diketone Decomposition. Classes: DiKetoAld-Decomp. The DiKetoAldDecomp class (Figure 13) describes the decomposition of a diketone to a ketone radical, where the radical is on the alpha position, and a ketyl radical. The diketone can be produced by pathways in which alkyl radicals and olefins are reduced to ketyl. If the ketyl groups are further away within the molecule, then this decomposition would be taken care of by the KetoAldCRadDecomp reaction class. The proximity of the two groups necessitates a new reaction pattern. In many simplified mechanisms, the path producing this species would simply not be included. The reaction constants of this class are similar to that of KetoAldCRadDecomp, meaning that, as a first guess, the influence of the adjacent ketyl group does not influence the rate.
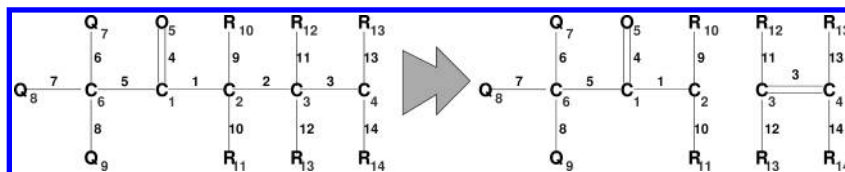
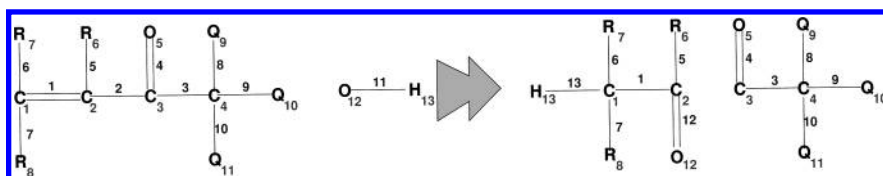**Figure 10. KetoneDecompToAlkeneAndch2co-Alkyl**.

Figure 11. KetoneAdditionOH−Alpha: This class represents the addition of a hydroxyl to an alkene next to a ketyl group. In this class, the oxygen is added to the alkene carbon next to the ketyl.
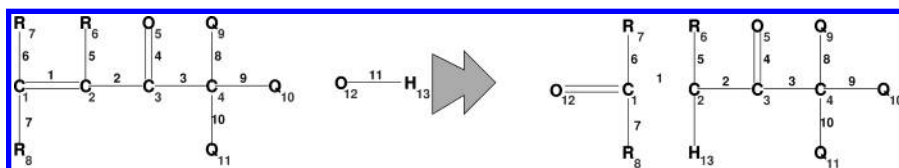

Figure 12. KetoneAdditionOH−Beta: This class represents the addition of a hydroxyl to an alkene next to a ketyl group. In this class, the oxygen is added to the alkene carbon next to the ketyl.
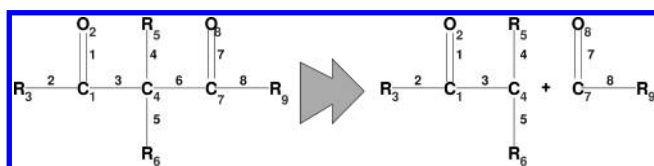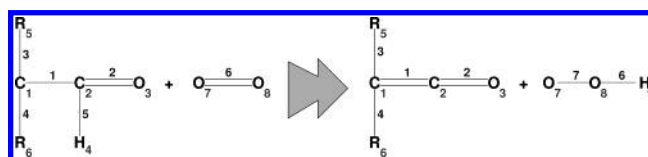

Figure 13. DiKetoAldDecomp: A diketone decomposes to two types of ketone radicals. The patterns are differentiated through the R_3, R_5, R_6, and R_9 groups making a total of 12 combinations of substituting H or C.

