SENSITIVITY ANALYSIS IN CHEMICAL KINETICS MODELING

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Abstract

Sensitivity analysis is a strong tool to solve engineering and science problems systematically. This paper describes the general theory of sensitivity analysis and its application to hydrocarbon chemistry.

The Green function method is extensively studied and used to develop a sensitivity analysis program. In particular, the pyrolysis and oxidation of acetaldehyde as well as the oxidation of n-butane are studied in detail and the usefulness of sensitivity analysis is shown in comparison with a simplified mechanism and a full mechanism of acetaldehyde combustion. Some of elementary sensitivity coefficients and Green function coefficients are shown in conjunction with an analysis of hydrocarbon mechanism.

CONTENTS

1. Introduction

Many engineering and science problems are described by a set of differential equations of complexity. Such a complicated model can be evaluated by systematic methods; for example, sensitivity analysis, which is an effective and efficient approach to the evaluation of models. Sensitivity analysis is basically an analysis to investigate the relationship between the output and input of a model through perturbation in parameters.

Sensitivity analysis was originally applied to the control theory by Tomovic and Vukobratovic[1] and to the chemical kinetics system by Cukier et al.[2] (Fourier method). Later Dickinson and Gelinas[3] established the sensitivity analysis using a direct method. Extensive work using the Green function method has been done recently by Hwang et al.[4] and Yetter et al.[5] who gave detailed interpretations of sensitivity analysis. Besides chemistry application, sensitivity analysis has been applied to economics, population dynamics, weather forecasting, system analysis, operation research, atmospheric science, combustion physics and engineering, chemical laser studies, biological systems, energy distribution etc.

Recent progress on the development of large scale chemical kinetic mechanisms and the modeling of chemical systems using developed mechanisms is remarkable[6~7]. However, there have not been any methods to evaluate such mechanisms quantitatively until sensitivity analysis appears, so that the mechanism may not be useful. As Yetter et al.[5] quoted, the model prediction becomes valid when a quantitative measurement of sensitivity analysis to the variation of an input parameter is done; for example, adding or subtracting reactions and changing rate constants are performed for the developed mechanism. When a chemical reaction modeling is performed with a large number of reactions, the computational cost becomes considerable. Sensitivity analysis may eliminate unnecessary reactions so that the reduction of the size of mechanism provides an economical computation.

This paper summarizes a general scope of sensitivity analysis and presents the sensitivity analysis of the Green function method in an attempt to apply to the hydrocarbon chemistry with a large reaction mechanism. Chap. 2 deals with a general theory of sensitivity analysis, especially concentrating into the Green function method, which is applied presently. Chap. 3 explains a sensitivity analysis program, which is originally developed for general purposes. Pyrolysis and oxidation mechanisms of hydrocarbon are investigated using the developed sensitivity program and their results are discussed in Chap. 4.

2. Sensitivity Analysis

Sensitivity analysis is developed by Tomovic[9] for the stability control in the field of automatic control in the 1960's. This method is recently used extensively for the stability control of large scale structures and the analysis of their structural dynamic modes in space. The mathematical treatment of sensitivity analysis is classified into the following three: (1) Fourier Amplitude Sensitivity Test (*FAST*), (2) Direct Method (*DM*) and (3) Green Function Method (*GFM*), which are explained below in detail.

2. 1. Fourier Amplitude Sensitivity Test (FAST)

This method is developed and extensively applied to actual chemistry problems by Cukier et al.[2]. Although the *FAST* method is applied to the same type of problems as the other methods, it handles a nonlinear coupled differential equation system using Fourier transformations and is considered more economical in calculation than the Direct Method as the number of chemical reactions increases.

Consider a general reacting system consisting of m species and n reactions;

$$\frac{dy_i}{dt}=\sum_{r=1}^{m} \nu_{r,i}\left[k_r \prod_{l=1}^{n} y_l^{\nu'_{r,l}} - k_{-r} \prod_{l=1}^{n} y_l^{\nu''_{r,l}} \right] ; \quad i=1, \cdots n \tag{2.1}$$

where the concentrations y_i are bounded, non-negative and continuous functions of time and rate constants. In order to formulate the relation between the concentrations and rate constants, the following functions are introduced;

$$k_r = k_r^{(0)} e^{\alpha_r} \tag{2.2}$$

and

$$\alpha_r = f_r(\sin \omega_r s) ; \qquad r=1, \cdots m \tag{2.3}$$

where $k_r^{(0)}$ are the known values of rate constants, ω_r the positive integer, s the parameter, and f_r the unknown function. The k_r depends upon the value of ω_r. Hence, when the concentrations y_i are the periodic function of s with the period of 2π at time t,

$$y_i(s ; t) = y_i(s+2\pi ; t) \tag{2.4}$$

then

$$y_i(s) = \frac{A_0^{(i)}}{2} + \sum_{r=1}^{\infty} (A_r^{(i)} \sin rs + B_r^{(i)} \cos rs) \tag{2.5}$$

If we are interested only in the sine series of period 2π in the present situation, then

$$A_{\omega_l}^{(i)} = \frac{1}{\pi} \int_0^{2\pi} y_i(s) \sin \omega_l s \, ds ; \quad l=1, 2, \cdots n \tag{2.6}$$

The $A_{\omega_l}^{(i)}$ is the first order derivative, the elementary sensitivity[2];

$$A_{\omega_l}^{(i)} = \frac{2}{a_l} \left\langle \frac{\partial y_i}{\partial \alpha_l} \right\rangle \tag{2.7}$$

where

$$\langle y(\alpha_1, \cdots \alpha_n)\rangle = \frac{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\prod_{i=1}^{n} p(\alpha_i; a_i)\, y(\alpha_1, \cdots \alpha_n)\, d\alpha_i}{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\prod_{i=1}^{n} p(\alpha_i; a_i)\, d\alpha_i} \tag{2.8}$$

and the probability function is defined as

$$p(\alpha_i; a_i) = \frac{a_i}{\cosh a_i\alpha_i}. \tag{2.9}$$

The paper by Cukier et al. (1973) treats only the first order derivatives, but higher order derivatives can be explained by a more complicated way using the *FAST* method. On this account the advantage of the Green Function Method is described and its economical computation is compared with the others.

2. 2. Direct Method (DM)

The direct method (*DM*) is much simpler (in its structure) than the *FAST* method, and is applied to chemical kinetic problems by Atherton et al.[10] and Dickinson and Gelinas, following the *FAST* method. Atherton uses the statistical averaging to sensitivity variables to solve the kinetic equations. As far as Dickinson and Gelinas are concerned, the statistical averaging produces some errors. Dickinson and Gelinas applied literally the direct method using a large computer to calculate not only the first order sensitivity coefficients but also the higher-order ones to explain their importance. The computational time of *DM* is, however, longer than the others since the method calculates Jacobian implicitly. The primary purpose of their paper is to show the usefulness of linear sensitivities to other users.

The basic theory of *DM* which Dickinson and Gelinas have developed is to give the general time-dependent nonlinear ordinary differential equations;

$$\dot{y}_i = f_i(y_k, \alpha_j, t); \quad i, \ k = 1, \cdots n, \ j = 1, \cdots, m \tag{2.10}$$

and to compute the following linear sensitivity function using the solution y_i of Eq. (2.10) according to the definition of first-order sensitivity Z_{ir};

$$Z_{ir} = \frac{\partial y_i}{\partial \alpha_r} \tag{2.11}$$

The differential equation system of Z_i is solved at the same time as the above system of Eq. (2.10); that is,

$$\dot{Z}_{ir} = \frac{\partial}{\partial t}\left(\frac{\partial y_i}{\partial \alpha_r}\right) = \frac{\partial}{\partial \alpha_r}(f_i(y(\alpha_j, t), t, \alpha_j)) = \frac{\partial f_i}{\partial \alpha_r} + \sum_{k=1}^{n} \frac{\partial f_i}{\partial y_k}\frac{\partial y_k}{\partial \alpha_r} \tag{2.12}$$

where $\frac{\partial f_i}{\partial y_k}$ is the Jacobian in Eq. (2.12) as well as of the original ordinary differential equations.

2. 3. Green Function Method (GFM)

The previous two methods, *FAST* and *DM*, have their limits of applicability and are expensive in computation for a large number of system parameters. The present report is based on a modified version of the direct method, the Green function

method (GFM)[4,5], where a system is assumed to consist of a large set of first-order ordinary differential equations with a large number of parameters. The GFM approach is applied to the same differential equations under consideration and replaces them by a set of integrals as shown later. These integrals are expected to be smooth for a well-defined system, providing a considerable amount of computational savings. Furthermore all the higher order sensitivity coefficients can be expressed in terms of certain integrals. This indicates that no additional differential equations need to be solved and the integrals are obtained from previous lower order sensitivity coefficient calculations.

We consider a general first-order differential equation

$$\dot{Y}_i = f(Y_k, \alpha_j, t) \; ; \quad i, \; k = 1, 2, \cdots, n \qquad (2.13)$$

with the initial condition

$$Y_i(0) = Y_i^0 \qquad (2.14)$$

where the dot indicates differentiation with respect to t, Y_i a species concentration and the m-vector α_j denotes a set of m parameters (say, the rate coefficients). Assuming the partial derivatives of Y_i with respect to α_j ($j = 1, 2, \cdots, m$) are continuous up to the pth order, Y_i can be expressed by a Taylor series as

$$Y_i(\alpha_j + d\alpha_j, t) = Y_i(\alpha_j, t) + dY_i(t) \qquad (2.15)$$

$$= Y_i(\alpha_j, t) + \sum_{k=1}^{p-1} \frac{1}{k!} d^k Y_i(\alpha_j; \; d\alpha_j) + \frac{1}{p!} d^p Y_i(\alpha_j^*; \; d\alpha_j)$$

where

$$d^k Y_i(\alpha_j; \; d\alpha_j) = \sum_{j_1=1}^{m} \sum_{j_2=1}^{m} \cdots \sum_{j_k=1}^{m} \frac{\partial^k Y_j(\alpha_j)}{\partial \alpha_{j_1} \partial \alpha_{j_2} \cdots \partial \alpha_{j_k}} d\alpha_{j_1} d\alpha_{j_2} \cdots d\alpha_{j_k} \qquad (2.16)$$

and

$$\alpha_j^* = \alpha_j + (1 - \hat{\varsigma}) d\alpha_j \; ; \; 0 < \hat{\varsigma} < 1 \qquad (2.17)$$

The analysis of first-order sensitivity coefficients, $\partial Y_i(\alpha_j)/\partial \alpha_j$ shows the important reactions and species in the observed mechanism. Second order sensitivity coefficients give the degree of non-linearity of variations in concentrations Y_i with respect to two rate constants k_j and k_l. In addition, it shows the first derivatives of the linear coefficient $\partial Y_i/\partial k_j$ with respect to k_l; a good tool for probing the mechanistic structure.

