J. Phys. Chem. **1988**, *92*, 661-671

Experimental Study and Kinetic Modeling of Propene Oxidation in a Jet Stirred Flow Reactor

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The oxidation of propene was studied in a jet stirred flow reactor in the temperature range 900–1200 K at pressures extending from 1 to 8 atm for a wide range of fuel–oxygen equivalence ratios (0.15–4.0). A computer program has been developed to model the experimental data by using a chemical kinetic reaction mechanism. A direct method to determine the first-order sensitivities of the mole fraction of each species with respect to the rate constants was used to develop the kinetic scheme. The present chemical kinetic reaction mechanism is able to reproduce the experimental results, although some discrepancies are observed for the minor products.

Introduction

Propene is an important intermediate olefin produced during fuel combustion[1] and plays an important role in the pyrolysis and oxidation of propane. Very few experimental results are available for propene oxidation,[2,3] and these results were obtained in relatively narrow conditions. For these reasons, we have carried out experiments in a jet stirred flow reactor to examine propene oxidation in a wide range of pressure (1–8 atm), temperature (900–1200 K), and equivalence ratio (0.15–4.0). In this paper we present the results of this study and we propose a detailed chemical kinetic mechanism to reproduce the experimental data obtained in the jet stirred reactor.

Experimental Section

The details of the experimental set up have been published elsewhere[4] and will only be reviewed briefly here.

The jet stirred reactor, built in fused silica to prevent wall catalytic reactions, is located inside a stainless steel pressure-resistant jacket, allowing work at pressures ranging from 1 to 10 atm and temperatures up to around 1200 K. The flow rates of the hydrocarbon and of oxygen are measured and regulated by thermal mass-flow controllers. These gases are diluted by a flow of nitrogen and mixed at the entrance of the injectors. Under these conditions, we can follow the evolution of the fuel oxidation from low conversion up to the formation of final products. The temperature of the gases inside the reactor is measured by a Chromel–Alumel thermocouple which is moved along a whole diameter, allowing checking of the reactor homogeneity. Preheating of the gases before their admission in the reactor and the high dilution (0.15–0.3% of the hydrocarbon by volume) of the fuel maintain the temperature gradient lower than 5 K. The pressure inside the reactor is kept constant in time by means of a pressure regulator on the exhaust line. A representation of the apparatus is given in Figure 1.

The propene (Phillips Petroleum Co.) was 99.9% pure; N_2 (less than 50 ppm of O_2 and H_2O, 5 ppm of H_2, and 1000 ppm of Ar) and O_2 (99.995% pure) were provided by Air Liquide.

By means of a sonic quartz probe, the gases within the reactor are sampled and stored in glass bottles. A multicolumn (molecular sieve, Porapack QS, Porapack R), multidetector (thermal conductivity, flame ionization) gas chromatograph working with helium as carrier gas, was used to determine O_2, CO, CO_2, aldehyde, and hydrocarbon contents of the samples. The hydrogen concentration was measured on another chromatograph using nitrogen as carrier gas and Carle microthermistors as detector. Beside the main chemical species (CO, H_2, CO_2, CH_4, C_2H_4, and C_3H_6), the concentrations of C_2H_6, C_2H_2, and CH_3CHO have been measured. The presence of allene, propyne, and C_4 hydrocarbons (1-butene, 2-butene, and 1,3-butadiene) in trace quantities was detected. The importance of these minor products, particularly allene and propyne, increased with increasing equivalence ratio and pressure.

TABLE I: Experimental Conditions for the Oxidation of Propene

mean residence time, s	press., atm	init temp, K	equiv ratio	init concn, %	
				C_3H_6	O_2
0.05–0.25	1	1033	0.15	0.15	4.500
0.05–0.25	1	1070	0.15	0.15	4.500
0.02–0.25	1	1140	0.50	0.15	1.350
0.03–0.25	1	1150	0.50	0.15	1.350
0.02–0.25	1	1160	0.50	0.15	1.350
0.03–0.25	1	1200	1.00	0.15	0.675
0.03–0.25	1	1210	1.50	0.15	0.450
0.15–1.20	5	1050	0.50	0.15	1.350
0.15–1.20	5	1100	1.00	0.15	0.675
0.20–1.20	5	1140	1.50	0.15	0.450
0.15–1.20	5	1160	2.00	0.15	0.337
0.20–1.20	5	1180	4.00	0.15	0.169
0.20–1.80	8	960	0.50	0.15	1.350
0.20–1.80	8	990	0.75	0.15	0.900
0.20–1.80	8	1020	1.00	0.15	0.675
0.20–1.80	8	1070	1.50	0.15	0.450
0.20–1.80	8	1100	2.00	0.15	0.337
0.20–1.80	8	1130	4.00	0.15	0.169

Table I presents the initial conditions of the experiments performed, covering a wide range of equivalence ratios and pressures.

Figures 2–8 show the evolutions of the concentrations of propene and the products of its oxidation versus mean residence time. It has been observed that the oxidation of lean and stoichiometric mixtures at atmospheric pressure (Figures 2 and 3) begins by an induction period during which propene is slowly consumed and the intermediate compounds accumulate. This induction periods ends with a dramatic decrease of propene and intermediate compound concentrations. At the same time, CO_2 accumulates very fast. However, at higher pressures (Figures 4, 5, and 7), the induction period is shorter and the evolution is more gradual.

Method of Calculation

Recently, we have developed a perfectly stirred reactor computer model where the reactor is assumed to be in the steady state. The gas concentrations within the reactor are determined from the balance between the net rate of production of each species by chemical reaction and the difference between the input and the output flow rates of the species:

$$\dot{m}(\sigma_i - \sigma_i^*)/v = R_j - R_{-j}$$

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(1) Brezinsky, K.; Dryer, F. L. *Combust. Sci. Technol.* **1986**, *45*, 199.

(2) Baldwin, R. R.; Hisham, M. W. M.; Walker, R. W. *Twentieth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1984; pp 743–750.

(3) Burcat, A.; Radhakrishnan, K. *Combust. Flame* **1985**, *60*, 157.

(4) Dagaut, P.; Cathonnet, M.; Rouan, J. P.; Foulatier, R.; Quilgars, A.; Boettner, J. C.; Gaillard, F.; James, H. *J. Phys. E: Sci. Instrum.* **1986**, *19*, 207.

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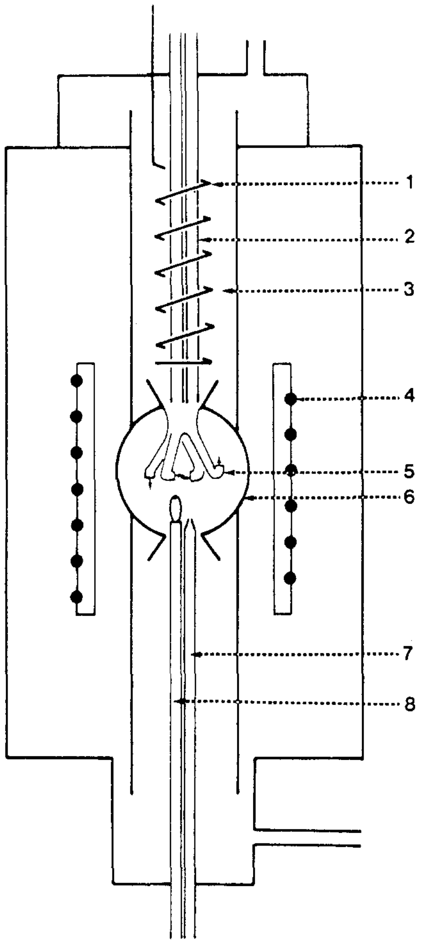


Figure 1. The jet stirred reactor: (1) the preheating resistor, (2) the capillary for introduction of the hydrocarbon diluted by nitrogen, (3) the oxygen–nitrogen flow, (4) the heating resistor, (5) the four injectors, (6) the fused-silica reactor of 29.5 cm^3, (7) the sonic quartz probe, and (8) the Chromel–Alumel thermocouple. Arrows symbolize the jet directions.

where σ_i^* and σ_i are the concentrations (moles per gram) of the species i respectively on input and output; $\dot{m}$ is the massic overall flow rate of the gases (grams per second), and v is the volume of the reactor. R_j and R_{-j} are the sums of the rates of elementary reactions respectively forming and consuming the species i.

These rates are computed from the chemical kinetic reaction mechanism and the rate constants of the elementary reactions at the experimental temperature according to the modified Arrhenius equation:

$$k = AT^b \exp(-E/RT)$$

At each mean residence time considered, $\tau = \rho V/\dot{m}$, where ρ is the mass density, we have to solve the set of nonlinear algebraic equations for the I species and J reaction of the kinetic scheme:

$$\dot{m}(\sigma_i^* - \sigma_i)/v - \sum_{j=1}^{J}(\alpha_{ij} - \beta_{ij})(R_j - R_{-j}) = 0 \qquad i = 1, 2, ..., I;\ j = 1, 2, ..., J$$

where α_{ij} and β_{ij} are the stoichiometric coefficients of species i in reaction j for the reactants and products, respectively.

The set of nonlinear algebraic equations is solved by the Newton–Raphson Method.

A sensitivity analysis computer program has been developed to calculate the first-order sensitivities for each species i in the reaction j, at a given mean residence time τ. The sensitivities are defined as

$$S_{i,j,\tau} = [\mathrm{d} \ln \sigma_i/\mathrm{d} \ln k_j]_\tau$$

assuming $\delta\sigma_i/\delta k_j = \Delta\sigma_i/\Delta k_j$ and using $\Delta k_j/k_j = 10^{-3}$.

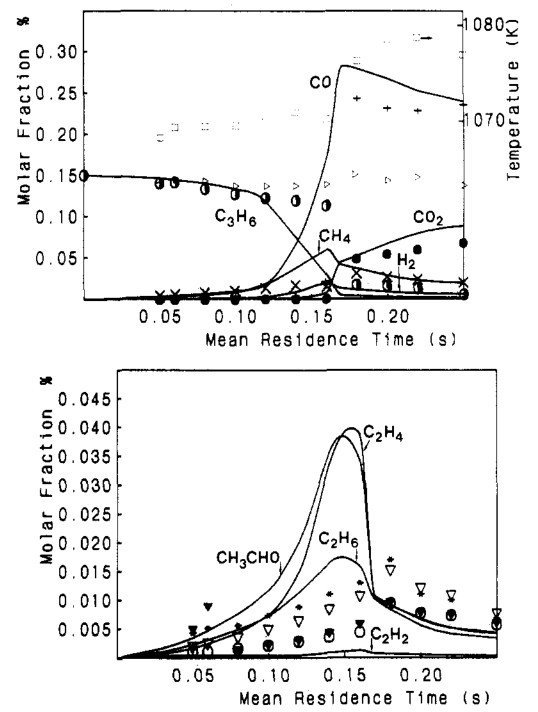


Figure 2. Oxidation in the jet stirred reactor of the mixture propene–oxygen–nitrogen = 0.15%–4.5%–95.35% at 1 atm (equivalence ratio = 0.15). Comparison between computed (lines) and experimental results (symbols): H_2 (▲), CO (+), CO_2 (●), CH_4 (×), C_2H_4 (▽), C_2H_6 (▼), C_2H_2 (○), CH_3CHO (*), and C_3H_6 (◑). Experimental temperature (□); total carbon/3 (▷). The concentration profiles for C_2H_6, C_2H_2, and CH_3CHO are multiplied by 10 and divided by 2 for CO_2.