A simple application of this reaction pattern is

```
REACTIONCLASS  = DiKetoAldDecomp-HHHH

  2 {1,3-dipropanal} = {ethanoyl-radical} + {formyl-radical}
END
```

The symmetry factor of 2 here represents the symmetry of the dipropanal and the two ways it can decompose.

4. KETENES

One intermediate of the various ketone/aldehyde decomposition pathways is the ketene. The ketene is formed in one of three ways, each requiring a radical one carbon away from an aldehyde or ketone. The three corresponding reaction classes represent the three different ways of producing the radical on the carbonyl group to finally form the ketene:

KeteneFormationO2Abstraction. Abstraction of a aldehyde hydrogen with an oxygen

KeteneFormation. Loss of aldehyde hydrogen by simple decomposition

KeteneFormationRadicalDecomp. Loss of an alkyl group from the ketone

Further decomposition of the ketene proceeds through three reaction classes, depending on the radical species that is added across the double bond:

Figure 14. KeteneFormationO2Abstraction: A ketene is formed through the abstraction of a hydrogen from a ketyl radical. The class is characterized by R_5 and R_6 giving three patterns.

KeteneDecompOTOCO2. Addition of a radical oxygen to form an alkene and carbon dioxide

KeteneDecompOHToCO2. Addition of hydroxyl radical to form an alkyl radical and carbon dioxide

KeteneDecompHToCO. Addition of hydrogen radical to form an alkyl radical and carbon monoxide.

The results of these ketene decompositions are simple molecules, such as carbon monoxide and carbon dioxide and alkyl radicals and olefins, which are dealt with in other submechanisms. The ketene functional group is reduced in such a way as to be compatible with other submechanisms (leading to no dead ends).

4.1. Ketene Formation by H Abstraction. Classes: KeteneFormationO2Abstraction. The KeteneFormation-O2Abstraction (Figure 14) uses an oxygen to abstract the hydrogen from an aldehyde with a radical on the adjoining carbon to form a ketene.

The rate constants of this pattern are based on the following reaction:

prototype	direction	A	n	E_a
ch3chcho+o2 = ch3chco+ho2 (rh)	forward	1.810E+11	0.00	7.69
	reverse	2.3060e+13	−0.5100	81.72

The (rh) refers to the having a hydrogen for R_5 and a carbon for R_6 in the pattern in Figure 14. The (rr) pattern also uses the same rate constant, and the (hh) is the specific reaction of the ethanal radical.

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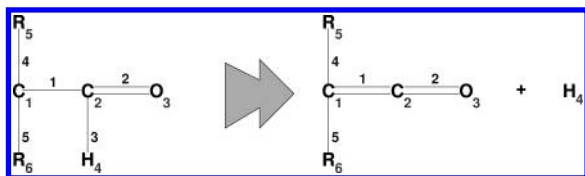*J. Chem. Inf. Comput. Sci., Vol. 44, No. 4, 2004* **1355**

Figure 15. KeteneFormation: The pattern describes the formation of a ketene through the loss of a hydrogen from an aldehyde with a radical on the adjoining carbon. The class, through the specification of R_5 and R_6, can differentiate the different alkyl radicals.
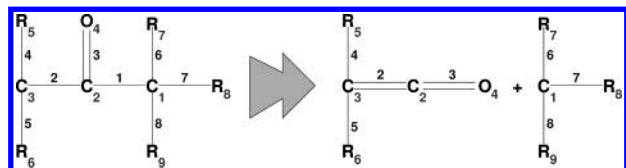

Figure 16. KeteneFormationRadicalDecomp: Through loss of an alkyl radical, a ketene is formed. The class is characterized by R_5 through R_9 giving a total of 12 patterns.

An example application of this reaction class on a three carbon and a four carbon aldehyde radical produces the following:

```
REACTIONCLASS = KeteneFormationO2Abstraction-(rh)
   1 {2-yl-1-propanal} + {oxygen} = {peroxyl-radical} + {1-propanal-1-ene}
   1 {2-yl-1-butanal} + {oxygen} = {peroxyl-radical} + {1-butanal-1-ene}
END
```

Since the abstraction occurs from the aldehyde, the symmetry factor is always one.