The vector function f in Eq. (2.13) is usually nonlinear but is a linear combination of reaction rates;

$$w_i = k_j \prod_{i=1}^{n} y_i^{\nu_{it}} \; ; \; \nu_{ij} \geq 0 \quad \text{and} \quad \sum_{i=1}^{n} \nu_{ji} \leq 3 \qquad (2.18)$$

where w_i is the rate of production of species i by chemical reactions, k_j the rate constant of chemical reaction j and ν_{ji} the stoichiometric coefficient of reaction j for species i. This condition means that the collision higher than trimolecular collision is neglected. The first-order sensitivity coefficient is related, among others, with the concentration sensitivity.

The system equation (2.13) is rewritten as:

$$\dot{Z}_{ij}(t) = \sum_{k=1}^{n} J_{ik}(t) \cdot Z_{kj}(t) + F_{ij}(t) \; ; \; Y_{ij}(0) = Y_{ij}^{0} \tag{2.19}$$

where

$$Z_{ij} = \partial Y_i / \partial \alpha_j, \; J_{ik} = \partial f_i / \partial Y_k, \; F_{ij} = \partial f_i / \partial \alpha_j \; ; \; i, \; k=1, \; 2, \; \cdots n \; \text{and} \; j=1, \; 2, \; \cdots m.$$

Eqs. (2.19) are "stiff" in chemical systems. Stiffness occurs when the system has both slow and fast variables. Step size is controlled by the fast ones, while the truncation errors are controlled by the slow variables.

Several methods have been developed to solve these stiff equations (Hindmarsh and Gear[11] etc.). Such solvers invert a matrix related to the Jacobian matrix of 2nd dimensions, spending a long time in the case of many species and parameters. The *GFM* reduces the number of differential equations using a Green function matrix $K_{ij}(t,\tau)$, which is defined by replacing $F_{ij}(t)$ in Eq. (2.19) with $\delta(t-\tau)$; in other words,

$$\frac{dK_{ij}}{dt} - \sum_{k=1}^{n} J_{ik}(t) K_{kj}(t, \; \tau) = \delta(t-\tau) \tag{2.20}$$

whence

$$K_{ij}(\tau, \; \tau) = 1$$

and

$$K_{ij}(t, \; \tau) = 0 \; ; \; t < \tau. \tag{2.21}$$

The integral expression of Eq. (2.19) then becomes

$$Z_{ij}(t) - \sum_{k=1}^{n} K_{ik}(t, \; 0) \cdot Z_{kj}^{0} = \sum_{k=1}^{n} \int_{0}^{t} K_{ik}(t, \; \tau) F_{kj}(\tau) d\tau \tag{2.22}$$

The sensitivity coefficients obtained by this expression should be identical to that by the *DM*. The difference between the two approaches is the numerical methods to obtain Z_{ij}.

In order to evaluate Z_{ij}, $K_{ij}(t, \; \tau)$ has to be calculated from $t=\tau_k$ to τ_N. However it is very slow to get $K_{ij}(t, \; \tau)$ using Eq. (2.20). There is another way to obtain $K_{ij}(t, \; \tau)$, which is to solve it by splitting the interval $[\tau_N, \; 0]$ into N parts. The integration is performed within each subinterval $[\tau_{k+1}, \; \tau_k]$, yielding the following initial-value equations;

$$\frac{d}{dt}K_{ij}(t, \; \tau_k) - J_{ik}(t) \cdot K_{kj}(t, \; \tau_k) = 0 \tag{2.23}$$

and

$$K_{ij}(\tau_k, \; \tau_k) = 1 \; ; \; k=0, \; 1, \; \cdots\cdots \; N-1. \tag{2.24}$$

$K_{ij}(\tau_N, \; \tau_k)$ is calculated from $K_{ij}(\tau_{k+1}, \; \tau_k)$ using the following relation;

$$K_{ij}(\tau_N, \; \tau_k) = K_{ij}(\tau_N, \; \tau_{N-1}) \cdot K_{ij}(\tau_{N-1}, \; \tau_{N-2}) \; \cdots\cdots \; K_{ij}(\tau_{k+1}, \; \tau_k) \tag{2.25}$$

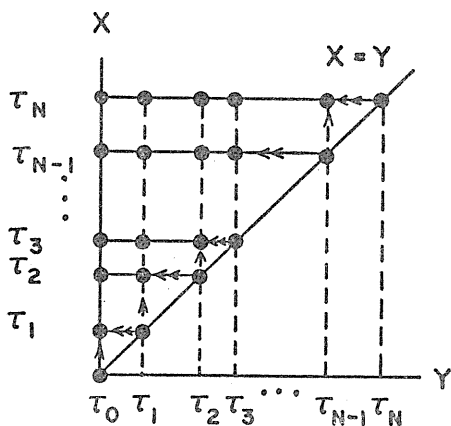The dots in Fig. 1 are the points calculated by this method.

Fig. 1. The x- and y- axis represent the two independent variables of the Green function $K(x, y)$. $K(x, y) = 1$ along the diagonal line $x=y$, and $K(x,y)=0$ for $x<y$. The single arrow indicates the first method of integration and the doubles are for the second way of integration.

Another method to evaluate $K_{ij}(\tau_N, \tau_k)$ is to solve the differential equation for the adjoint Green function

$$-\frac{d}{d\tau}K^+(\tau,\ t_l) + K^+(\tau,\ t_l) \cdot J(\tau)$$

$$=\delta(\tau-t_l) \qquad (2.26)$$

and

$$K^+(t_l,\ t_l)=1 \qquad (2.27)$$

where time is proceeded backwards from any t_l to zero. Using the relation

$$K^+(\tau,\ t)=K(t,\ \tau) \qquad (2.28)$$

the general equation (2.22) can be solved by integrating the adjoint Green function K^+ row by row as a function at a fixed value of t (the integration is performed in the direction of the double arrow in Fig. 1) rather than by evaluating the usual Green function K through the multiplication relation (2.25) (in the direction of single arrow in Fig. 1). Because Eq. (2.22) necessitates $K(t, \tau)$ to be evaluated as a continuous function of τ, the adjoint Green function method is better in computational time and accuracy than the usual Green function method. Once K^+ or K is obtained, then the first-order sensitivity coefficients are computed.

The higher order sensitivity coefficients can be evaluated from the information of one order lower values. A detailed discussion is presented elsewhere[4].

2. 3. 1. First Order Sensitivity Coefficients

The so-called elementary sensitivity in a chemical reaction system means the first order derivative when a species concentration and a system parameter relate each other as dependent and independent variables respectively. In an actual operation, a subset of concentrations is measured in experiments to determine the same number of rate constants, and then these concentrations are considered known and are treated as independent variables. Thus the same number of rate constants can be converted to dependent variables from independent variables. Hence the most appropriate rate constants to be determined are the ones showing the highest sensitivity $\partial y/\partial \alpha$. The change of variables in system parameters such as α_k to T, α_k to α_j, α_k to p, etc., provides the information on the parameter interdependence, parameter-observation interdependence, correlation between different observations, etc., according to Yetter et al.[5].

Precautions have to be paid when a mechanism is developed by interchanging dependent variables with the equal number of independent variables. The concentrations are linearly dependent from atom conservation. For example, CO and CO_2 concentrations can be obtained by two independent measurements, but these two measurements are not independent in the considered model.

Relation between Two Rate Constants

The parameter $\partial \ln k_i / \partial \ln k_j$ gives an information to the correlation among system parameters. For example, when a rate canstant k_i has a large uncertainty and is measured experimentally, another k_j has to be known if there is a high correlation between k_i and k_j, since $\partial \ln k_i / \partial \text{in} k_j$ is the sensitivity of k_i with respect to another parameter of the system k_j.

Another example explains that the obtained rate constants have to be updated everytime, and then the concentration profiles of chemical species obtained by many experiments are supposed to be modeled using a mechanism containing the rate constants k_j. If the values of k_j are updated and yet the modeling does not agree with the experiment, the coefficient $\partial \ln k_i / \partial \ln k_j$ provides the magnitude and direction of updated change in a rate constant k_i to reproduce the species concentration profiles obtained experimantally. This type of analysis suggests whether the reaction rate constants have to be investigated further.

Relation between Rates and Concentrations

The parameter-observation sensitivity $\partial \ln k_i / \partial \ln y_j$ is not the reciprocal of an elementary coefficient $\partial \ln y_i / \partial \ln k_j$, since the other concentrations are fixed when the quantity $\partial \ln k_i / \partial \ln y_j$ is calculated. $\partial \ln k_i / \partial \ln y_j$ indicates the dependency of a rate constant on the measured concentration. This type of coefficient as well as the coefficient $\partial \ln k_i / \partial \ln k_j$ is important in performing a statistical error analysis regarding a particular parameter k_i.

As an example, $\partial k_i / \partial y_j$ must be minimized when a species concentration is measured to obtain the data related to a rate constant k_i, since the uncertainties of the measured species concentration should not be transferred to the obtained rate constant k_i or magnified. Furthermore the choice of a concentration profile as rate data is made by comparing the derived coefficients $\partial k_i / \partial k_j$ and $\partial k_i / \partial y_j$.

Relation between Two Concentrations

The parameter-parameter coefficient shows the parameter interdependence, whereas the observation-observation sensitivities $\partial y_i / \partial y_j$ do the observation interdependence.