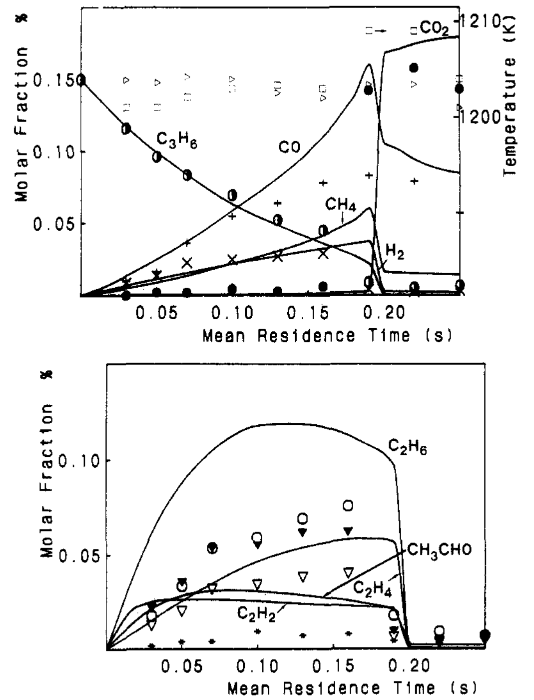


Figure 3. Oxidation in the jet stirred-reactor of the mixture propene–oxygen–nitrogen = 0.15%–0.675%–99.175% at 1 atm (equivalence ratio = 1.0). Comparison between computed (lines) and experimental results (symbols): H_2 (▲), CO (+), CO_2 (●), CH_4 (×), C_2H_4 (▽), C_2H_6 (▼), C_2H_2 (○), CH_3CHO (*), and C_3H_6 (◑). Experimental temperature (□); total carbon/3 (▷). The concentration profiles for C_2H_6, C_2H_2, and CH_3CHO are multiplied by 10 and divided by 2 for CO_2.

Reaction Mechanism

The present chemical kinetic reaction mechanism was built to model the oxidation of ethylene, propene, and propane.[10] It was assembled from the compilation of Warnatz[24] and from previous

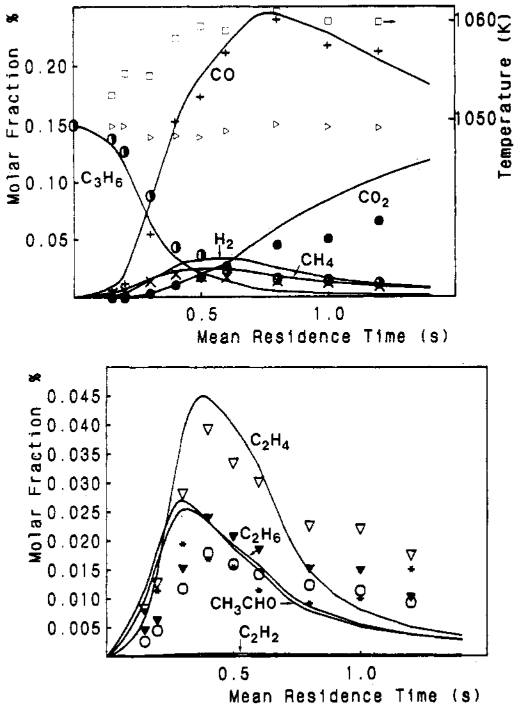


Figure 4. Oxidation in the jet stirred reactor of the mixture propene–oxygen–nitrogen = 0.15%–1.35%–98.50% at 5 atmospheres (equivalence ratio = 0.5). Comparison between computed (lines) and experimental results (symbols): H_2 (▲), CO (+), CO_2 (●), CH_4 (×), C_2H_4 (▽), C_2H_6 (▼), C_2H_2 (○), CH_3CHO (*), and C_3H_6 (◑). Experimental temperature (□); total carbon/3 (▷). The concentration profiles for C_2H_6, C_2H_2, and CH_3CHO are multiplied by 10 and divided by 2 for CO_2.

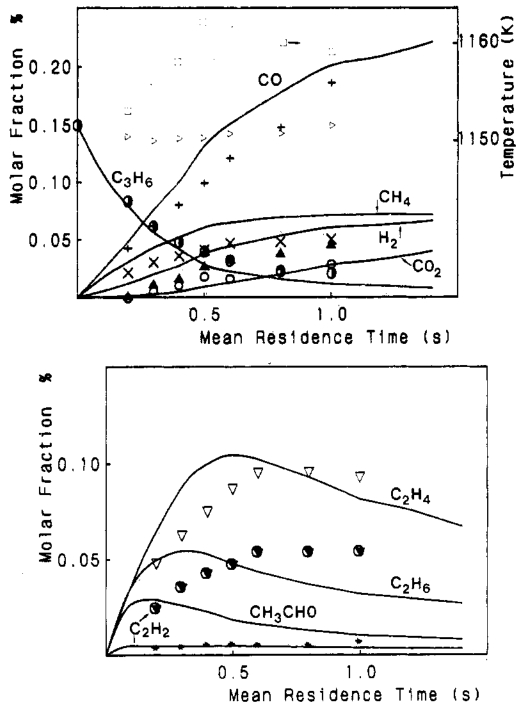


Figure 6. Oxidation in the jet stirred reactor of the mixture propene–oxygen–nitrogen = 0.15%–0.45%–99.40% at 5 atm (equivalence ratio = 1.5). Comparison between computed (lines) and experimental results (symbols): H_2 (▲), CO (+), CO_2 (●), CH_4 (×), C_2H_4 (▽), C_2H_6 (▼), C_2H_2 (○), CH_3CHO (*), and C_3H_6 (◑). Experimental temperature (□); total carbon/3 (▷). The concentration profiles for C_2H_4, C_2H_6, C_2H_2, and CH_3CHO are respectively multiplied by 2, 10, 10, and 10.

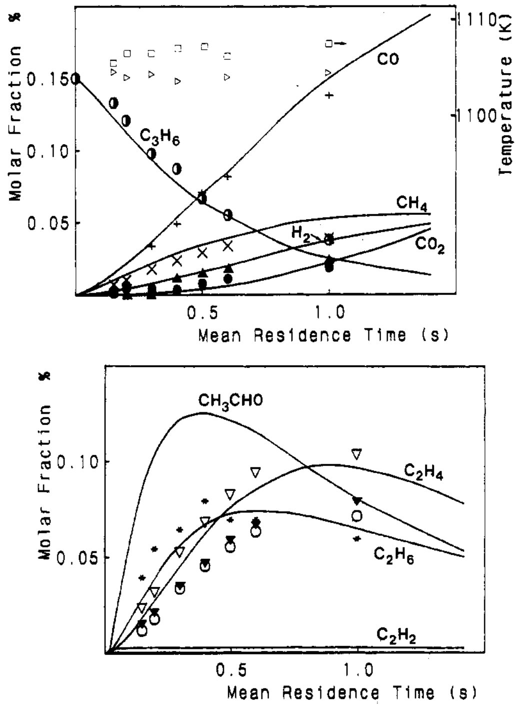


Figure 5. Oxidation in the jet stirred reactor of the mixture propene–oxygen–nitrogen = 0.15%–0.675%–99.175% at 5 atm (equivalence ratio = 1.0). Comparison between computed (lines) and experimental results (symbols): H_2 (▲), CO (+), CO_2 (●), CH_4 (×), C_2H_4 (▽), C_2H_6 (▼), C_2H_2 (○), CH_3CHO (*), and C_3H_6 (◑). Experimental temperature (□); total carbon/3 (▷). The concentration profiles for C_2H_4, C_2H_6, C_2H_2, and CH_3CHO are respectively multiplied by 2, 20, 20, and 50.

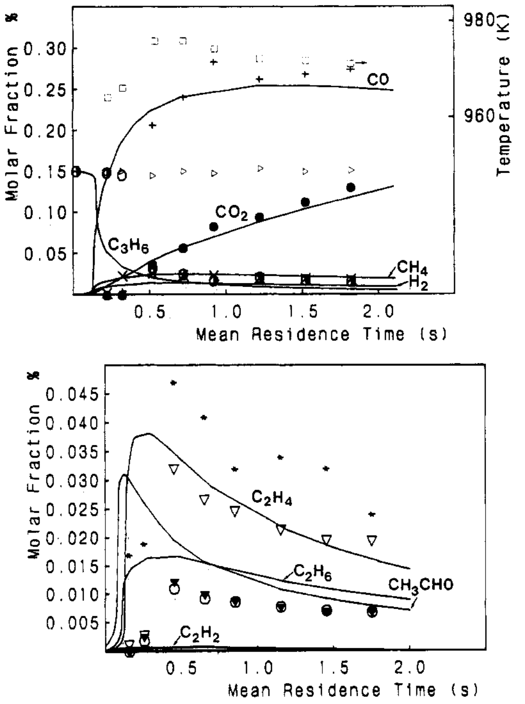


Figure 7. Oxidation in the jet stirred reactor of the mixture propene–oxygen–nitrogen = 0.15%–1.35%–98.50% at 8 atm (equivalence ratio = 0.5). Comparison between computed (lines) and experimental results (symbols): H_2 (▲), CO (+), CO_2 (●), CH_4 (×), C_2H_4 (▽), C_2H_6 (▼), C_2H_2 (○), CH3CHO (*), and C_3H_6 (◑). Experimental temperature (□); total carbon/3 (▷). The concentration profiles for C_2H_6, C_2H_2, and CH_3CHO are multiplied by 10 and divided by 2 for CH_4.

mechanisms for the oxidation of propane in flames.[5,6] The reaction mechanism developed by Westbrook and co-workers[8,26,27] was also considered, since it was built to model experiments in the same temperature range as the present one. However, some parts of the mechanism of C_3 hydrocarbons oxidation remain obscure, i.e., the reactions forming and consuming the intermediate species C_3H_5, C_3H_4, and C_3H_3, and additional data were taken from Baldwin et al.[2,25] and other authors whose references are given later. In the present mechanism, we introduced several new species, in comparison with previous kinetic schemes proposed for