4.2. Ketene Formation Through loss of Hydrogen. Classes: KeteneFormation. The KeteneFormation reaction class (Figure 15) forms a ketene by simple loss of a hydrogen from an aldehyde with a radical on the adjoining carbon. The reaction constants are based on a single reaction:

prototype	direction	A	n	E_a
c3h6cho-3 = c2h5chco+h (rh)	forward	8.431E+15	−0.60	169.
	reverse	2.3060e+13	−0.51	5.

The (rh) refers to (R_5R_6) in Figure 15.

An example application of this reaction class on a three carbon and a four carbon aldehyde radical produces the following:

```
REACTIONCLASS = KeteneFormation-(rh)
   1 2-yl-1-propanal = hydrogen-radical + 1-propanal-1-ene
   1 2-yl-1-butanal = hydrogen-radical + 1-butanal-1-ene
END
```

Since this is a decomposition, the symmetry factor is always one.

4.3. Ketene Formation Through Loss of a Alkyl Radical. Classes: KeteneFormationRadicalDecomp. The KeteneFormationRadicalDecomp reaction class (Figure 16) produces a ketene through the loss of a alkyl radical from a ketone with a radical on the adjoining carbon.

prototype	direction	A	n	E_a
c2h5coch2 = ch2co+c2h5 (hh)(rhh)	forward	1.000E+14	0.0	130.
	reverse	2.110E+11	0.0	30.

The pattern specification refers to the substitution of C_3 and C_1 of Figure 16, namely, (R_5R_6)($R_7R_8R_9$). All combinations of substitutions use the same rate constant.
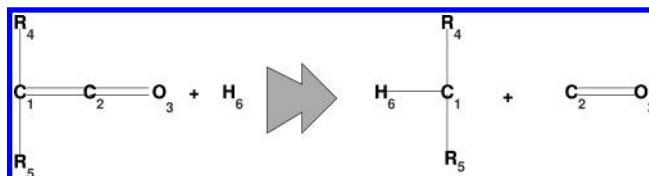

Figure 17. KeteneDecompHToCO: Through the addition of a hydrogen to the carbon double bond, the ketene decomposes to an alkyl radical and carbon monoxide. The class is characterized by R_4 and R_5 giving a total of three patterns.
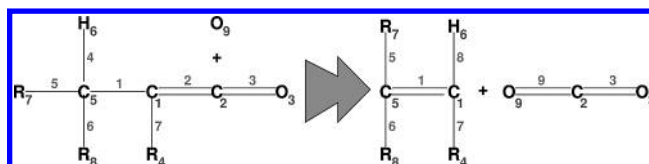

Figure 18. KeteneDecompOToCO2: Through the addition of molecular oxygen to the carbon double bond, the ketene decomposes to an alkene and carbon monoxide. H_6 migrates from C_5 to C_1. The class is characterized by R_4, R_7, and R_8 giving a total of six patterns.

An example of the application of this class to a butanal radical is

```
REACTIONCLASS = KeteneFormationRadicalDecomp-(hh)(rhh)
   1 1-yl-2-butanal = ethyl-radical + allenal
END
```

Since this reaction class is a decomposition, the symmetry value is always one.

4.4. Ketene Decomposition with Hydrogen Radical. Classes: KeteneDecompHToCO. The KeteneDecompHToCO class (Figure 17) produces an alkyl radical and carbon monoxide after the addition of a hydrogen radical to the double bond. The rate constants are based on the following reaction:

prototype	direction	A	n	E_a
c2h5chco+h = nc3h7+co (rh)	forward	4.400E+12	0.0	130.
	reverse	0.0	0.0	0.0

The (rh) refers to the substitution of R_4R_5 of Figure 17. Currently, (rr) uses the same rate constant. Examples applied to branched species are

```
REACTIONCLASS = KeteneDecompHToCO-(rh)
   1 PP39 + hydrogen-radical = carbonmonoxide + 2-methyl-1-propyl-radical
END
REACTIONCLASS = KeteneDecompHToCO-(rr)
   1 PP40 + hydrogen-radical = carbonmonoxide + 2-propyl-radical
END
```

The species PP39 and PP40 (generated species names) are the ketenes $C(CH_3)_2CHCO$ and $C(CH_3)_2CO$, respectively.