For instance, consider an already measured set of species concentrations. Which concentration has to be investigated to maximize the effect of rate constants acting as independent variables? As an example of $\partial y_i / \partial y_j$, the independence of y_j is an important information when y_i is known and y_j is being measured.

2. 3. 2. Higher Order Sensitivity Coefficients

Second order sensitivities have the same relationship to the first order sensitivities as first order sensitivities. In other words, second order sensitivities show the extent of linearity between independent and dependent variables.

$\partial (\partial \alpha_i / \partial \alpha_j) / \partial \alpha_s$ expresses how the uncertainty of a rate constant k_s influences the correlation between k_i and k_j. If this sensitivity has a large value, the sensitivity of k_i to k_j is dependent upon the value of k_s. $\partial^2 y_i / \partial \alpha_j^2$ gives the extent of non-linearity for the change of species concentration y_i with respect to the change of an input parameter α_j. This coefficient is useful to determine the range of accuracy in predicting from first order elementary sensitivity coefficients. Another understanding is that a second order sensitivity coefficient is the sensitivity

of the first order sensitivity coefficient.

2. 3. 3. Green Function Coefficients

The physical interpretation of Green function matrix $K_{ij}(t, \tau)$, which is calculated for the case of acetaldehyde oxidation, may be recognized as a memory function of the sensitivity of species i at time t with respect to species j at prior time τ. The calculated Green function coefficients show the reaction path of a complex chemical system during the entire reaction time. Yetter et al. explain that perturbations of the chemical species can be introduced at varying times and the response at later times can be studied to deduce mechanistic informations.

An example calculation is successfully performed to explain CO oxidation exactly as Yetter did.

The Green function coefficient gives a relation between two observable parameters, and hence this sensitivity can be measured in laboratory. Fig. 2 shows the perturbation of $[H_2O]$ on $[CO]$ concentration in carbon monoxide oxidation. The perturbation in $[H_2O]$ occurs along $\log \tau = \log t$ and its sensitivity shows zero at $\log t < \log \tau$. In laboratory $[H_2O]$ can be added at $t=0$, and then $[CO]$ concentration shows the response until time becomes 10 msec as shown in Fig. 2.

The sensitivity of $[OH]$ by perturbing $[H_2]$ in CO oxidation is shown in Fig. 3. The response of $[OH]$ to $[H_2]$ concentration is different from that of $[CO]$ to $[H_2O]$ concentration shown in Fig. 2. The Green function sensitivity of $[OH]$ shows a late response to $[H_2]$ perturbation until $t=10$ msec, and then $[OH]$ corresponds to $[H_2]$ variation without delay. The maximum sensitivity occurs near 10 msec.

The Green function coefficient calculation performed by our sensitivity analysis program shows the same results as Yetter et al.[5]. Thus, except for some details, our program written for a general chemical reaction mechanism shown in appendix can calculate the sensitivity and Green function coefficients properly.
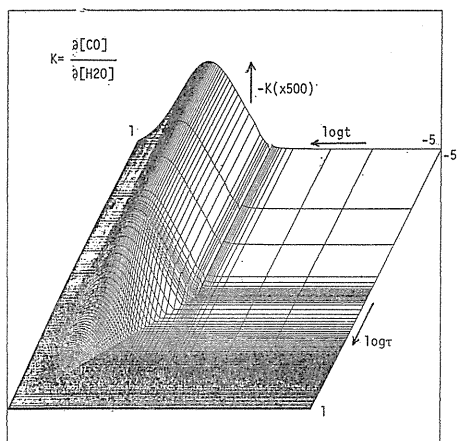

Fig. 2. Green function coefficient, $\partial [CO]/\partial [H_2O]$ versus $\log (\tau)$ and $\log (t)$ in CO oxidation.
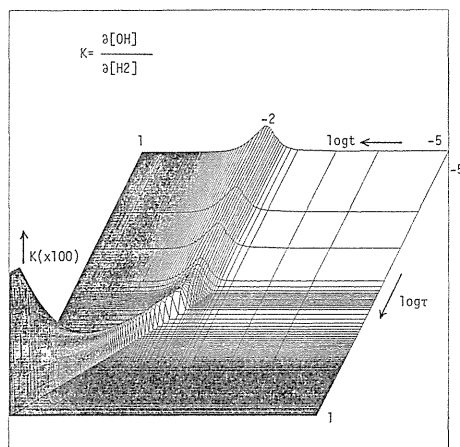
Fig. 3. Green function coefficient, $\partial [OH]/\partial [H_2]$ versus $\log (\tau)$ and $\log (t)$ in CO oxidation.

2. 4. The Comparison of Sensitivity Analyses among Three Methods; FAST, DM and GFM.

An example of the mechanism of methane oxidation (Table 1) was treated by GFM. This system has been studied by Boni and Penner [12], using FAST method, whereas Dougherty et al.[14] compared the results obtained by GFM with that by FAST at 2.3×10^{-5} sec. Dougherty et al. confirmed that their kinetics matched with that by Boni and Penner under the same initial condition, and then recognized that their GFM results were almost identical with their DM results, as expected, and were different from FAST results. They concluded that Reactions 1, 6, 10 and 18 in Table 1 were the four most dominant ones affecting all the species concentrations. Reaction 13 was important for only CO_2 while Reactions 8, 11, 16, 17, 18, 20, 21, 22 and 23 were insensitive. GFM calculations showed the improvement from DM; no overflows were detected in GFM calculations while DM showed the overflows related to Reaction 6. Dougherty et al. compared the computing time among the three methods; GFM took 24 sec for one case, DM 2.8 min and FAST 1 hour, indicating that GFM was the best to compute sensitivity coefficients.

Table 1. Methane oxidation mechanism (units in cc-mole-cal-K-sec).

No.	Reaction	A	n	Ea
1(41)	CH4+M=CH3+H+M	2.0E17	0.	88400.
2(44)	CH4+OH=CH3+H2O	6.0E14	0.	12500.
3(43)	CH4+H=CH3+H2	2.2E4	3.	8740.
4(45)	CH4+O=CH3OH	2.1E13	0.	9060.
5(51)	CH3+O=CH2O+H	1.0E14	0.	0.
6(−)	CH3+O2=CH2O+OH	2.0E10	0.	0.
7(33)	CH2O+O=HCO+H2O	5.0E13	0.	4570.
8(31)	CH2O+OH=HCO+H2O	5.4E14	0.	6300.
9(32)	CH2O+H=HCO+H2	1.4E13	0.	3750.
10(30)	CH2O+M=HCO+H+M	4.0E12	0.	36700.
11(39)	HCO+O=CO+OH	1.0E14	0.	0.
12(37)	HCO+OH=CO+H2O	1.0E14	0.	0.
13(38)	HCO+H=CO+H2	2.0E14	0.	0.
14(35)	HCO+M=CO+H+M	5.0E12	0.	19000.
15(28)	CO+OH=CO2+H	4.0E12	0.	8000.
16(3)	H2+OH=H+H2O	2.9E14	0.	11000.
17(2)	H2+O=H+OH	3.2E14	0.	15000.
18(1)	H+O2=H+OH	2.2E14	0.	16800.
19(8)	H+OH+AR=H2O+AR	8.4E21	−2.	0.
20(8')	H+OH+H2O=H2O+H2O	1.4E23	−2.	0.
21(11)	H+HO2=OH+OH	2.5E14	0.	1890.
22(9)	H+O2+M=HO2+M	1.5E15	0.	990.
23(−4)	OH+OH=O+H2O	5.5E13	0.	7000.

3. Sensitivity Analysis Program

The computational method used in this study is the Green Function Method, which is the most effective way to obtain sensitivity coefficients described in the previous chapter. The computational scheme for the present sensitivity analysis is the one developed by Kramer et al.[14].

The sensitivity program consists of four major parts (Fig. 4); (i) the initial value input which is executed by a general purpose program, *CHEMKIN*, developed by Kee et al. [15]. This code, among others, calculates sensitivity parameters; (ii) ODE-solver, originally developed by Gear[16], to calculate concentrations, (iii) the calculation of Green function and (iv) the integration of Green function.

As shown later, the shock tube data are analyzed by Shock Tube Program. The importance of this comprehensive program is that the sensitivity coefficients of a general chemical kinetics mechanism can be calculated automatically.
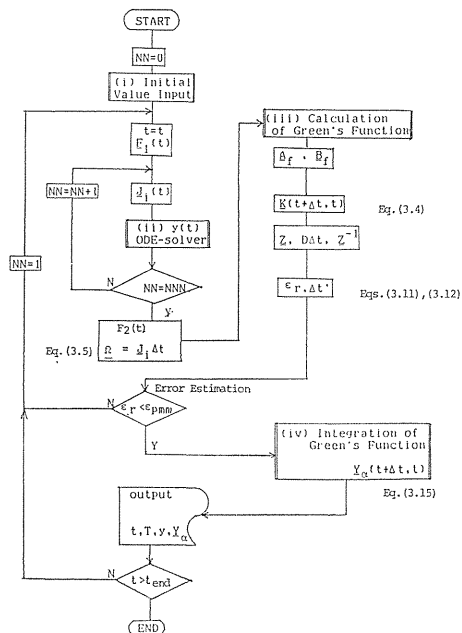

Fig. 4. Algorithm of sensitivity analysis program.

3. 1. *Calculation of Green Function K.*

The Green function K is evaluated by the following Magnus solution to Eq. (2.20);

$$K(t,\ \tau)=e^{\Omega(t,\ \tau)}K(\tau,\ \tau)=e^{\Omega(t,\ \tau)}, \tag{3.1}$$

where Ω is a matrix,

$$\Omega(t+\varDelta t,\ t)=X(D\varDelta t)X^{-1} \tag{3.2}$$

and

$$D\varDelta t=\begin{pmatrix} \lambda_1 & & 0 \\ & \cdot & \\ & & \cdot \\ 0 & & \lambda_n \end{pmatrix}. \tag{3.3}$$

Using these matrices, K can be calculated as follows:

$$K(t+\varDelta t,\ t)=e^{\Omega}=X\cdot\begin{pmatrix} e^{D_1\varDelta t} & & 0 \\ & \cdot & \\ & & \cdot \\ 0 & & e^{D_n\varDelta t} \end{pmatrix}\cdot X^{-1} \tag{3.4}$$

the procedure of which is shown in Fig. 4.