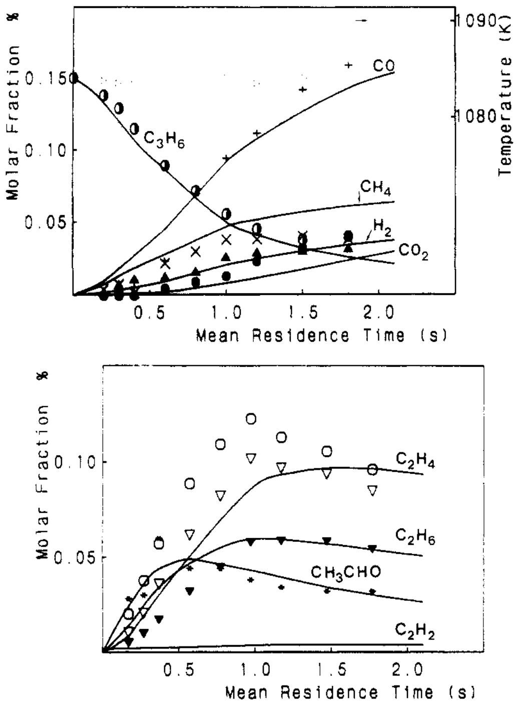


Figure 8. Oxidation in the jet stirred reactor of the mixture propene–oxygen–nitrogen = 0.15%–0.45%–99.50% at 8 atm (equivalence ratio = 1.5). Comparison between computed (lines) and experimental results (symbols): H_2 (▲), CO (+), CO_2 (●), CH_4 (×), C_2H_4 (▽), C_2H_6 (▼), C_2H_2 (○), CH_3CHO (×), and C_3H_6 (◑). Experimental temperature (□); total carbon/3 (▷). The concentration profiles for C_2H_4, C_2H_6, C_2H_2, and CH_3CHO are respectively multiplied by 2, 20, 40, and 20.

propane and propene oxidation.[3,5-9] These species are listed in Table II with their formulas.

The complete mechanism consists of 277 reactions among 48 species and is presented in Table III. Reverse rates were computed from forward rates and the appropriate equilibrium constants, calculated by using the thermochemical coefficients of Burcat.[13] The data of compounds not found in Burcat's compilation were taken from Bahn.[14]

The species CH_3CO has been neglected in the present kinetic scheme and replaced by $CH_3 + CO$, assuming a rapid thermal decomposition of CH_3CO. We have verified that this simplification has no effect on computed results in the conditions of the present work.

In addition, the rates of a number of reactions have been adjusted within their uncertainty range or estimated by using sensitivity studies; they are identified in Table III. Table III also shows the most sensitive reactions in the oxidation of ethylene,[11] propane,[12] and propene.

The submechanism of C_1 and C_2 species—reactions 1–160—is discussed elsewhere.[11] In the present paper, we detail the reactions of the unsaturated C_3 species involved in the mechanism of Table III.

Reactions of Propene. Initiation. We have considered initiation reactions involving propene:

$$C_3H_6 = AC_3H_5 + H \tag{189}$$

$$C_3H_6 = SC_3H_5 + H \tag{190}$$

$$C_3H_6 = C_2H_3 + CH_3 \tag{191}$$

$$C_3H_6 + O_2 = SC_3H_5 + HO_2 \tag{204}$$

$$C_3H_6 + O_2 = TC_3H_5 + HO_2 \tag{205}$$

$$C_3H_6 + O_2 = AC_3H_5 + HO_2 \tag{206}$$

For reaction 189, we used the rate constant proposed by Simmie et al.;[15] the rate constant for reaction 190 was proposed by Roscoe and Thompson.[16] We used their rate constant value at 1038 K and the same activation energy as for reaction 189. Kinetic parameters for reaction 191 were initially taken from Westbrook and Pitz[8] and adjusted to fit our experimental results. Arrhenius parameters for reactions 204–206 are derived from Walker.[17]

Reactions 192–199 have been proposed by Baldwin et al.,[2] and the rate expressions determined by these authors are used here, except for reactions 193–195 estimated from Walker.[17]

The modeling results are insensitive to the values of the rate constants of these initiation reactions, except reaction 191.

Reactions with Hydroxyl Radicals. These reactions have been studied by Baldwin et al.,[2] who have proposed the mechanism

$$C_3H_6 + OH = AC_3H_5 + H_2O \tag{196}$$

$$C_3H_6 + OH = SC_3H_5 + H_2O \tag{197}$$

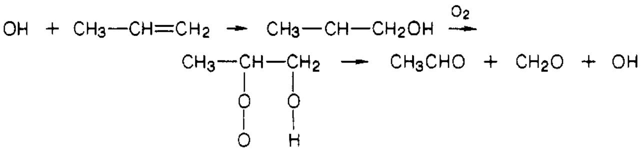
and the complex route

$$C_3H_6 + OH = C_2H_5 + CH_2O \tag{198}$$

Acetaldehyde formation route via reaction of C_3H_6 and OH used by Westbrook and Pitz[8] and Warnatz[5-7]

$$C_3H_6 + OH = CH_3CHO + CH_3 \tag{i}$$

has not been considered here, because of a great lack of information. However, we have considered the mechanism proposed by Baldwin et al.[2]



$$OH + CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CH{-}CH_2OH \xrightarrow{O_2} CH_3{-}\underset{\substack{|\\O\\|\\O}}{CH}{-}\underset{\substack{|\\O\\|\\H}}{CH_2} \rightarrow CH_3CHO + CH_2O + OH$$

which we have written as a global reaction:

$$C_3H_6 + OH + O_2 = CH_3CHO + CH_2O + OH \tag{199}$$

The rate constants of reactions 196–198 have a sensitive effect on the computation, but k_{199} has no effect. Their values have been taken from Baldwin et al.[2]

Reactions with Oxygen Atoms. Reactions of propene with atomic oxygen include the steps

$$C_3H_6 + O = C_2H_5 + HCO \tag{200}$$

$$C_3H_6 + O = C_2H_4 + CH_2O \tag{201}$$

$$C_3H_6 + O = CH_3 + CH_3 + CO \tag{202}$$

also used by Westbrook and Pitz.[8]

Kanofsky et al.[18] in their high-intensity crossed molecular beams experiments determined that reactions 200 and 202 were the main

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(5) Warnatz, J. *Eighteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1981; pp 369–384.

(6) Warnatz, J. *Combust. Sci. Technol.* **1983**, *34*, 177.

(7) Warnatz, J. *Twentieth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1984; pp 845–856.

(8) Westbrook, C. K.; Pitz, W. J. *Combust. Sci. Technol.* **1984**, *37*, 117.

(9) Cathonnet, M.; Boettner, J. C.; James, H. *Eighteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1981; p 903.

(10) Dagaut, P. Thèse de l'Université Pierre et Marie Curie, Paris, 1986.

(11) Dagaut, P.; Cathonnet, M.; Boettner, J. C.; Gaillard, F. *Combust. Flame*, in press.

(12) Dagaut, P.; Cathonnet, M.; Boettner, J. C.; Gaillard, F. *Combust. Sci. Technol.* **1987**, *56*, 23.

(13) Burcat, A. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer Verlag: New York, 1984; Chapter 8, pp 455–473.

(14) Bahn, G. S. *Approximate Thermochemical Tables for some C–H and C–H–O Species*; National Technical Information Service, Springfield, VA, 1973; NASA CR-2178.

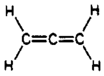
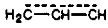
(15) Simmie, J. M.; Gardiner, W. C., Jr.; Eubank, C. S. *J. Phys. Chem.* **1982**, *86*, 799.

(16) Roscoe, J. M.; Thompson, M. J. *Int. J. Chem. Kinet.* **1985**, *17*, 967.

(17) Walker, R. W. In *Reaction Kinetics*; Specialist Periodical Report 1; The Chemical Society: London, 1975; pp 161–211. Walker, R. W. In *Reaction Kinetics and Energy Transfer*; Specialist Periodical Report 2; The Chemical Society: London, 1977; pp 296–330.

(18) Kanofsky, J. R.; Lucas, D.; Gutman, D. *Fourteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1973; p 285.

TABLE II: The C_3H_4 and C_3H_5 Species

symbol	name	formula
AC_3H_4	allene or propadiene	
PC_3H_4	propyne or methylacetylene	$HC\equiv C—CH_3$
SC_3H_5	2-methylvinyl radical	$H_3C—CH=\dot{C}H$
AC_3H_5	allyl radical	 $H_2\dot{C}\overline{—CH—}CH_2$
TC_3H_5	1-methylvinyl radical	$H_3C—\dot{C}=CH_2$

routes for the reaction of oxygen atoms with propene and that reactions 201 and

$$C_3H_6 + O = C_3H_4O + H_2 \qquad \text{(ii)}$$

were the minor routes, in agreement with the general mechanism for O + olefin reactions proposed by Cvetanovic.[19,20] Blumenberg et al.[21] proposed the same reactions as Kanofsky did and pointed out that reaction ii is of lower importance than reaction 201; hence, reaction ii was neglected in the present work. The Arrhenius expressions used here for reactions 200–202 are derived from the determination of Perry[22] in the 258–861 K temperature range. Perry proposed the expression

$$k(T) = (2.05 \times 10^5)T^{2.56} \exp(+568.6/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for the global reaction of C_3H_6 with oxygen atoms. In the absence of further information about the branching ratio versus temperature for each route, we used the same rate constant for each reaction 200–202, dividing Perry's preexponential factor by 3, as already done in ref 8.

The modeling is sensitive to the values of rate constants of reactions 200–202, at 1 atm, but their sensitivity decreases at higher pressure.

Reactions with Hydroperoxyl Radicals. The reactions considered were

$$C_3H_6 + HO_2 = C_3H_6O + OH \qquad (192)$$

$$C_3H_6 + HO_2 = AC_3H_5 + H_2O_2 \qquad (193)$$

$$C_3H_6 + HO_2 = SC_3H_5 + H_2O_2 \qquad (194)$$

$$C_3H_6 + HO_2 = TC_3H_5 + H_2O_2 \qquad (195)$$

According to Baldwin et al.,[2] $k_{193} \gg k_{194} \simeq k_{195}$; hence reactions 194 and 195 may be neglected. We used the rate expressions of Baldwin et al.[2] for reactions 192 and 193, and we derived k_{194} and k_{195} from Walker 17. None of these rate constants has an effect on the computation.