4.5. Ketene Decomposition with Oxygen Radical. Classes: KeteneDecompOToCO2. The KeteneDecompOToCO2 class (Figure 18) decomposes the ketene to an olefin and carbon dioxide after the addition of an oxygen. All the rate constants were based on the following:

prototype	direction	A	n	E_a
c2h5chco+o = c3h6+co2 (rhh)(h)	forward	3.200E+12	0.0	−1.83
	reverse	0.0	0.0	0.0

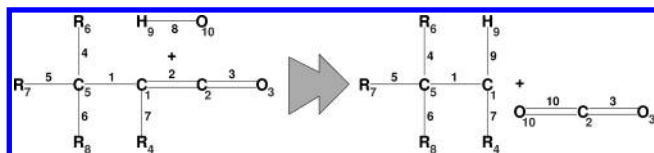The (rhh)(h) refers to ($R_6R_7R_8$)(R_4) in Figure 18. Due to the

Figure 19. KeteneDecompOHToCO2: Through the addition of a hydroxyl radical across the carbon double bond, a ketene decomposes to an alkyl radical and carbon monoxide. The class is characterized by R_6, R_7, R_8, and R_4 giving eight patterns.

complex nature of the valence rearrangement, this reaction is considered irreversible. Examples of two patterns within this class applied to branched species are

```
REACTIONCLASS  = KeteneDecompOToCO2-(rrh)(h)
    1 PP39 + oxygen-atom = carbondioxide + 2-methyl-1-butene
END
REACTIONCLASS  = KeteneDecompOToCO2-(hhh)(r)
    2 PP40 + oxygen-atom = carbondioxide + propene
END
```

The species PP39 and PP40 are the ketenes $C(CH_3)_2CHCO$ and $C(CH_3)_2CO$, respectively. The symmetry factor of 2 comes from the symmetry of the reactant molecule; there are two choices to form the propene.

4.6. Ketene Decomposition with Hydroxyl Radical. Classes: KeteneDecompOHToCO2. The reaction class KeteneDecompOHToCO2 (Figure 19) adds a hydroxyl across the double carbon bond of the ketene activating a decomposition to carbon monoxide and a simple alkyl radical.

Currently, no distinction is made in how the ketene is substituted, so the rate is based on a single reaction.

prototype	direction	A	n	E_a
ch3chco+oh = c2h5+co2	forward	1.730E+12	0.0	−4.22
(hhh)(h)	reverse	0.0	0.0	0.0

The (hhh)(h) refers to $(R_6R_7R_8)(R_4)$ in Figure 19. Due to the complex nature of the valence rearrangement, this reaction is considered irreversible.

Examples applied to branched species are

```
REACTIONCLASS  = KeteneDecompHOToCO2-(rrh)(h)
    1 PP39 + hydroxyl-radical = 2-methyl-1-propyl-radical + carbondioxide
END
REACTIONCLASS  = KeteneDecompHOToCO2-(hhh)(r)
    2 PP40 + hydroxyl-radical = 2-propyl-radical + carbondioxide
END
```

The species PP39 and PP40 are the ketenes $C(CH_3)_2CHCO$ and $C(CH_3)_2CO$, respectively. The symmetry factor of 2 comes from the symmetry of the reactant molecule; there are two ways to form the 2-propyl-radical.