3. 2. Error Estimation

When Δt is small enough, Ω is obtained from the first approximation

$$\Omega \simeq \int_t^\tau J(t_\iota)\,dt_\iota. \tag{3.5}$$

In view of accuracy the developed program calculates the error in $K(t+\Delta t,\ t)$ and judges whether the estimated error is larger than a certain level. If the error is large, the time step is reduced to give better accuracy in K.

The crude Green function approximately satisfying Eq. (2.23) can give the error matrix E through the following equation:

$$E(t,\ \tau) = \frac{d}{dt}K(t,\ \tau) - J(t)K(t,\ \tau). \tag{3.6}$$

Hence the relative error is of the order of

$$\varepsilon_r = \frac{\|E(t,\ \tau)\|}{\|J(t)K(t,\ \tau)\|}, \tag{3.7}$$

where

$$\|A\| = \max\left(\sum_{i=1}^{n} |A_{ij}|;\ j=1,\ \cdots,\ m\right). \tag{3.8}$$

The maximum error occurs at the end of integration in Eq. (2.23), and then the error should be estimated at $(t+\Delta t,\ t)$. It is more convenient to rewrite Eq. (3.6) into the following form;

$$E(t+\Delta t,\ t) = \frac{d}{d\Delta t}K(t+\Delta t,\ t) - J(t+\Delta t)K(t+\Delta t,\ t). \tag{3.9}$$

Since K is given by Eq.(3.4),

$$E(t+\Delta t,\ t) = X\left(\frac{d}{d\Delta t}e^{D\Delta t}\right)X^{-1} - J(t+\Delta t)Xe^{D\Delta t}X^{-1}$$

$$= (\Omega(t+\Delta t)/\Delta t - J(t+\Delta t))K(t+\Delta t,\ t). \tag{3.10}$$

Hence ε_r is rewritten as

$$\varepsilon_r = \frac{\|(\Omega(t+\Delta t)/\Delta t - J(t+\Delta t))K(t+\Delta t,\ t)\|}{\|J(t+\Delta t)K(t+\Delta t,\ t)\|} \tag{3.11}$$

It depends on the relative magnitude of ε_r comparing with the error allowance ε_{pmm} whether the time step Δt should be reduced or increased;

$$(\Delta t)_{new} = \min[\Delta t(\varepsilon_{pmm}/\varepsilon_r),\ 3\Delta t]. \tag{3.12}$$

3. 3. Integration of Green Function

The integration of Green function is approximated by the linear interpolation of Eq. (2.22) in the interval between t and $t+\Delta t$;

$$Z(t+\Delta t) = \int_t^{t+\Delta t} F(\tau) K(t+\Delta t,\ \tau) d\tau + K(t+\Delta t,\ t) Z(t). \qquad (3.13)$$

Using the transformation $\tilde{\tau} = \tau - t$,

$$F(\tau) = A_f + B_f \tilde{\tau} = F(0) + \frac{F(\Delta t) - F(0)}{\Delta t} \tilde{\tau} \qquad (3.14)$$

Substituting Eq. (3.14) into Eq. (3.13)

$$Z(t+\Delta t) = \int_0^{\Delta t} (A_f + B_f \tau) X e^{D\tau} X^{-1} d\tau + X e^{D\Delta t} X^{-1} Z(t). \qquad (3.15)$$

Letting the first term of Eq. (3.15) be I_{ij} and integrating it analytically,

$$I_{ij} = \sum_{l=1}^n \left\{ \sum_{k=1}^n Z_{ik} Z_{kl} C_{jkl} \right\} \qquad (3.16)$$

where

$$C_{jkl} = \left[\left(A_{lj} - \frac{B_{lj}}{D_k} + B\Delta t \right) \exp(D_k \Delta t) - \left(A_{lj} - \frac{B_{lj}}{D_k} \right) \right] / D_k \qquad (3.17)$$

for $D_k \neq 0$, and

$$C_{jkl} = A_{lj} \Delta t + \frac{1}{2} B_{lj} \Delta t^2 \qquad (3.18)$$

for $D_k = 0$. Eq. (3.16) is the result of integrating the Green function.

3. 4. Preliminary Calculation Using a Developed Program

The accuracy of calculation using the newly developed sensitivity program is studied in view of the results of methane oxidation (Dougherty et al.[13]) and carbon monoxide oxidation (Yetter et al.[5]). The same results are expected when compared with that by Yetter et al., since the computing technique is identical. The present method calculates the Green function by integrating Eq. (2.23), whereas the method of Dougherty et al. treats it differently.

3. 4. 1. Methane Oxidation

In order to examine a new sensitivity analysis program, a methane oxidation mechanism in Table 1, which is the same as that used by Dougherty et al., is explored to perform a sensitivity analysis and to compare with their results. The

Table 2.   Initial conditions of methane oxidation.

	This study	Dougherty et al.
Temperature (K)	2001	2000
Pressure (atm)	4.75	1.00
Mole fraction CH_4	0.01	0.092
O_2	0.02	0.183
Ar	0.97	0.725

initial conditions of the present study and of Dougherty et al. are listed in Table 2, where their initial pressure and concentrations are somewhat different from ours.

The non-dimensional sensitivity coefficients in both cases, defined by

$$\frac{k_j}{y_i}\left(\frac{\partial y_i}{\partial k_j}\right) = \frac{\partial l_n y_i}{\partial l_n k_j}, \tag{3.19}$$

are compared in Table 3. The number of each species in Table 3 is Reaction Number and is listed in the order of sensitiveness. The upper and lower lines are the results of the present study and Dougherty et al., respectively.

The results show that Reaction 14 (or Reaction 33 in Appendix) using our model is the most sensitive unlike in the model of Dougherty et al..

Table 3. Sensitivity analysis of methane oxidation.

Species	Most sensitive rate constants									
	1	2	3	4	5	6	7	8	9	10
1 CH_4	18	14	3	2	1	8	13	5	6	10
	1	6	18	14	10	3	13	4	8	2
2 CH_3	14	18	3	1	2	8	5	6	13	10
	1	6	14	5	8	2	13	4	18	10
3 H	1	18	3	14	2	13	10	6	8	17
	1	6	14	10	18	13	3	12	8	4
4 OH	18	1	2	8	3	13	6	5	16	17
	1	18	6	14	2	8	10	13	5	7
5 H_2O	14	18	1	2	8	10	3	6	13	16
	1	6	18	3	10	14	4	5	13	7
6 H_2	14	1	3	10	13	8	18	2	16	11
	1	6	14	10	8	18	2	5	13	12
7 CO	1	14	18	10	3	2	13	8	6	5
	1	6	18	8	10	14	3	2	5	13
8 O	18	1	5	3	2	13	8	6	10	14
	18	1	6	5	14	10	8	3	4	2
9 CO_2	14	1	10	18	2	5	13	6	22	16
	1	6	18	15	2	10	14	3	8	5
10 O_2	1	3	2	5	13	8	18	10	17	14
	1	6	18	10	3	14	13	4	5	12
11 CH_2O	14	18	2	8	3	17	5	6	16	10
	6	8	1	2	5	18	7	14	10	13
12 CHO	8	18	13	5	14	1	10	17	2	12
	6	1	18	14	13	8	10	12	3	4
13 HO_2	14	10	1	18	3	21	5	13	22	2
	1	6	14	22	10	21	13	3	18	8

For each species, the upper and the lower lines give the ten most sensitive reactions according to this study and Dougherty, respectively.

3. 4. 2. Carbon Monoxide Oxidation

The sensitivity analysis is performed for carbon monoxide oxidation under the same initial conditions as that of Yetter et al.[5] for the purpose of comparison. In spite of the same initial conditions, both results show that the qualitative behaviors of normal sensitivity coefficients are alike each other, while their quantitative value $\partial \ln y_1 / \partial \ln k_3$ of Yetter et al. is three times as large as ours. This difference comes not only from the difference in the Green function integration but also from the concentration calculation, since our backward rates are obtained from equilibrium constants whereas Yetter et al. use independent backward rates.

4. Detailed Hydrocarbon Combustion Mechanism (up to C4)

This chapter deals with the application of sensitivity analysis to the hydrocarbon combustion and the discussion on the hydrocarbon combustion mechanism. The pyrolysis and/or oxidation of normal butane, acetaldehyde and methane are studied.

4. 1. Normal Butane Oxidation Mechanism

Normal butane has been studied by Pitz et al.[17], discussing its reaction mechanism in detail without any sensitivity analysis. Although it was mentioned in their paper that the initiation reactions

$$nC4H10 = C2H5 + C2H5 \tag{216}$$

and

$$nC4H10 = nC3H7 + CH3, \tag{217}$$

were sensitive, a quantitative description was not given; their rates might be studied further.

Hence it is important to provide a sensitivity analysis in butane mechanism. The normal butane mechanism pursued in the present study is based on a mechanism developed by Pitz et al.[17]. A developed sensitivity program is used for the present analysis.

Oxidation of stoichiometric 2 % n-butane diluted with Ar was studied by the sensitivity analysis program. The initial conditions of temperature and pressure were 1468 K and 3.48 atm respectively. The sensitivity calculation for n-butane oxidation was performed until 3.5×10^{-5} sec when 50 % of n-butane was decomposed. Since temperature did not rise until 3.5×10^{-5} sec, this reaction was rather of pyrolysis type.

Reactions (216) and (217) are the two possible paths of initiation. In order to examine which path is more sensitive to n-butane decomposition, the elementary sensitivity coefficients of n-butane to Reactions (216) and (217) are plotted in Fig. 5. It is apparent that Reaction (217) is more sensitive than Reaction (216).