Propene oxide, formed in reaction 192, is assumed to react principally by thermal decomposition via the reaction

$$C_3H_6O = C_2H_6 + CO \qquad (211)$$

with the rate constant proposed by Benson,[23] but the computation is insensitive to the value of k_{211}.

Reactions with Hydrogen Atoms. The main addition reactions occurs on the terminal carbon side of the double bond:

$$C_3H_6 + H = i\text{-}C_3H_7 \qquad (187)$$

Another process is the abstraction of an H atom. Because of the lack of experimental data, only one reaction was considered:

$$C_3H_6 + H = AC_3H_5 + H_2 \qquad (203)$$

For k_{187}, we used the recommended value of Warnatz;[24] for reaction 203, we used the rate constant proposed by Simmie et al.[15] The computation is insensitive to the values of k_{187} but sensitive to that of k_{203}. Both rate constants have an effect on the modeling of propane oxidation.[12]

Reactions with Methyl Radicals. Abstraction of an H atom can give three different C_3H_5 radicals by the processes

$$C_3H_6 + CH_3 = A_3H_5 + CH_4 \qquad (208)$$

$$C_3H_6 + CH_3 = SC_3H_5 + CH_4 \qquad (209)$$

$$C_3H_6 + CH_3 = TC_3H_5 + CH_4 \qquad (210)$$

The value of k_{208} was taken from Allara and Shaw[43] and the values of k_{209} and k_{210} were derived from Walker.[17]

The computation is sensitive to the values of k_{208} and k_{209}. Direct investigations of these reactions are needed.

Reactions of C_3H_5 Radicals. The reactions of C_3H_5 radicals with molecular oxygen considered were

$$SC_3H_5 + O_2 = CH_3CHO + HCO \qquad (213)$$

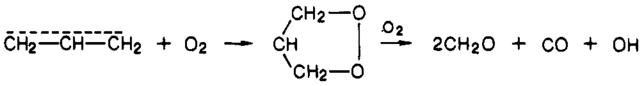
$$SC_3H_5 + O_2 = CH_3 + CO + CH_2O \qquad (214)$$

$$AC_3H_5 + O_2 + O_2 \rightarrow CO + OH + 2CH_2O \qquad (218)$$

$$TC_3H_5 + O_2 = CH_3 + CO + CH_2O \qquad (219)$$

Reaction 214 represents a global reaction early proposed by Baldwin and Walker.[25]

Baldwin et al.[2] proposed a mechanism for reaction 218:



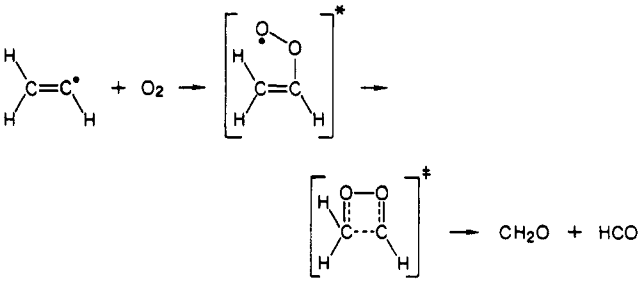
but they did not measure its rate constant. By analogy with the reaction of vinyl radical with molecular oxygen

$$C_2H_3 + O_2 = CH_2O + HCO \qquad (118)$$

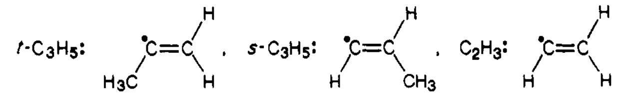
the rate constant of reaction 218 was initially taken equal to k_{118}. This value was divided by a factor of 2 in order to fit experimental results. This reaction appeared to be essential to model propene oxidation in very lean mixture, at atmospheric pressure in our temperature range. The H-transfer reaction

$$AC_3H_5 + O_2 = AC_3H_4 + HO_2 \qquad \text{(iii)}$$

generally considered in modeling studies,[8,26,27] instead of reaction 218, leads to an overestimation of the reactivity of propene in lean mixtures and is excluded by Baldwin and Walker.[25] For reactions 213, 214, and 219, we assumed that the mechanism was similar to that proposed by Baldwin and Walker[25] and confirmed by Slagle et al.[28] for the reaction of vinyl radical with molecular oxygen. According to these authors, vinyl radicals react with molecular oxygen via an addition–decomposition channel:



The molecular structures of the C_3H_5 and C_2H_3 radicals can be compared:



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(19) Cvetanovic, R. J. *Adv. Photochem.* **1963**, *1*, 115.

(20) Cvetanovic, R. J. *Can. J. Chem.* **1955**, *23*, 1375.

(21) Blumenberg, B.; Hoyermann, K.; Sievert, R. *Sixteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1976; p 841.

(22) Perry, R. A. *J. Chem. Phys.* **1984**, *80*, 153.

(23) Benson, S. W. *J. Chem. Phys.* **1964**, *40*, 105.

(24) Warnatz, J. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer Verlag, New York, 1984; Chapter 5, pp 197–360.

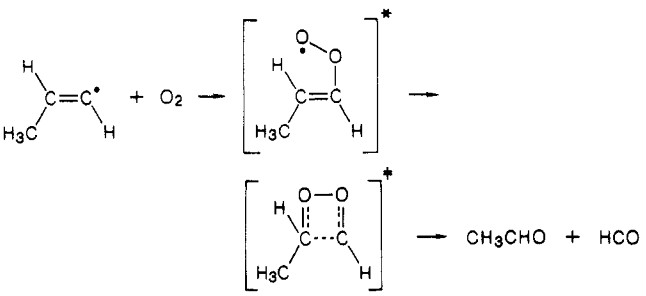
(25) Baldwin, R. R.; Walker, R. W. *Eighteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1981; pp 819–829.

(26) Pitz, W. J.; Westbrook, C. K.; Proscia, W. M.; Dryer, F. L. *Twentieth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1984; pp 831–843.

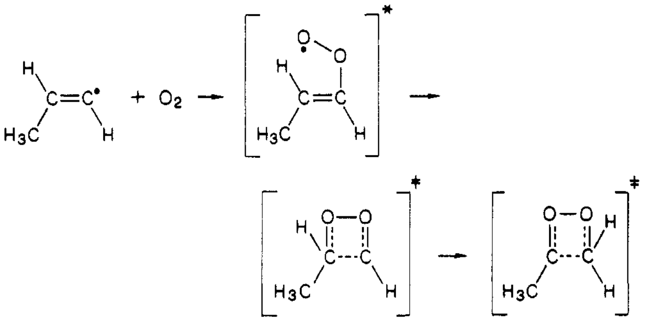
(27) Pitz, W. J.; Westbrook, C. K. *Combust. Flame* **1986**, *63*, 113.

(28) Slagle, I. R.; Park, J. Y.; Heaven, M. C.; Gutman, D. *J. Am. Chem. Soc.* **1984**, *106*, 4356.

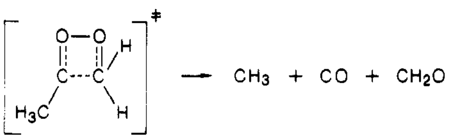
For the reactions of sC_3H_5 with O_2, we propose the following steps: The classical route



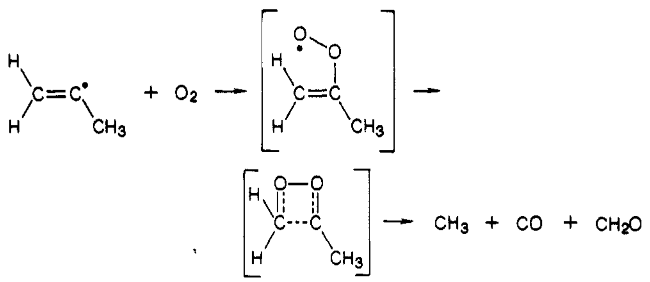
or the possible H transfer in the activated complex



followed by the decomposition of the new activated complex.



For tC_3H_5 radicals, the proposed mechanism is



The rate constants for these reactions were initially taken equal to k_{118} and adjusted to fit our experimental results. Although according to Slagle and Gutman[42] the rate constant of the reaction $C_3H_5 + O_2$ should be very low, reactions 213 and 214 have an influence on the computation at low conversion and reaction 218 appeared to be essential to model propene oxidation in very lean mixture, at atmospheric pressure in our temperature range. We also considered C_3H_5 radical thermal decomposition reactions:

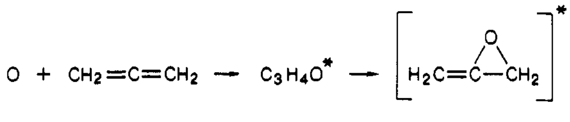
$$SC_3H_5 = C_2H_2 + CH_3 \qquad (212)$$

$$AC_3H_5 = AC_3H_4 + H \qquad (215)$$

$$TC_3H_5 = PC_3H_4 + H \qquad (-231)$$

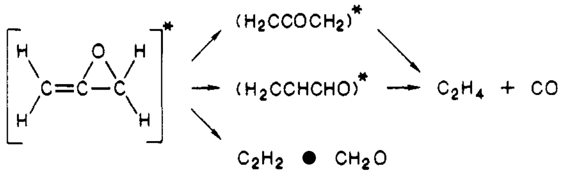
For reaction 212, we used the rate constant value proposed by Sundaram and Froment,[29] while for k_{215}, we used the value proposed by Dente and Ranzi.[30] Arrhenius parameters for reaction −231 are computed from the value of k_{231} determined by Wagner and Zellner.[31] From these three rate constants only k_{215} has a sensitive effect on the computation.

Reactions of Allene. Allene consumption includes its reactions with O, H, OH, and HO_2. The reactions of allene with oxygen atoms have been studied by Havel[32] and Herbrechtsmeier.[33-35] Herbreichtsmeier proposed a mechanism:



(A)

Then, (A) may rearrange or decompose:



We considered only the main route according to Herbrechtsmeier:

$$AC_3H_4 + O = CO + C_2H_4 \qquad (224)$$

with the rate constant proposed in ref 33.

Reactions of allene with hydrogen atoms have been studied by Wagner and Zellner.[36] They determined the steps

$$AC_3H_4 + H = TC_3H_5 \qquad (225)$$

$$AC_3H_4 + H = SC_3H_5 \qquad (226)$$

included in the present mechanism, with the rate constants determined by these authors in the temperature range 273–470 K.