5. CONCLUSION

The reaction classes described in this paper are supplementary to the basic classes for hydrocarbon chemistry of the Curran et al. of heptane[1] and isooctane[2] mechanisms. This set of supplementary reaction classes primarily describes the complete set of reactions needed to consume the products of the low-temperature pathway (products of Curran et al. type 24), the cyclic ether pathway (products of the Curran et al. type 25), and the oxidation of alkenes (products of Curran et al. type 7). All of the product species are aldehyde/ketones or aldehyde/ketones with one radical center. The set

of reaction classes needed to consume these species is of two basic types. The first set of classes abstracts a hydrogen from all possible carbons of the aldehyde/ketones, starting with the hydrogen directly on the ketyl group to the hydrogens on the alpha, beta, and further positions along the aliphatic chain from the ketyl group. The second set of classes consumes the ketyl radicals. If the radical is on the ketyl group itself, through loss of carbon monoxide a simple radical is left. For the radicals along the aliphatic chain from the ketyl group, a set of classes analogous to the Curran et al. type 3 (reaction class **PropylRadicalToEthene** of blurock), loss of an alkyl radical to form an alkene, are designed. The new derived classes take into account the presence of the ketyl group. Another set of classes converts the radical to a ketene group.

The set of classes defined in this paper are able to describe, with a few exceptions, all the aldehyde/ketone chemistry of the C_4, C_5, and C_6 of the Curran et al. heptane mechanism. The few exceptions involve more complex rearrangements or multistep reactions. The set of reactions generated by the aldehyde/ketone chemistry consisting of these new classes are somewhat more extensive than those in the hand generated heptane mechanism. However, if the reactions in the list of "insignificant" (or too complex) species are ignored, then the hand produced and the automatically generated set can be quite close. The combination of the aldehyde/ketone chemistry described here and the reaction classes derived from the 25 types of Curran et al. effectively describes the C_5 through C_7 chemistry of the heptane mechanism.

In contrast to translating already generalized types, the classes developed here reflect another form of generalization. Instead of the database only reflecting established general reaction types defined in the literature, additional reaction classes were extracted from specific examples found within mechanisms published in the literature. Given a specific reaction, the reactive center, i.e., the bonds being made and broken, can be identified (in fact it can be automated) by the "graphical" representation of the reaction.

The final reaction class description supplements the reactive center by the "environment", i.e., neighboring functional groups. This requires the developer to analyze level of accuracy and generalization the reaction class is to represent. These "functional groups" do not change structure through the course of the reaction, i.e., they exist both in the products and in the reactants. They do, however, provide an influence which effects the rate of the reaction, for example, the "electronic" effects caused by oxygenated groups, multiple bonded atoms, or resonance. These groups have to be included within the reaction class to ensure the appropriate accuracy. In the design of the reaction class, especially from specific reactions, one tries to find a compromise between "complexity", i.e., including many structural influences (the largest being the specific reaction itself), and "generality", including only the "major" influences. Many of the classes involving ketyl groups are actually special cases of reaction classes involving just alkyl species, i.e., species with no extra functionality. As seen in the previous sections, including these influences creates a set of more complex reaction classes due to variety of relative positions of the ketyl group and the reactive center. Quite a few specialized reaction classes emerge.

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Though the chosen rate constants will be improved as more experience, experimental data, and physical principles are gathered, the work in this paper has shown that reasonable and usable reaction classes can be derived from sources in the literature and can represent the current stand of chemical knowledge in the production of complex reaction mechanisms.

The purpose of this paper, to provide a complete set of reaction classes to describe the additional chemistry beyond the 25 types of Curran et al., has been accomplished. Furthermore, when these classes are used within properly defined aldehyde/ketone pathways, they are able to mimic the C_5, C_6, and C_7 chemistry of the hand produced heptane mechanism. The work presented here, in conjunction with the previous paper in this series, provides a substantiation that automated reaction generation techniques can be used to produce mechanisms that are close to those that would be produced by hand.

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