Hydrogen abstraction reactions are dominant in the propagating reaction mechanism. For a given mechanism the normalized sensitivity coefficients of
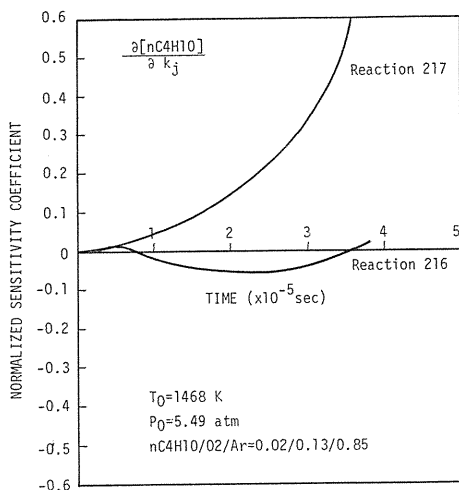
Fig. 5. Elementary sensitivity coefficients; $\partial[C_4H_{10}]/\partial k_{216}$ and $\partial[C_4H_{10}]/\partial k_{217}$ in normal butane oxidation.

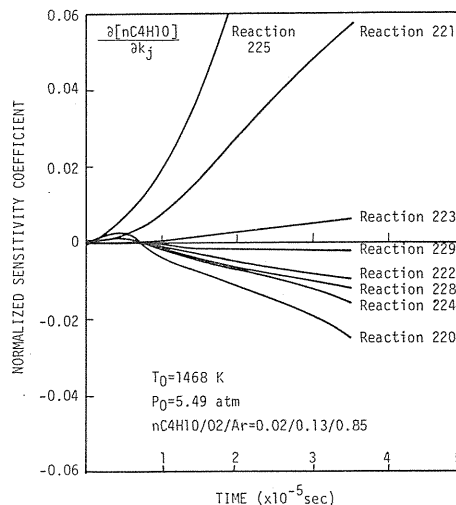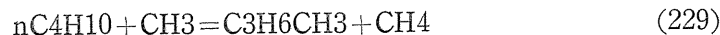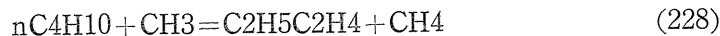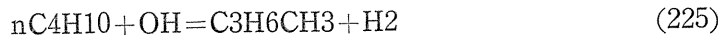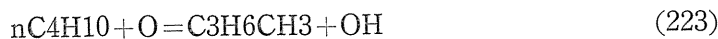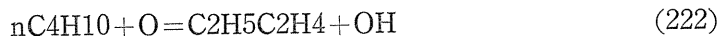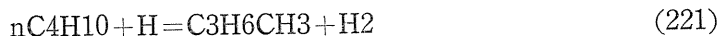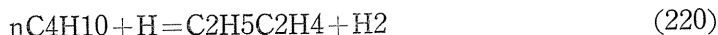Fig. 6. Eementary sensitivity coefficients; $\partial[C4H10]/\partial k_{220}$, $\partial[C4H10]/\partial k_{221}$, $\partial[C4H10]/\partial k_{222}$, $\partial[C4H10]/\partial k_{223}$, $\partial[C4H10]/\partial k_{224}$, $\partial[C4H10]/\partial k_{225}$, $\partial[C4H10]/\partial k_{228}$, $\partial[C4H10]/\partial k_{229}$, in normal butane oxidation.

n-butane by perturbing hydrogen abstraction reactions are investigated to know how these reactions affect the n-butane concentration. Fig. 6 shows the sensitivity coefficients of n-butane to the following eight reactions;

$$nC4H10 + H = C2H5C2H4 + H2 \qquad (220)$$

$$nC4H10 + H = C3H6CH3 + H2 \qquad (221)$$

$$nC4H10 + O = C2H5C2H4 + OH \qquad (222)$$

$$nC4H10 + O = C3H6CH3 + OH \qquad (223)$$

$$nC4H10 + OH = C2H5C2H4 + H2O \qquad (224)$$

$$nC4H10 + OH = C3H6CH3 + H2 \qquad (225)$$

$$nC4H10 + CH3 = C2H5C2H4 + CH4 \qquad (228)$$

$$nC4H10 + CH3 = C3H6CH3 + CH4 \qquad (229)$$
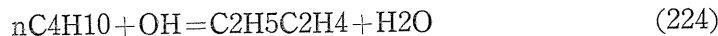
Reactions (221) and (225) provide the high sensitivity of n-butane. Hence the importance of these reactions in the stoichiometric n-butane oxidation can be pinpointed from this analysis.
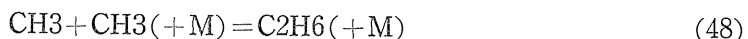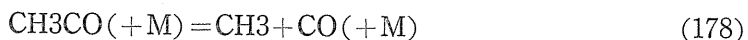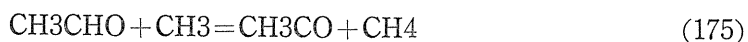
4. 2. Acetaldehyde Pyrolysis and Oxidation Mechanism

The comprehensive study on the sensitivity analysis of acetaldehyde pyrolysis and oxidation is performed to see the mechanism and behavior of acetaldehyde

combustion. Several applications of sensitivity analysis are conducted; (i) the elementary sensitivity coefficients for the pyrolysis mechanism, (ii) the experimental determination of unknown rate constants using sensitivity analysis, and (iii) the Green function coefficients calculation. The mechanism used in this section is simplified from the one in Appendix.

4. 2. 1. Elementary Sensitivity Coefficients for a Pyrolysis Mechanism

An acetaldehyde high temperature pyrolysis mechanism is proposed by Rice and Herzfeld[18] in 1934, consisting of the following six elementary reactions;

$$CH3CHO(+M) = CH3 + HCO(+M) \tag{169}$$

$$HCO + M = H + CO + M \tag{35}$$

$$CH3CHO + H = CH3CO + H2 \tag{172}$$

$$CH3CHO + CH3 = CH3CO + CH4 \tag{175}$$

$$CH3CO(+M) = CH3 + CO(+M) \tag{178}$$

$$CH3 + CH3(+M) = C2H6(+M) \tag{48}$$

In this mechanism acetaldehyde pyrolysis is initiated by Reaction (169), propagated by the chain reactions (35), (172), (175), (178), and terminated by Reaction (48).

A mechanism extended from the Rice-Herzfeld one is considered by adding the following three elementary reactions (*ERH* mechanism);

$$C2H6 + H = C2H5 + H2 \tag{68}$$

$$C2H6 + CH3 = C2H5 + CH4 \tag{67}$$

$$C2H5 + M = C2H4 + H + M \tag{72}$$
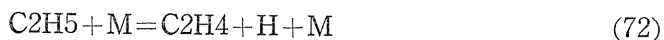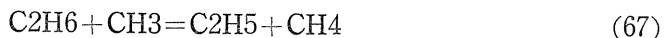
The *ERH* mechanism is investigated numerically for the pyrolysis of 1 % acataldehyde diluted with 99% argon by comparing with the acetaldehyde mechanism of 87 reactions (Table 4). Both results are shown in Figs. 7-(a) and (b), where the solid lines are the results using the 87 reactions whereas the broken ones using 9 reactions. Figs. 7-(a) and (b) clearly explain the difference between the full and simple mechanisms. The full mechanism verifies that the acetaldehyde pyrolysis and oxidation agree with the experimental data[19]. The yields of methane and ethylene are well simulated by the simple mechanism, where methane yields mainly from Reactions (175) and (67) and ethylene from Reaction (72).

Then a sensitivity analysis of acetaldehyde pyrolysis is performed for the full acetaldehyde mechanism under the condition listed in Table 5. The results of sensitivity analysis show that the following three plus the nine reactions in the *ERH* mechanism have large sensitivity coefficients;
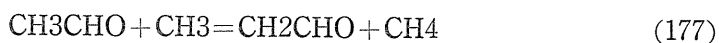
$$CH3CHO + CH3 = CH2CHO + CH4 \tag{177}$$

$$CH4 + M = CH3 + H + M \tag{41}$$

$$CH4 + H = CH3 + H2 \tag{43}$$

Table 4. Acetaldehyde oxidation mechanism (units in cc-mole-cal-K-sec).