Reaction of allene with hydroxyl radicals was studied by several groups.[37-39] Bradley et al.[37] have observed the production of crotonaldehyde, methanol, ketene, and carbon monoxide. Hoyermann et al.[38] proposed a mechanism including five steps:

$$OH + CH_2{=}C{=}CH_2 \rightarrow CH_3 + CH_2CO \qquad (a)$$

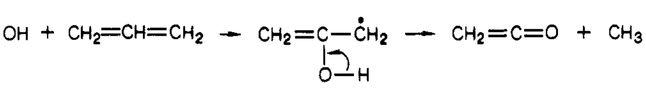
$$\rightarrow C_3H_3 + H_2O \qquad (b)$$

$$\rightarrow C_2H_4 + HCO \qquad (c)$$

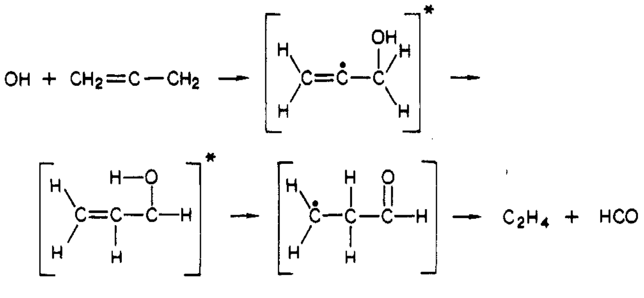
$$\rightarrow C_2H_5 + CO \qquad (d)$$

$$\rightarrow C_3H_4OH \qquad (e)$$

with (a) being the main route that is supposed to occur via



Slagle et al.[39] proposed a route



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(29) Sundaram, K. M.; Froment, G. F. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 174.

(30) Dente, M. E.; Ranzi, E. M. In *Pyrolysis, Theory* and *Industrial Practice*; Albright, L. F.; Crynes, B. L.; Corcoran, W. H., Eds.; Academic: New York, 1983; Chapter 7, pp 133–175.

(31) Wagner, H. G.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 518.

(32) Havel, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 530.

(33) Herbrechtsmeier, P. *Combustion Institute European Symposium*; Weinberg, F. J., Ed.; Academic: London, 1973; pp 13–18.

(34) Herbrechtsmeier, P.; Wagner, H. G. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 517.

(35) Herbrechtsmeier, P.; Wagner, H. G. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *79*, 461.

(36) Wagner, H. G.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 667.

(37) Bradley, J. N.; Hack, W.; Hoyermann, K.; Wagner, H. G. *J. Chem. Soc., Faraday Trans. 1*, **1973**, *11*, 1889.

(38) Hoyermann, K.; Sievert, R.; Wagner, H. G. *Oxid. Commun.* **1980**, *1*, 145.

(39) Slagle, I. R.; Gilbert, J. R.; Graham, R. E.; Gutman, D. *Int. J. Chem. Kinet., Symp.* **1975**, *1*, 317.

to explain the formation of ethylene. We retained the main routes of Hoyermann et al.[38] and Slagle et al.:[39]

$$\mathrm{AC_3H_4 + OH = CH_2CO + CH_3} \qquad (222)$$

$$\mathrm{AC_3H_4 + OH = C_2H_4 + HCO} \qquad (223)$$

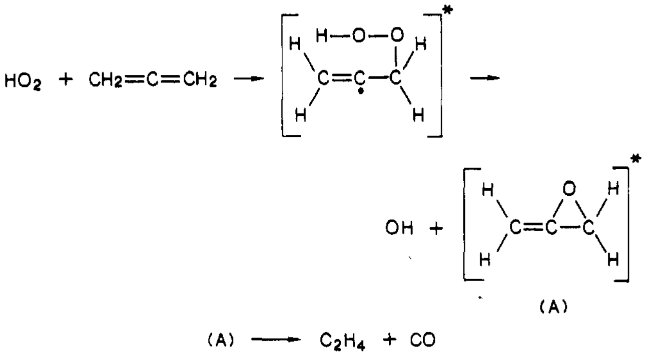
The rate constants for these reactions have been estimated and derived from Walker[17] and Westbrook and Pitz.[8]

We also considered the reactions of allene with hydroperoxyl radicals:

$$\mathrm{AC_3H_4 + HO_2 = C_2H_4 + CO + OH} \qquad (220)$$

$$\mathrm{AC_3H_4 + HO_2 = C_3H_3 + H_2O_2} \qquad (221)$$

Reaction 220 is supposed to occur via the mechanism



In this scheme, the species A formed intermediately is the same that is formed in the mechanism of Herbrechtsmeier in the reaction of allene with oxygen atoms, presented above. Arrhenius parameters for reaction 220 are assumed to be similar to that of

$$\mathrm{C_3H_6 + HO_2 = C_3H_6O + OH} \qquad (192)$$

and the rate constant for reaction 221 is assumed to be close to that of

$$\mathrm{C_2H_4 + HO_2 = C_2H_4O + OH} \qquad (103)$$

The model predictions are not very sensitive to the rate constants of the reactions of allene, but if reactions 220 and 221 are not included in the mechanism, the model underpredicts the reactivity of propene–oxygen mixtures at high pressure.

Propyne Reactions. Propyne consumption includes reactions with OH, O, and H; no reaction with HO_2 has been included.

We considered the reactions of propyne with OH proposed by Kanofsky et al.:[40]

$$\mathrm{PC_3H_4 + OH = C_3H_3 + H_2O} \qquad (228)$$

$$\mathrm{PC_3H_4 + OH = CH_2CO + CH_3} \qquad (229)$$

These authors pointed out that reaction 228 is predominant. Arrhenius parameters for this step are derived from Walker;[17] k_{229} has been estimated.

The reactions of propyne with oxygen atoms have been studied by Herbrechtsmeier,[33] Kanofsky et al.,[40] and Blumenberg et al.[21] In the present mechanism, we used the reaction of Herbrechtsmeier[33] with Arrhenius parameters determined by these authors:

$$\mathrm{PC_3H_4 + O = C_2H_2 + H_2 + CO} \qquad (230)$$

The reactions of propyne with atomic hydrogen have been studied by Wagner and Zellner:[31]

$$\mathrm{PC_3H_4 + H = TC_3H_5} \qquad (231)$$

$$\mathrm{PC_3H_4 + H = SC_3H_5} \qquad (232)$$

The Arrhenius parameters determined in ref 31 are used in the present mechanism. We also considered the isomerization reaction:

$$\mathrm{PC_3H_4 = AC_3H_4} \qquad (227)$$

with the rate constant determined by Hidaka et al.[41] at high temperature. The model predictions are insensitive to the rate constants of the reactions of propyne.

Reactions of C_3H_3 Radicals. Reactions of C_3H_3 radicals include reaction with hydrogen atoms

$$\mathrm{C_3H_3 + H = PC_3H_4} \qquad (235)$$

and with oxygen atoms

$$\mathrm{C_3H_3 + O = C_2H_3 + CO} \qquad (236)$$

with the rate constants proposed by Warnatz.[5]

We also considered the initiation step with molecular oxygen:

$$\mathrm{C_3H_3 + O_2 = CH_2CO + HCO} \qquad (237)$$

with the rate constant recently determined by Slagle and Gutman.[42] The computations are insensitive to the reactions of C_3H_3 radicals.

Reactions of C_4 Species. The rates of reactions involving C_4 species have a small effect on the model predictions, for C_3H_6 oxidation in lean mixture. Their influence increases with increasing pressure and equivalence ratio. That is the case for

$$\mathrm{1C_4H_8 = AC_3H_5 + CH_3} \qquad (270)$$

This part of the mechanism was initially taken from Pitz et al.[26]

Mechanism Evaluation

The detailed chemical kinetic reaction mechanism was tested and refined by comparison between computed results and experimental data obtained in the jet stirred reactor.

Figures 2–8 show examples of comparison between experimental data and computed composition profiles for mixtures of propene–O_2–N_2 studied between 1 and 8 atm. The composition profiles of CH_4, CO, CO_2, H_2, C_2H_4, and C_3H_6 are correctly reproduced by the computation, but as we noticed in our kinetic study on ethylene oxidation,[11] the computed acetylene concentrations are generally lower than the experimental ones, which indicates that this part of the mechanism has to be improved.

The most sensitive reactions have been reported in Table III. Among them, all the computed mole fractions of the major species were very sensitive to the rate of the reactions of hydrogen submechanism

$$\mathrm{H + O_2 = OH + O} \qquad (6)$$

$$\mathrm{H + O_2 + M = HO_2 + M} \qquad (7)$$

and to the rates of these reactions of CO submechanism

$$\mathrm{HCO + M = H + CO + M} \qquad (26)$$

$$\mathrm{HCO + O_2 = CO + HO_2} \qquad (31)$$

as already observed in our kinetic study of ethylene oxidation under similar conditions.[10,11]

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(40) Kanofsky, J. R.; Lucas, D.; Pruss, F.; Gutman, D. *J. Phys. Chem.* **1974**, *78*, 311.

(41) Hidaka, Y.; Chimori, T.; Suga, M. *Chem. Phys. Lett.* **1985**, *119*, 435.

(42) Slagle, I. R.; Gutman, D. *Twenty-First Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1986, in press.

(43) Allara, D. L.; Schaw, R. *J. Phys. Chem. Ref. Data* **1980**, *9*, 523.

(44) Cohen, N.; Westberg, K. R. *Int. J. Chem. Kinet.* **1986**, *18*, 99.

(45) Baldwin, R. R.; Bennett, J. P.; Walker, R. W. *Sixteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1977; pp 1041–1051.

(46) Ebert, K. H.; Ederer, H. J.; Isbarn, G. *Int. J. Chem. Kinet.* **1983**, *15*, 475.

(47) Hautman, D. J.; Santoro, R. J.; Dryer, F. L.; Glassman, I. *Int. J. Chem. Kinet.* **1981**, *13*, 149.

(48) Edelson, D.; Allara, D. L. *Int. J. Chem. Kinet.* **1980**, *12*, 605.

(49) Homann, K. H.; Schweinfurth, H. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 569.

(50) Warnatz, J.; Bockhorn, G.; Moser, A.; Wenz, H. W. *Nineteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1982; pp 197–209.

(51) Benson, S. W.; Haugen, G. R. *J. Phys. Chem.* **1967**, *71*, 1735.

(52) Tanzawa, T.; Gardiner, W. C., Jr. *Combust. Flame* **1980**, *39*, 241.

(53) Tanzawa, T.; Gardiner, W. C., Jr. *Seventeenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1979; pp 563–573.

(54) Huie, R. E.; Herron, J. T. *Prog. React. Kinet.* **1975**, *8*, 1.

(55) Kiefer, J. H.; Budach, K. A. *Int. J. Chem. Kinet.* **1984**, *16*, 679.

TABLE III: The Chemical Kinetic Reaction Mechanism[a]

no.	chemical reaction	A^b	b	E	ref[c]	sensitivity[d]		
1	$H + H + M = H_2 + M$	7.310E+017	-1.0	0.00				
2	$O + O + M = O_2 + M$	1.140E+017	-1.0	0.00				
3	$O + H + M = OH + M$	6.200E+016	-0.6	0.00				
4	$H_2 + O_2 = OH + OH$	1.700E+013	0.0	47.78				P
5	$O + H_2 = OH + H$	1.500E+007	2.0	7.55				
6	$H + O_2 = OH + O$	1.200E+017	-0.91	16.52		E	p	P
7	$H + O_2 + M = HO_2 + M$	8.000E+017	-0.8	0.00		E	p	P
8	$H + O_2 + O_2 = HO_2 + O_2$	6.700E+019	-1.42	0.00				
9	$H + OH + M = H_2O + M$	8.615E+021	-2.0	0.00				
10	$H_2 + OH = H_2O + H$	1.000E+008	1.6	3.30				P
11	$H_2O + O = OH + OH$	1.500E+010	1.14	17.26				
12	$HO_2 + OH = H_2O + O_2$	5.000E+013	0.0	1.00		E	p	P
13	$HO_2 + O = OH + O_2$	2.000E+013	0.0	0.00				
14	$H + HO_2 = H_2 + O_2$	2.500E+013	0.0	0.69		E		P
15	$H + HO_2 = OH + OH$	1.500E+014	0.0	1.00				
16[e]	$HO_2 + HO_2 = H_2O_2 + O_2$	2.800E+012	0.0	0.00		E	p	P
17	$H_2O_2 + M = OH + OH + M$	1.300E+017	0.0	45.41		E	p	P
18	$H_2O_2 + OH = HO_2 + H_2O$	7.000E+012	0.0	1.43		E		
19	$H_2O_2 + H = H_2O + OH$	1.000E+013	0.0	3.59				
20	$H_2O_2 + H = HO_2 + H_2$	1.700E+012	0.0	3.75				
21	$H_2O_2 + O = HO_2 + OH$	2.800E+013	0.0	6.40				
22[e]	$CO + HO_2 = CO_2 + OH$	4.570E+014	0.0	25.24		E	p	P
23	$CO + OH = CO_2 + H$	4.400E+006	1.5	-0.74		E	p	P
24	$CO + O + M = CO_2 + M$	2.830E+013	0.0	-4.54				
25	$CO + O_2 = CO_2 + O$	2.530E+012	0.0	47.70				
26	$HCO + M = H + CO + M$	2.860E+014	0.0	16.80		E	p	P
27	$HCO + OH = CO + H_2O$	5.000E+013	0.0	0.00				
28	$HCO + O = CO + OH$	3.000E+013	0.0	0.00				
29	$HCO + O = CO_2 + H$	3.000E+013	0.0	0.00				
30	$HCO + H = CO + H_2$	7.224E+013	0.0	0.00				
31[e]	$HCO + O_2 = CO + HO_2$	3.313E+013	-0.34	0.00		E	p	P
32	$HCO + CH_3 = CO + CH_4$	3.000E+011	0.5	0.00				
33[e]	$CH_4 = CH_3 + H$	1.000E+015	0.0	100.38		E	p	P
34	$CH_4 + HO_2 = CH_3 + H_2O_2$	4.000E+012	0.0	19.36				
35	$CH_4 + OH = CH_3 + H_2O$	1.090E+005	2.4	2.11				P
36[e]	$CH_4 + O = CH_3 + OH$	1.400E+007	2.1	7.62				
37[e]	$CH_4 + H = CH_3 + H_2$	2.600E+004	3.0	8.75				P
38	$CH_4 + CH_2 = CH_3 + CH_3$	6.000E+014	0.0	14.00				
39	$CH_3 + M = CH_2 + H + M$	1.900E+016	0.0	91.60				
40[e]	$CH_3 + HO_2 = CH_3O + OH$	3.000E+013	0.0	1.08		E	p	P
41	$CH_3 + HO_2 = CH_4 + O_2$	1.000E+012	0.0	0.40		E	p	P
42	$CH_3 + OH = CH_2O + H_2$	4.000E+012	0.0	0.00				
43	$CH_3 + OH = CH_3O + H$	9.000E+014	0.0	15.40		E	p	P
44	$CH_3 + OH = CH_2 + H_2O$	3.000E+013	0.0	3.00				
45	$CH_3 + O = CH_2O + H$	6.000E+013	0.0	0.00				
46	$CH_3 + O = CH_2 + OH$	5.000E+013	0.0	12.00				
47	$CH_3 + H = CH_2 + H_2$	7.000E+013	0.0	15.10				
48	$CH_3 + O_2 = CH_3O + O$	2.239E+014	0.0	33.70				
49	$CH_3 + CH_3 = C_2H_5 + H$	8.000E+013	0.0	26.53				
50	$CH_3 + CH_3 = C_2H_4 + H_2$	2.100E+014	0.0	19.20				
51[e]	$C_2H_6 = CH_3 + CH_3$	1.400E+016	0.0	87.48		E	p	P
52	$CH_2 + OH = CH + H_2O$	4.000E+013	0.0	0.00				
53	$CH_2 + OH = CH_2O + H$	2.000E+013	0.0	0.00				
54	$CH_2 + O = CO + H + H$	3.000E+013	0.0	0.00				
55	$CH_2 + O = CO + H_2$	5.000E+013	0.0	0.00				
56	$CH_2 + O = CH + OH$	5.000E+013	0.7	12.00				
57	$CH_2 + O = HCO + H$	5.000E+013	0.0	0.00				
58	$CH_2 + H = CH + H_2$	4.000E+013	0.0	0.00				
59	$CH_2 + O_2 = HCO + OH$	4.300E+010	0.0	-0.50				
60	$CH_2 + O_2 = CO_2 + H_2$	6.900E+011	0.0	0.50				
61	$CH_2 + O_2 = CO_2 + H + H$	1.600E+012	0.0	1.00				
62	$CH_2 + O_2 = CO + H_2O$	1.870E+010	0.0	-1.00				
63	$CH_2 + O_2 = CO + OH + H$	8.640E+010	0.0	-0.50				
64	$CH_2 + O_2 = CH_2O + O$	5.000E+013	0.0	9.00				
65	$CH_2 + CO_2 = CH_2O + CO$	1.100E+011	0.0	1.00				
66	$CH_2 + CH_2 = C_2H_2 + H_2$	3.200E+013	0.0	0.00				
67	$CH_2 + CH_3 = C_2H_4 + H$	4.000E+013	0.0	0.00				
68	$CH_2 + CH = C_2H_2 + H$	4.000E+013	0.0	0.00				
69	$CH + OH = HCO + H$	3.000E+013	0.0	0.00				
70	$CH + O = CO + H$	4.000E+013	0.0	0.00				
71	$CH + O_2 = HCO + O$	3.300E+013	0.0	0.00				
72	$CH + O_2 = CO + OH$	2.000E+013	0.0	0.00				
73	$CH + CO_2 = HCO + CO$	3.400E+012	0.0	0.69				
74	$CH + CH_4 = C_2H_4 + H$	6.000E+013	0.0	0.00				
75	$CH + CH_3 = C_2H_3 + H$	3.000E+013	0.0	0.00				
76[e]	$CH_3O + M = CH_2O + H + M$	1.800E+014	0.0	25.10				

TABLE III (Continued)