| No.	Reaction	A	n	E	Reference
1	$CH_3CHO = CH_3 + HCO$	1.4E16	0.0	85800.	This studay
2	$O_2 + CH_3CHO = HO_2 + CH_3CO$	2.0E13	0.5	42200.	Colket (1977)
3	$O + CH_3CHO = OH + CH_3CO$	1.1E13	0.	2300.	Schofield (1967)
4	$HO_2 + CH_3CHO = H_2O_2 + CH_3CO$	1.2E12	0.	10700.	Colket (1975)
5	$OH + CH_3CHO = H_2O + CH_3CO$	3.2E14	0.	4240.	Schofield (1967)
6	$H + CH_3CHO = H_2 + CH_3CO$	5.9E-5	5.6	-1360.	Colket (1975)
7	$CH_3 + CH_3CHO = CH_4 + CH_3CO$	6.0E-8	6.1	1720.	Colket (1975)
8	$CH_3 + CH_3CHO = CH_4 + CH_2CHO$	5.5E-1	4.0	8280.	Watkins and Word (1974)
9	$CH_3CO = CH_3 + CO$	3.2E13	0.0	17240.	Colket (1977)
10	$CH_2CHO = H + CH_2CO$	1.6E13	0.0	35000.	Colket (1977)
11	$CH_3O + M = CH_2O + H + M$	5.0E13	0.	21000.	Brabbs and Brokaw (1975)
12	$CH_3O + O_2 = CH_2O + HO_2$	1.0E12	0.	6000.	Engleman (1976)
13	$CH_3O = H + CH_2O$	8.9E13	0.	30000.	Gray et al. (1967)
14	$CH_2O + M = HCO + H + M$	3.3E16	0.	81000.	Dean et al. (1980)
15	$CH_2O + CH_3 = HCO + CH_4$	1.0E10	0.5	19000.	Colket (1977)
16	$CH_2O + H = HCO + H_2$	3.3E14	0.	10500.	Dean et al. (1980)
17	$CH_2O + OH = HCO + H_2O$	7.6E12	0.	170.	Atkinson and Pitts (1978)
18	$C_2H_6 + O = C_2H_5 + OH$	2.5E13	0.	6360.	Herron and Huie (1973)
19	$C_2H_6 + OH = C_2H_5 + H_2O$	1.1E13	0.	2450.	Greiner (1973)
20	$C_2H_6 + H = H_2 + C_2H_5$	5.4E2	3.5	5200.	Clark and Dove (1973)
21	$C_2H_6 + CH_3 = CH_4 + C_2H_5$	5.5E-1	4.0	8280.	Clark and Dove (1973)
22	$C_2H_5 + O_2 = C_2H_4 + HO_2$	1.0E12	0.	5000.	Westbrook (1979)
23	$C_2H_5 = H + C_2H_4$	2.0E15	0.0	30000.	Olson et al. (1979).
24	$C_2H_4 + M = C_2H_2 + H_2 + M$	2.6E17	0.	79280.	Hartig et al. (1971)
25	$C_2H_4 + M = C_2H_3 + H + M$	3.8E17	0.	98160.	Baldwin et al. (1970)
26	$C_2H_3 + M = C_2H_2 + H + M$	7.9E14	0.	31500.	Herron (1969)
27	$CH_4 + M = CH_3 + H + M$	1.4E17	0.	88400.	Zellner et al. (1976)
28	$CH_4 + H = CH_3 + H_2$	1.3E14	0.	11900.	Skinner et al. (1972)
29	$CH_4 + O = CH_3 + OH$	2.0E13	0.	9200.	Brabbs and Brakaw (1975)
30	$CH_4 + OH = CH_3 + H_2O$	3.5E3	3.1	2000.	Shepp (1956)
31	$CH_4 + HO_2 = CH_3 + H_2O_2$	2.0E13	0.	18000.	Peeters and Mahnen (1973)
32	$CH_3 + O_2 = CH_3O + O$	2.4E13	0.	29000.	Fenimore (1969)
33	$CH_3 + CH_3 = C_2H_6$	2.2E13	0.0	0.	Tunder et al. (1967)
34	$CH_3 + O = CH_2O + H$	1.3E14	0.	2000.	Hayashi (1983)
35	$CH_3 + OH = CH_2O + H_2$	4.0E12	0.	0.	Just et al. (1977)
36	$CH_3 + HCO = CH_4 + CO$	3.0E11	0.5	0.	Benson and Haugen (1976)
37	$C_2H_4 + H = C_2H_3 + H_2$	1.5E7	2.0	6000.	Westbrook et al. (1967)
38	$C_2H_4 + O = CH_3 + HCO$	3.3E12	0.	1130.	Davis et al. (1972)
39	$C_2H_4 + O = CH_2O + CH_2$	2.5E13	0.	5000.	Westbrook et al. (1982)
40	$C_2H_4 + OH = CH_3 + CH_2O$	2.0E12	0.	960.	Westbrook et al. (1982)
41	$C_2H_4 + OH = C_2H_3 + H_2O$	4.8E12	0.	1230.	Westbrook et al. (1982)
42	$C_2H_4 + C_2H_4 = C_2H_3 + C_2H_5$	5.0E14	0.	64700.	Benson and Hougen (1967)
43	$C_2H_2 + O_2 = HCO + HCO$	1.0E14	0.	38000.	Gardiner and Walker (1968)
44	$C_2H_2 + H = C_2H + H_2$	2.0E14	0.	19000.	Browne et al. (1969)
45	$C_2H_2 + O = C_2H + OH$	3.2E15	-0.6	17000.	Browne et al. (1969)
46	$C_2H_2 + O = CH_2 + CO$	6.8E13	0.	4000.	Vandooren and Von Tiggelen (1977)
47	$C_2H_2 + OH = C_2H + H_2O$	6.0E12	0.	7000.	Vandooren and Von Tiggelen (1977)
48	$C_2H_2 + M = C_2H + H + M$	1.0E14	0.	114000.	Jachmowski (1977)
49	$C_2H_3 + OH = CH_3 + CO$	1.2E12	0.	500.	Smith and Zellner (1973)
50	$C_2H + O_2 = HCO + CO$	1.0E13	0.	7000.	Browne et al. (1969)
51	$C_2H + O = CH + CO$	5.0E13	0.	0.	Browne et al. (1969)
52	$CH_2 + O_2 = HCO + OH$	1.0E14	0.	3700.	Benson and Haugen (1967)
53	$CH_2 + H = CH + H_2$	2.7E11	0.7	25700.	Mayer et al. (1967)
54	$CH_2 + O = CH + OH$	1.9E11	0.7	25000.	Mayer et al. (1967)
55	$CH_2 + OH = CH + H_2O$	2.7E11	0.7	25700.	Peeters and Vicker (1975)
56	$CH_2 + HO_2 = HCO + H_2O$	1.0E12	0.	8000.	Engleman (1976)
57	$CH + O_2 = HCO + O$	1.0E13	0.0	0.	Jachimoski (1977)
58	$CH + O_2 = CO + OH$	1.3E11	0.7	25700.	Peeters and Vicker (1975)
59	$CO + OH = CO_2 + H$	1.3E7	1.3	-770.	Baulch and Drysdale (1974)
60	$CO + HO_2 = CO_2 + OH$	1.0E14	0.	23000.	Baldwin et al. (1970)
61	$CO + O + M = CO_2 + M$	5.9E15	0.	4100.	Simonaitis and Heicklen (1974)
62	$CO_2 + O = CO + O_2$	2.8E12	0.	43830.	Gardiner et al.
63	$HCO + M = H + CO + M$	1.4E14	0.5	19000.	Westbrook et al. (1977)
64	$HCO + O_2 = HO_2 + CO$	3.3E12	0.0	7000.	Westbrook et al. (1977)
65	$HCO + H = CO + H_2$	2.0E14	0.	0.	Niki et al. (1969)
66	$HCO + O = CO + OH$	1.0E14	0.	0.	Westenberg and de Haas (1972)
67	$HCO + OH = CH_2O + O$	1.0E14	0.	3000.	Baldwin and Walker (1973)
68	$HCO + OH = CO + H_2O$	1.0E14	0.	0.	Bowman (1970)
69	$H_2 + O = H + OH$	1.8E10	0.	8900.	Baulch et al. (1973)
70	$O_2 + M = O + O + M$	5.1E15	0.	115000.	Jenkins et al. (1967)
71	$H + O + M = OH + M$	1.0E16	0.	0.	Moretti (1965)
72	$H_2 + M = H + H + M$	2.2E14	0.	96000.	Baulch et al. (1973)
73	$H + O_2 = OH + O$	2.2E14	0.	16800.	Baulch et al. (1973)
74	$H + O_2 + M = HO_2 + M$	3.2E15	0.	-1000.	Baulch et al. (1973)
75	$H_2O_2 + M = OH + OH + M$	1.2E17	0.	45500.	Baulch et al. (1973)
76	$H_2O_2 + H = H_2 + HO_2$	1.7E12	0.	3750.	Baulch et al. (1973)
77	$H_2O_2 + OH = H_2O + HO_2$	1.0E13	0.	1800.	Baulch et al. (1973)
78	$HO_2 + H = OH + OH$	2.5E14	0.	1900.	Baulch et al. (1973)
79	$HO_2 + O = O_2 + OH$	5.0E13	0.	1000.	Lloyd (1974)
80	$HO_2 + H = H_2 + O_2$	2.5E13	0.	700.	Baulch et al. (1973)
81	$HO_2 + OH = H_2O + O_2$	5.0E13	0.	1000.	Lloyd (1974)
82	$HO_2 + HO_2 = H_2O_2 + O_2$	1.0E13	0.	1000.	Lloyd (1974)
83	$HO_2 + CH_3 = CH_3O + OH$	2.0E12	0.	0.	Colket (1975)
84	$HO_2 + CH_3 = CH_4 + O_2$	2.0E12	0.	0.	Skinner et al. (1972)
85	$H_2O + M = H + OH + M$	2.2E16	0.	105000.	Baulch et al. (1973)
86	$H_2O + H = H_2 + OH$	9.5E13	0.	20300.	Baulch et al. (1973)
87	$H_2O + O = OH + OH$	6.8E13	0.	18350.	Baulch et al. (1973)
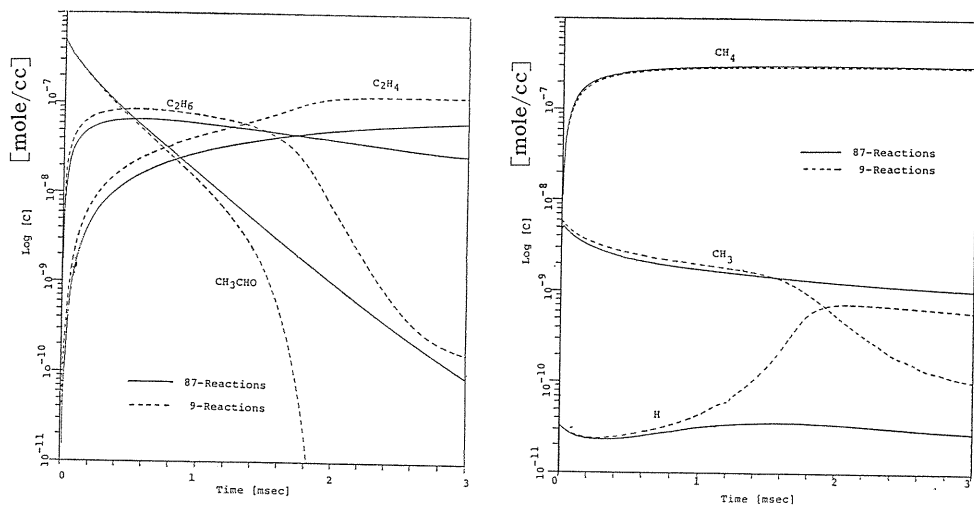
(a) Results for CH3CHO, C2H6 and C2H4   (b) Results for CH4, CH3, and H concent-
    concentrations.   rations.

Fig. 7. Comparison of computational results for acetaldehyde pyrolysis between
        two mechanisms; the mechanism of 87 reactions (solid lines) and that
        of 9 reactions (broken lines), at $CH_3CHO/Ar=0.01/0.99$, T=1385K and
        P=7.12 atm.

Table 5.   Conditions and some results of sensitivity analysis for
           acetaldehyde pyrolysis and oxidation.