no.	chemical reaction	*A*[b]	*b*	*E*	ref[c]	sensitivity[d]		
77	$CH_3O + OH = CH_2O + H_2O$	1.000E+013	0.0	0.00				
78	$CH_3O + O = CH_2O + OH$	1.000E+013	0.0	0.00				
79	$CH_3O + H = CH_2O + H_2$	2.000E+013	0.0	0.00				
80[e]	$CH_3O + O_2 = CH_2O + HO_2$	1.500E+013	0.0	7.17			p	P
81	$CH_3O + CH_2O = CH_3OH + HCO$	1.150E+011	0.0	1.28				
82	$CH_3O + CH_4 = CH_3OH + CH_3$	1.995E+011	0.0	7.00				
83	$CH_2O + M = HCO + H + M$	5.720E+016	0.0	76.48				
84[e]	$CH_2O + HO_2 = HCO + H_2O_2$	1.000E+012	0.0	9.60		E	p	P
85[e]	$CH_2O + OH = HCO + H_2O$	7.000E+013	0.0	1.25		E	p	P
86	$CH_2O + O = HCO + OH$	3.500E+013	0.0	3.51				
87	$CH_2O + H = HCO + H_2$	2.500E+013	0.0	3.99		E	p	P
88	$CH_2O + O_2 = HCO + HO_2$	2.040E+013	0.0	39.00			p	
89	$CH_2O + CH_3 = HCO + CH_4$	1.000E+011	0.0	6.10				
90	$C_2H_6 + HO_2 = C_2H_5 + H_2O_2$	1.690E+013	0.0	20.46				
91	$C_2H_6 + OH = C_2H_5 + H_2O$	5.125E+005	2.06	0.86				
92[e]	$C_2H_6 + O = C_2H_5 + OH$	4.400E+007	2.02	5.12				
93	$C_2H_6 + H = C_2H_5 + H_2$	5.400E+002	3.5	5.21		E	p	P
94	$C_2H_6 + O_2 = C_2H_5 + HO_2$	1.000E+013	0.0	51.00				
95	$C_2H_6 + CH_3O = C_2H_5 + CH_3OH$	3.020E+011	0.0	7.00				
96	$C_2H_6 + CH_3 = C_2H_5 + CH_4$	5.500E-001	4.0	8.29			p	
97	$C_2H_5 + O = CH_3CHO + H$	5.000E+013	0.0	0.00				
98	$C_2H_5 + H = C_2H_4 + H_2$	1.250E+014	0.0	8.00				
99	$C_2H_5 + O_2 = C_2H_4 + HO_2$	1.580E+010	0.0	-1.90		E	p	P
100	$C_2H_5 + C_2H_5 = C_2H_4 + C_2H_6$	1.400E+012	0.0	0.00				
101	$C_2H_4 + M = C_2H_2 + H_2 + M$	3.000E+017	0.0	79.35				
102	$C_2H_4 + M = C_2H_3 + H + M$	2.970E+017	0.0	96.56				
103	$C_2H_4 + HO_2 = C_2H_4O + OH$	1.000E+013	0.0	18.28		E	p	P
104	$C_2H_4 + OH = C_2H_3 + H_2O$	4.900E+012	0.0	1.23		E	p	P
105[e]	$C_2H_4 + OH = CH_2O + CH_3$	1.500E+012	0.0	0.96		E	p	P
106[e]	$C_2H_4 + O = CH_2O + CH_2$	4.000E+013	0.0	5.00		E	p	P
107[e]	$C_2H_4 + O = CH_3 + HCO$	2.200E+009	1.2	0.74		E	p	P
108[e]	$C_2H_4 + H = C_2H_3 + H_2$	4.000E+006	2.0	6.00		E	p	P
109	$C_2H_5 + M = C_2H_4 + H + M$	2.000E+015	0.0	30.12		E	p	P
110	$C_2H_4 + O_2 = C_2H_3 + HO_2$	4.000E+013	0.0	61.50				
111	$C_2H_4 + C_2H_4 = C_2H_5 + C_2H_3$	5.000E+014	0.0	64.70				
112[e]	$C_2H_4 + CH_3 = C_2H_3 + CH_4$	5.600E+011	0.0	11.11		E	p	
113	$C_2H_4O = CH_4 + CO$	2.000E+014	0.0	58.00		E		
114[e]	$C_2H_3 = C_2H_2 + H$	2.200E+014	0.0	38.00				
115	$C_2H_3 + OH = C_2H_2 + H_2O$	5.000E+012	0.0	0.00				
116	$C_2H_3 + O = CH_2CO + H$	3.300E+013	0.0	0.00				
117[e]	$C_2H_3 + H = C_2H_2 + H_2$	2.500E+013	0.0	0.00				
118[e]	$C_2H_3 + O_2 = CH_2O + HCO$	3.200E+012	0.0	-0.35		E	p	P
119	$C_2H_3 + C_2H_6 = C_2H_4 + C_2H_5$	1.500E+013	0.0	10.00		E	p	P
120	$C_2H_2 + M = C_2H + H + M$	4.570E+016	0.0	106.84				
121	$C_2H_2 + OH = C_2H + H_2O$	1.000E+013	0.0	7.00				
122	$C_2H_2 + OH = CH_2CO + H$	3.200E+010	0.0	0.20				
123	$C_2H_2 + H = C_2H + H_2$	6.000E+013	0.0	23.66				
124	$C_2H_2 + O = CH_2 + CO$	4.100E+008	1.5	1.70				
125	$C_2H_2 + O = C_2H + OH$	3.200E+015	-0.6	15.00				
126	$C_2H_2 + O = HCCO + H$	4.300E+014	0.0	12.12				
127	$C_2H_2 + O_2 = HCCO + OH$	2.000E+008	1.5	30.10			p	
128	$C_2H_2 + O_2 = HCO + HCO$	4.000E+012	0.0	28.00			p	
129	$C_2H + OH = HCCO + H$	2.000E+013	0.0	0.00				
130	$C_2H + O = CO + CH$	1.000E+013	0.0	0.00				
131	$C_2H + O_2 = HCCO + O$	5.000E+013	0.0	1.50				
132	$C_2H + O_2 = HCO + CO$	5.000E+013	0.0	1.51				
133	$CH_2CO + M = CH_2 + CO + M$	4.110E+015	0.0	59.27				
134	$CH_2CO + OH = CH_2O + HCO$	1.000E+013	0.0	0.00				
135	$CH_2CO + O = HCO + HCO$	2.000E+013	0.0	2.30				
136	$CH_2CO + O = CH_2O + CO$	2.000E+013	0.0	0.00				
137	$CH_2CO + H = CH_3 + CO$	7.000E+012	0.0	3.01				
138	$HCCO + OH = HCO + CO + H$	1.000E+013	0.0	0.00				
139	$HCCO + O = CO + CO + H$	1.930E+014	0.0	0.59				
140	$HCCO + H = CH_2 + CO$	3.000E+013	0.0	0.00				
141	$HCCO + O_2 = CO + CO + OH$	1.460E+012	0.0	2.50				
142	$HCCO + CH_2 = C_2H + CH_2O$	1.000E+013	0.0	2.00				
143	$HCCO + CH_2 = C_2H_3 + CO$	3.000E+013	0.0	0.00				
144	$CH_3OH = CH_3 + OH$	6.000E+016	0.0	91.06		E		P
145	$CH_3OH + HO_2 = CH_2OH + H_2O_2$	6.300E+012	0.0	19.36				
146	$CH_3OH + OH = CH_2OH + H_2O$	1.000E+013	0.0	1.70				
147	$CH_3OH + O = CH_2OH + OH$	1.000E+013	0.0	4.69				
148	$CH_3OH + H = CH_2OH + H_2$	4.000E+013	0.0	6.10				
149	$CH_3OH + CH_2O = CH_3O + CH_3O$	1.549E+012	0.0	79.57				
150	$CH_3OH + CH_3 = CH_2OH + CH_4$	1.820E+011	0.0	9.80				
151	$CH_2OH + M = CH_2O + H + M$	1.000E+014	0.0	25.10				
152	$CH_2OH + H = CH_2O + H_2$	3.000E+013	0.0	0.00				

TABLE III (Continued)

no.	chemical reaction	A[b]	b	E	ref[c]	sensitivity[d]	
153	$CH_2OH + O_2 = CH_2O + HO_2$	1.000E+013	0.0	7.17			
154	$CH_3CHO = CH_3 + HCO$	2.000E+015	0.0	79.11			
155	$CH_3CHO + HO_2 = CH_3 + CO + H_2O_2$	1.700E+012	0.0	10.70			
156	$CH_3CHO + OH = CH_3 + CO + H_2O$	1.000E+013	0.0	0.00			
157	$CH_3CHO + O = CH_3 + CO + OH$	5.000E+012	0.0	1.79			
158	$CH_3CHO + H = CH_3 + CO + H_2$	4.000E+013	0.0	4.21			
159	$CH_3CHO + O_2 = CH_3 + CO + HO_2$	2.000E+013	0.5	42.20			
160	$CH_3CHO + CH_3 = CH_3 + CO + CH_4$	8.500E+011	0.0	6.00			
161	$C_3H_8 = C_2H_5 + CH_3$	7.940E+016	0.0	85.10	43	p	P
162[e]	$C_3H_8 + HO_2 = NC_3H_7 + H_2O_2$	4.500E+011	0.0	14.90	see ref 17	p	P
163[e]	$C_3H_8 + HO_2 = IC_3H_7 + H_2O_2$	2.000E+011	0.0	12.50	see ref 17	p	P
164	$C_3H_8 + OH = NC_3H_7 + H_2O$	4.710E+005	2.366	0.39	12	p	P
165	$C_3H_8 + OH = IC_3H_7 + H_2O$	3.580E+002	3.231	−1.60	12		P
166	$C_3H_8 + O = NC_3H_7 + OH$	3.715E+006	2.4	1.39	44		
167	$C_3H_8 + O = IC_3H_7 + OH$	5.495E+005	2.5	0.79	44		
168	$C_3H_8 + H = NC_3H_7 + H_2$	1.350E+014	0.0	9.68	45	p	P
169[e]	$C_3H_8 + H = IC_3H_7 + H_2$	2.000E+014	0.0	8.30	12	p	P
170[e]	$C_3H_8 + O_2 = NC_3H_7 + HO_2$	4.000E+013	0.0	47.50	17		
171	$C_3H_8 + O_2 = IC_3H_7 + HO_2$	4.000E+013	0.0	47.50	17		
172	$C_3H_8 + IC_3H_7 = NC_3H_7 + C_3H_8$	1.000E+011	0.0	12.90	43		
173	$C_3H_8 + AC_3H_5 = NC_3H_7 + C_3H_6$	7.940E+011	0.0	20.50	43		
174	$C_3H_8 + AC_3H_5 = IC_3H_7 + C_3H_6$	7.940E+011	0.0	16.20	46	p	
175	$C_3H_8 + C_2H_5 = NC_3H_7 + C_2H_6$	3.160E+011	0.0	12.30	43		
176	$C_3H_8 + C_2H_5 = IC_3H_7 + C_2H_6$	5.010E+010	0.0	10.40	43		
177	$C_3H_8 + C_2H_3 = NC_3H_7 + C_2H_4$	1.000E+011	0.0	10.40	47		
178	$C_3H_8 + C_2H_3 = IC_3H_7 + C_2H_4$	1.000E+011	0.0	10.40	47		
179	$C_3H_8 + CH_3O = NC_3H_7 + CH_3OH$	3.180E+011	0.0	7.05	17		
180	$C_3H_8 + CH_3O = IC_3H_7 + CH_3OH$	7.200E+010	0.0	4.47	17		
181[e]	$C_3H_8 + CH_3 = NC_3H_7 + CH_4$	3.000E+012	0.0	11.71	12	p	P
182	$C_3H_8 + CH_3 = IC_3H_7 + CH_4$	8.070E+011	0.0	10.11	17		
183	$NC_3H_7 = C_2H_4 + CH_3$	3.000E+014	0.0	33.22	24		
184	$NC_3H_7 = C_3H_6 + H$	1.000E+014	0.0	37.28	24	p	P
185	$NC_3H_7 + O_2 = C_3H_6 + HO_2$	1.000E+012	0.0	5.00	24		
186	$IC_3H_7 = C_2H_4 + CH_3$	1.000E+014	0.0	45.00	17		P
187[e]	$C_3H_6 + H = IC_3H_7$	3.000E+012	0.0	0.96	24		P
188	$IC_3H_7 + O_2 = C_3H_6 + HO_2$	3.000E+012	0.0	3.00	12	p	P
189	$C_3H_6 = AC_3H_5 + H$	1.000E+015	0.0	88.04	15		
190[e]	$C_3H_6 = SC_3H_5 + H$	3.333E+014	0.0	88.04	this work		
191[e]	$C_3H_6 = C_2H_3 + CH_3$	7.000E+015	0.0	85.80	this work	p	
192[e]	$C_3H_6 + HO_2 = C_3H_6O + OH$	1.050E+012	0.0	14.19	2		P
193[e]	$C_3H_6 + HO_2 = AC_3H_5 + H_2O_2$	1.500E+011	0.0	14.19	2		
194[e]	$C_3H_6 + HO_2 = SC_3H_5 + H_2O_2$	7.500E+009	0.0	12.57	17		
195[e]	$C_3H_6 + HO_2 = TC_3H_5 + H_2O_2$	3.000E+009	0.0	9.93	17		
196[e]	$C_3H_6 + OH = AC_3H_5 + H_2O$	1.150E+013	0.0	0.60	2	p	P
197	$C_3H_6 + OH = SC_3H_5 + H_2O$	9.000E+013	0.0	6.45	2	p	P
198	$C_3H_6 + OH = C_2H_5 + CH_2O$	1.000E+013	0.0	0.00	2	p	P
199[e]	$C_3H_6 + OH + O_2 = CH_3CHO + CH_2O + OH$	3.000E+010	0.0	−8.23	2		
200[e]	$C_3H_6 + O = C_2H_5 + HCO$	6.833E+004	2.56	−1.13	this work	p	P
201[e]	$C_3H_6 + O = C_2H_4 + CH_2O$	6.833E+004	2.56	−1.13	this work	p	P
202[e]	$C_3H_6 + O = CH_3 + CH_3 + CO$	6.833E+004	2.56	−1.13	this work		P
203	$C_3H_6 + H = AC_3H_5 + H_2$	2.500E+012	0.0	1.10	15	p	P
204[e]	$C_3H_6 + O_2 = SC_3H_5 + HO_2$	4.000E+013	0.0	47.56	this work		
205[e]	$C_3H_6 + O_2 = TC_3H_5 + HO_2$	4.000E+013	0.0	44.00	this work	p	
206[e]	$C_3H_6 + O_2 = AC_3H_5 + HO_2$	4.000E+013	0.0	50.90	this work		
207	$C_3H_6 + C_2H_5 = AC_3H_5 + C_2H_6$	1.000E+011	0.0	9.80	48		
208	$C_3H_6 + CH_3 = AC_3H_5 + CH_4$	1.400E+011	0.0	8.80	43	p	
209[e]	$C_3H_6 + CH_3 = SC_3H_5 + CH_4$	6.600E+011	0.0	10.11	17	p	
210[e]	$C_3H_6 + CH_3 = TC_3H_5 + CH_4$	2.400E+011	0.0	8.03	17		
211[e]	$C_3H_6O = C_2H_6 + CO$	1.260E+014	0.0	58.00	23		
212	$SC_3H_5 = C_2H_2 + CH_3$	3.000E+010	0.0	36.20	29		
213[e]	$SC_3H_5 + O_2 = CH_3CHO + HCO$	3.000E+012	0.0	−0.25	this work	p	
214[e]	$SC_3H_5 + O_2 = CH_3 + CO + CH_2O$	2.000E+012	0.0	−0.25	this work	p	
215	$AC_3H_5 = AC_3H_4 + H$	8.910E+012	0.0	59.00	30	p	P
216[e]	$AC_3H_5 + H = AC_3H_4 + H_2$	3.333E+012	0.0	0.00	this work	p	P
217[e]	$AC_3H_5 + CH_3 = AC_3H_4 + CH_4$	5.000E+011	0.0	0.00	this work	p	P
218[e]	$AC_3H_5 + O_2 + O_2 \rightarrow COOH + CH_2O + CH_2O$	1.500E+013	0.0	−0.25	this work	p	P
219[e]	$TC_3H_5 + O_2 = CH_3 + CO + CH_2O$	3.200E+012	0.0	−0.25	this work		
220[e]	$AC_3H_4 + HO_2 = C_2H_4 + CO + OH$	1.000E+012	0.0	14.00	this work		
221[e]	$AC_3H_4 + HO_2 = C_3H_3 + H_2O_2$	3.000E+013	0.0	14.00	this work	p	P
222[e]	$AC_3H_4 + OH = CH_2CO + CH_3$	2.000E+012	0.0	0.86	this work		
223[e]	$AC_3H_4 + OH = C_2H_4 + HCO$	1.000E+012	0.0	0.90	this work		
224	$AC_3H_4 + O = CO + C_2H_4$	7.800E+012	0.0	1.60	33, 34		
225	$AC_3H_4 + H = TC_3H_5$	8.500E+012	0.0	2.00	36		
226	$AC_3H_4 + H = SC_3H_5$	4.000E+012	0.0	2.70	36		
227	$PC_3H_4 = AC_3H_4$	7.760E+011	0.0	55.70	41		
228	$PC_3H_4 + OH = C_3H_3 + H_2O$	1.845E+012	0.0	1.65	this work		

TABLE III (Continued)

no.	chemical reaction	A^b	b	E	ref^c	sensitivity^d	
229	$PC_3H_4 + OH = CH_2CO + CH_3$	4.500E+011	0.0	0.00	this work		
230	$PC_3H_4 + O = C_2H_2 + H_2 + CO$	1.600E+013	0.0	2.01	33		
231	$PC_3H_4 + H = TC_3H_5$	6.630E+012	0.0	2.00	31		
232	$PC_3H_4 + H = SC_3H_5$	5.780E+012	0.0	3.10	31		
233	$C_2H_2 + CH_2 = C_3H_3 + H$	1.800E+012	0.0	0.00	49		
234	$C_2H_2 + CH = C_3H_3$	3.000E+013	0.0	0.00	49		
235	$C_3H_3 + H = PC_3H_4$	2.000E+013	0.0	0.00	50		
236	$C_3H_3 + O = C_2H_3 + CO$	3.800E+013	0.0	0.00	50		
237	$C_3H_3 + O_2 = CH_2CO + HCO$	3.010E+010	0.0	2.87	42		
238	$C_2H_3 + C_2H_4 = C_4H_6 + H$	1.000E+012	0.0	7.30	51		
239	$C_2H_2 + C_2H_2 = C_4H_3 + H$	2.000E+012	0.0	45.90	52		
240	$C_2H_2 + C_2H = C_4H_2 + H$	3.500E+013	0.0	0.00	24		
241	$C_4H_3 + M = C_4H_2 + H + M$	1.000E+016	0.0	59.70	53		
242	$C_4H_2 + M = C_4H + H + M$	3.500E+017	0.0	80.00	53		
243	$C_4H_7 = C_4H_6 + H$	1.200E+014	0.0	49.30	43		
244	$C_4H_7 = C_2H_4 + C_2H_3$	1.000E+012	0.0	28.00	29		
245	$C_4H_7 + H = C_4H_6 + H_2$	3.160E+013	0.0	0.00	27		
246	$C_4H_7 + O_2 = C_4H_6 + HO_2$	1.000E+011	0.0	0.00	27		
247	$C_4H_7 + C_2H_3 = C_4H_6 + C_2H_4$	4.000E+012	0.0	0.00	27		
248	$C_4H_7 + C_2H_5 = C_4H_6 + C_2H_6$	4.000E+012	0.0	0.00	27		
249	$C_4H_7 + C_2H_5 = 1C_4H_8 + C_2H_4$	5.000E+011	0.0	0.00	27		
250	$C_4H_7 + C_2H_5 = 2C_4H_8 + C_2H_4$	5.000E+011	0.0	0.00	27		
251	$C_4H_6 = C_2H_3 + C_2H_3$	3.981E+019	-1.0	98.15	27		
252	$C_4H_6 + OH = C_2H_5 + CH_2CO$	1.000E+012	0.0	0.00	27		
253	$C_4H_6 + OH = SC_3H_5 + CH_2O$	1.000E+012	0.0	0.00	27		
254	$C_4H_6 + OH = CH_3CHO + C_2H_3$	1.000E+012	0.0	0.00	27		
255	$C_4H_6 + O = C_2H_4 + CH_2CO$	1.000E+012	0.0	0.00	27		
256	$C_4H_6 + O = PC_3H_4 + CH_2O$	1.000E+012	0.0	0.00	27		
257	$1C_4H_8 = C_4H_7 + H$	4.078E+018	-1.0	97.35	27		
258	$2C_4H_8 = C_4H_7 + H$	4.074E+018	-1.0	97.35	27	p	
259	$1C_4H_8 + H = C_4H_7 + H_2$	1.000E+014	0.0	3.90	43		
260	$2C_4H_8 + H = C_4H_7 + H_2$	2.000E+014	0.0	3.50	43		
261	$1C_4H_8 + OH = C_4H_7 + H_2O$	1.410E+013	0.0	3.06	27		
262	$2C_4H_8 + OH = C_4H_7 + H_2O$	2.290E+013	0.0	3.06	27		
263	$1C_4H_8 + CH_3 = C_4H_7 + CH_4$	1.000E+011	0.0	7.30	43		
264	$2C_4H_8 + CH_3 = C_4H_7 + CH_4$	1.000E+011	0.0	8.20	29		
265	$1C_4H_8 + O = C_3H_6 + CH_2O$	5.010E+012	0.0	0.00	54		
266	$2C_4H_8 + O = IC3H7 + HCO$	6.030E+012	0.0	0.00	54		
267	$2C_4H_8 + O = CH_3CHO + C_2H_4$	1.000E+012	0.0	0.00	27		
268	$1C_4H_8 + OH = NC_3H_7 + CH_2O$	1.514E+012	0.0	0.00	27		
269	$2C_4H_8 + OH = CH_3CHO + C_2H_5$	3.020E+012	0.0	0.00	27	p	P
270^e	$1C_4H_8 = AC_3H_5 + CH_3$	1.000E+016	0.0	73.40	43		
271	$1C_4H_8 = C_2H_3 + C_2H_5$	1.000E+019	-1.0	96.77	26		
272^e	$1C_4H_8 + O = CH_3CHO + C_2H_4$	1.500E+013	0.0	0.85	26		P
273	$1C_4H_8 + O = C_2H_5 + CH_3 + CO$	1.288E+013	0.0	0.85	26		
274	$1C_4H_8 + OH = CH_3CHO + C_2H_5$	1.000E+011	0.0	0.00	26		
275	$1C_4H_8 + OH = C_2H_6 + CH_3 + CO$	1.000E+010	0.0	0.00	26		
276	$C_2H_5 + CH_3 = C_2H_4 + CH_4$	4.365E-004	5.0	8.30	55		
277	$C_2H_3 + CH_3 = C_2H_2 + CH_4$	4.365E-004	5.0	8.30	55		

[a] Reaction rates in cm^3-mol-kcal units; $k = AT^b \exp(-E/RT)$. [b] e.g., 7.310E+017 = 7.310 × 10^{17}. [c] References of reactions 1–160 are given in ref 11. [d] Sensitive reactions: E, ethylene oxidation; p, propene oxidation; P, propane oxidation. [e] Rate constant adjusted or estimated.

The general trend of this mechanism is to overpredict CH_3CHO and C_2H_6 concentrations. Acetaldehyde concentrations are very sensitive to the reactions of CH_3CHO submechanism (reactions 154–160) and to the reactions involving 2-methylvinyl radicals and particularly the steps

$$C_3H_6 + OH = SC_3H_5 + H_2O \qquad (197)$$

$$SC_3H_5 + O_2 = CH_3CHO + HCO \qquad (213)$$

$$SC_3H_5 + O_2 = CH_3 + CO + CH_2O \qquad (214)$$

$$PC_3H_4 = AC_3H_4 \qquad (227)$$

Furthermore, we noticed that the overprediction of acetaldehyde concentrations decreases with increasing pressure.

The overprediction of ethane is mainly due to the simplification of propene oxide consumption via the single reaction

$$C_3H_6O = C_2H_6 + CO \qquad (211)$$

An improvement of this part of the mechanism seems to be necessary, and an experimental study of the oxidation of allene and propyne is scheduled.

Registry No. C_3H_6, 115-07-1.