Case	Shock 1	Shock 2	Shock 3	Shock 4
Mechanism	Simple	Full	Full	Full
T_0 (K)	1450	1432	1450	1667
P_0 (atm)	6.277	6.324	6.277	6.558
Mole fraction CH_3CHO	0.010	0.010	0.010	0.010
O_2	—	0.030	—	0.015
Ar	0.990	0.960	0.990	0.975
ε_{pmm} Eq. (3.12)	0.02	—	—	—
ε_r(max)Eq. (3.11)	0.02	1.00	0.966	1.16
t_{end} (sec)	3.0×10^{-6}	1.0×10^{-6}	1.0×10^{-6}	1.0×10^{-6}

The final simplified mechanism of acetaldehyde pyrolysis (12 reactions) is
used to calculate acetaldehyde thermal decomposition to be compared with the full
mechanism simulation. Figs. 8-(a) and (b) show the comparison between the two
mechanisms, and reveal a good agreement. The following two facts are found from
the sensitivity analysis of acetaldehyde pyrolysis;
  (1)   the Rice-Herzfeld mechanism is not adequate for acetaldehyde pyrolysis,
  (2)   the sensitivity analysis of elementary coefficients gives a simple way of
       finding important reactions.
  When the same procedure is applied to acetaldehyde oxidation, additional reac-
tions are added to the simplified pyrolysis mechanism, showing an agreement between
the simplified oxidation and full mechanisms (Figs. 9-(a) and (b)).

(a) Results for CH3CHO, C2H6 and CH4 concentrations.

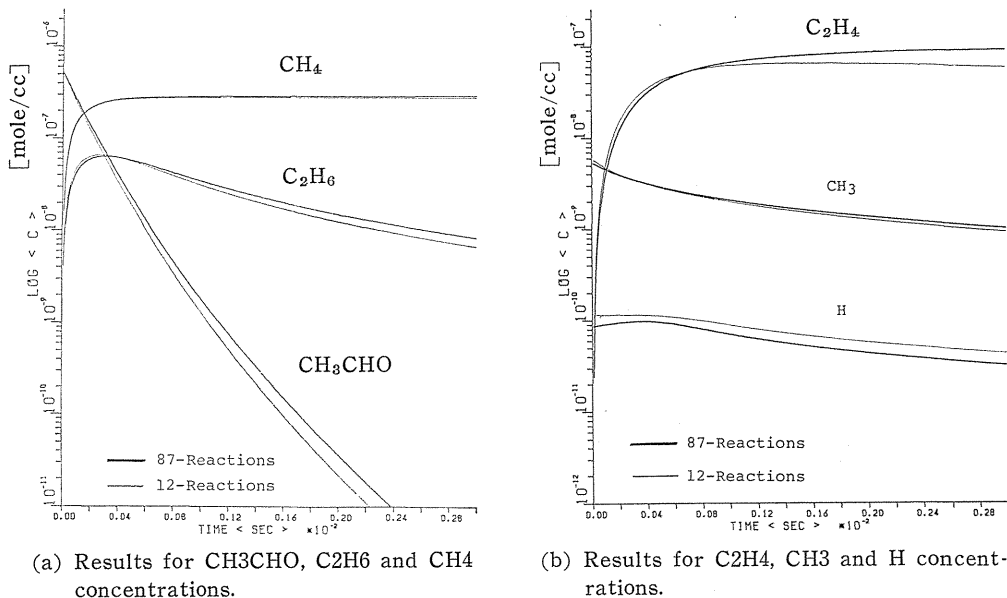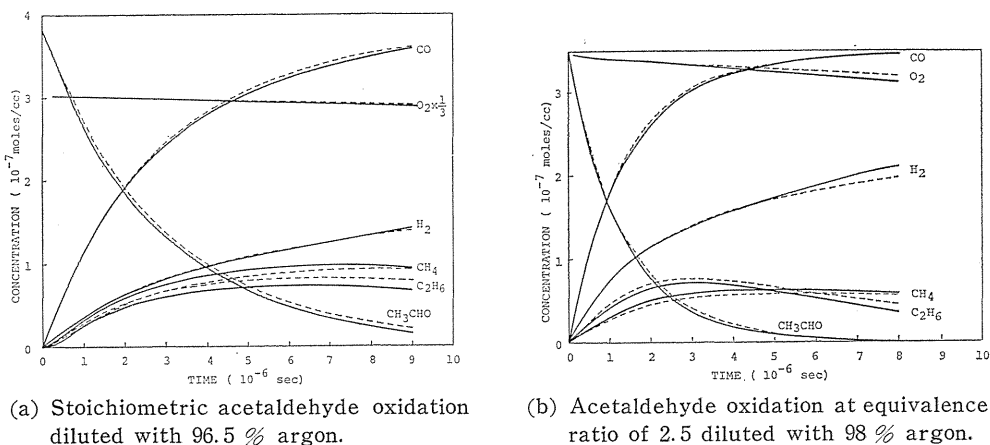(b) Results for C2H4, CH3 and H concentrations.

Fig. 8. Comparison of computational results for acetaldehyde pyrolysis between the two mechanisms; 87 reactions (thick lines) and 12 reactions (thin lines), at $CH_3CHO/Ar=0.01/0.99$, $T=1450$ K and $P=6.28$ atm.

(a) Stoichiometric acetaldehyde oxidation diluted with 96.5 % argon.

(b) Acetaldehyde oxidation at equivalence ratio of 2.5 diluted with 98 % argon.

Fig. 9. Comparison of computational results for acetaldehyde oxidation between two mechanisms; the mechanism of 87 reactions (solid lines) and that of 19 reactions (broken lines), $T=1700$ K and $P=5.00$ atm.

4. 2. 2. *Experimental Determination of Unknown Rate Constants Using Sensitivity Analysis*

The sensitivity analysis can be used to experimentally determine the rates of unknown reactions in an acetaldehyde oxidation system. The concentrations of O-atom and CO-and OH-molecules in the reaction system are measured behind a reflected shock wave using ultraviolet and infrared emission spectroscopies. Two

types of $CH_3CHO/O_2/Ar$ mixtures, the equivalence ratios 0.94 and 2.5, are used to study the concentrations of O, CO and OH species at the temperature 1470–1960K and the pressure 0.46–0.67 MPa. A H_2/O_2 mixture was used to calibrate OH concentrations and a CO/O_2 mixture for O and CO concentrations.

Experiment

The experiment is conducted using a single-pulse shock tube of 50.8 mm i. d. and 5.86 m length. In order to produce a single-pulse shock wave, a $0.1 m^3$ dump tank is installed 10 cm downstream of a plastic diaphragm, which separates the stainless steel driver section from the pyrex glass test one. The shock tube shows a leak rate of less than $1.0 Pa/min$ and is evacuated down to less than $0.1 Pa$.

A ball valve is used to open the dump tank, pressurized up to the driven section pressure, just before rupturing the diaphragm by a needle. Acetaldehyde is Merck Grade 99.5 % pure with water as the most probable impurity. Argon, hydrogen, carbon monoxide and oxygen are Nihon Oxygen Grade 99.99 % pure. Prepared are the stoichiometric hydrogen/oxygen mixture diluted with argon, stoichiometric carbon monoxide/oxygen mixture diluted with argon and acetaldehyde/oxygen mixtures at the equivalence ratios 0.94 and 2.5 diluted with argon. The shock speed is measured by a multichannel time counter signaled from a piezoelectric pressure transducer (Kistler 601 H). The initial temperature and pressure immediately behind a reflected shock wave are calculated from shock relations taking account of the temperature dependency of enthalpies. A schematic diagram of the experimental setup is shown in Fig. 10.

The OH concentration was measured using the emission of the R^2 branches of $^2\Sigma - ^2\Pi$ (0,0) band system at 3064 A. The OH ultraviolet emission was focused on the entrance slit of a 10cm monochromator (*JASCO CT*-10). Entrance and exit slits were set to 200 μm width to supply enough emission into a photomultiplier (Hamamatsu Photonics R106). A stoichiometric hydrogen/oxygen mixture was used to obtain a calibration curve for OH emission comparing experimental data with the computational results. A least square fit of the calibration results is shown in
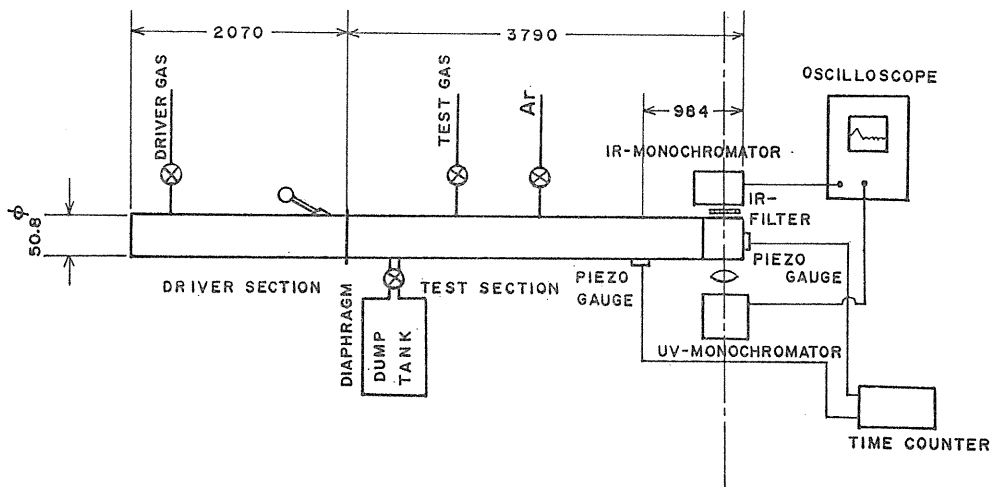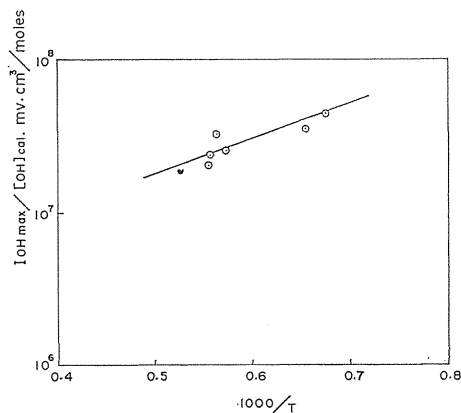

Fig. 10. Schematic diagram of experimental setup.

Fig. 11. A least square fit of the calibration curve for the OH ultraviolet emission at 3064 A and concentration by a stoichiometric H_2/O_2 mixture diluted with argon.

Fig. 11, confirming that the observed emission intensity is proportional to the computed OH concentrations using nine well-known elementary reactions listed on Table 6.

The measurement of O-atom concentration was conducted using the same methodology as Bowman[22] in 1975. The chemiluminescent emission of $O+CO \rightarrow CO_2$ at 3660 A passed through a quartz window and was focused on the entrance slit of a 10 cm monochromator. A photomultiplier (Hamamatsu Photonics $R106$) detected the ultraviolet light from the exit of the monochromator. In order to determine the O-atom concentration, the infrared emission from the fundamental band of CO molecules at 4.8 μm was measured simultaneously with the above ultraviolet emission. The infrared light passed through a CaF_2 window and focused on the entrance slit of a 25 cm infrared monochromator ($JASCO$ CT-25). A cryogenically cooled infrared detector (Santa Barbara Research Center PbSe LTO Detector 4311) sensed the infrared emission from the exit slit. All the slit widths used in this experiment were 200 μm. The following relation between the intensity of chemiluminescent emission and the O-atom and CO-molecule concentrations was used;

$$I = k\,[O][CO],$$

where k is a temperature and total pressure-dependent constant[20,21].

The emission from this $O+CO \rightarrow CO_2 + h\nu$ reaction was measured in a stoichiometric CO/O_2 mixture diluted with argon and compared with the computational results using three elementary reactions listed on Table 7. The least-square fits of the data on the intensity of the chemiluminescent emission from $O+CO$ reaction and on the intensity of the CO infrared emission are shown in Figs. 12 and 13,

Table 6. H2/O2 reaction mechanism (units in cc-mole-cal-K-sec).

Reaction	A	n	E
$H+O_2=O+OH$	2.2×10^{14}	0.0	16790.
$H_2+O=H+OH$	3.2×10^{14}	1.0	104800.
$O+H_2O=OH+OH$	5.4×10^{14}	0.0	24239.
$H+H_2O=OH+H_2$	1.26×10^{15}	0.0	31932.
$O_2=O+O$	7.9×10^{13}	0.0	104800.
$H_2=H+H$	2.2×10^{14}	0.0	96000.
$H_2O=H+OH$	6.86×10^{26}	-3.0	122590.
$HO_2=H+O_2$	2.3×10^{15}	0.0	45900.
$H+HO_2=OH+OH$	2.5×10^{14}	0.0	1900.

respectively.

When an Arrhenius-type rate constant was assumed, the activation energy of O+CO reaction was 4570 cal/mole, which agreed with the result obtained by Bowman[22]. Thus the curves in Figs. 12 and 13 can be used for calibration.

Table 7.   CO/O2 reaction mechanism (units in cc-mole-cal-K-sec)

Reaction	A	n	E
$CO+O_2=CO_2+O$	3.1×10^{11}	0.0	37600.
$O_2+M=O+O+M$	1.7×10^{15}	0.0	115000.
$CO+O+M=CO_2+M$	5.9×10^{15}	0.0	4100.
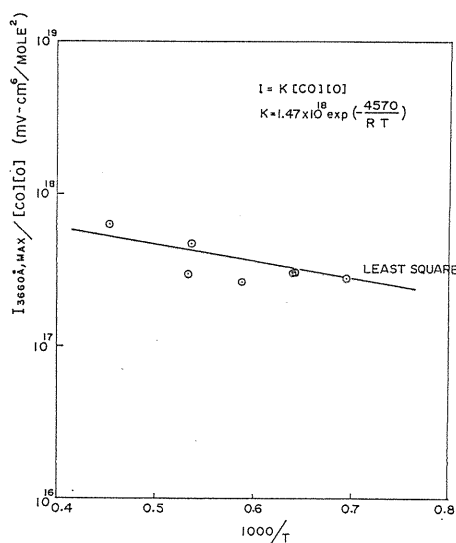
Fig. 12. A least square fit of the calibration curve for the O+CO reaction using 3660 A emission from a stoichiometric CO/O$_2$ mixture diluted with argon.
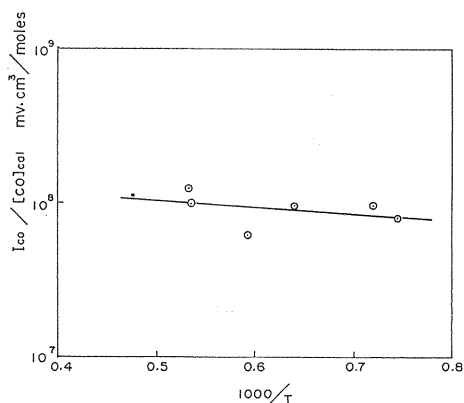
Fig. 13. A least square fit of the calibration curve for the CO infrared emission at 4.8 μm emission from a stoichiometric CO/O$_2$ mixture diluted with argon.

Experimental Results

The concentrations of O-atom and CO- and OH-molecules were obtained behind a reflected shock wave using near-stoichiometric and rich acetaldehyde/oxygen/argon mixtures. The ranges of temperature, pressure and total species concentrations were $1470-1960K$, $0.46-0.67MPa$ and $(2.89-6.19) \times 10^{-5}$ mole/cc.

A typical experimental output of radiation intensities on an oscilloscope is shown in Fig. 14, indicating OH ultraviolet emission at 3064 A for the acetaldehyde/oxygen/argon mixture at the equivalence ratio 2.5, temperature 1760 K and pressure 0.503 MPa. Fig. 14-(b) is an example of the chemiluminescent emission from O+CO reaction at 3660 A and the infrared radiation of CO-molecule at 4.8 μm for the
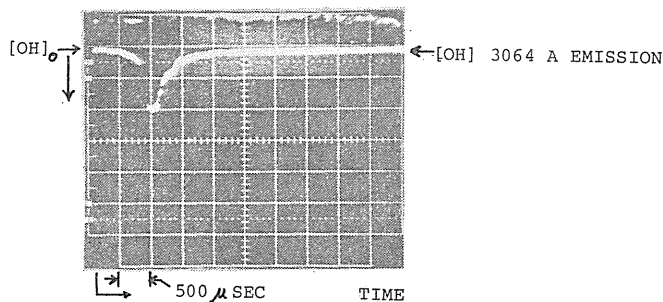
(a) ϕ =2.5, $CH_3CHO/O_2/Ar$=1/1/98, T=1760K, P=4.97 atm.
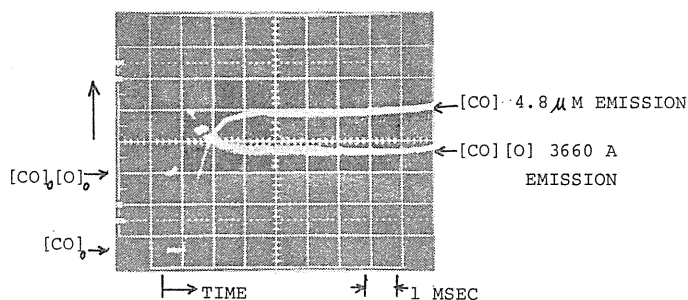
(b) ϕ =0.94, $CH_3CHO/O_2/Ar$=2/4.9/93.1, T=1830K, P=4.66 atm.

Fig. 14. A typical experimental output of radiation intensities on an oscilloscope.

acetaldehyde/oxygen/argon mixture at the equivalence ratio 0.94, temperature 1830 K and pressure 0.472 MPa.   The transient spikes in O+CO and OH emissions are observed in the experiments on near-stoichiometric and rich mixtures.   This transient spike in O+CO chemiluminescence contains unknown hydrocarbon emissions as Jachimowski pointed out in the study of a methane oxidation system.   Hence the maximum intensity of O+CO emission is extrapolated from its equilibrium value. The concentration of CO is obtained from the extrapolated maximum O+CO emission.

The extrapolated maximum O-atom and OH-molecule and the simultaneous CO-molecule concentrations as well as the temperature, pressure and spike-time are tabulated for the near-stoichiometric and rich $CH_3CHO/O_2/Ar$ mixtures in Table 8.   The uncertainties in the measurement of concentration are at most 20 % considering the optical systems, pressure and temperature calculations and the data calibration.

Table 8. Experimental results.

Equivalence Ratio	T_5 (K) $\pm 30K$	P_5 (atm) $\pm 3\%$	t, spike (msec)	Total Concentration (10^{-5}, mole/cc)	$[O]_{MAX}$ (10^{-8}) $\pm 20\%$	$[CO]$ (10^{-6}) $\pm 20\%$	$[OH]_{MAX}$ (10^{-9}) $\pm 15\%$
0.94	1275	5.88	2.21	5.625			0.097
0.94	1376	6.65	1.06	5.891			1.20
0.94	1470	5.60	0.49	4.647			9.19
0.94	1680	5.84	0.20	4.241			20.2
0.94	1683	4.73	0.14	3.428			23.2
0.94	1924	4.58	0.02	2.900			38.1
0.94	1385	7.03	1.14	6.186	0.261	3.93	
0.94	1523	6.29	0.41	5.031	0.785	1.12	
0.94	1566	5.46	0.29	4.249	1.15	0.67	
0.94	1595	5.69	0.23	4.346	0.88	0.35	
0.94	1709	5.40	0.13	3.852	4.16	0.22	
0.94	1727	5.54	0.14	3.911	1.76	0.60	
0.94	1833	4.66	0.04	3.100	3.81	0.22	
2.50	1334	6.28	1.43	5.739			0.265
2.50	1400	5.95	0.76	5.183			0.766
2.50	1569	6.11	0.29	4.747			7.01
2.50	1684	5.76	0.15	4.167			12.1
2.50	1762	4.97	0.09	3.441			15.1
2.50	1880	4.27	0.03	2.770			24.3
2.50	1962	4.65	0.03	2.888			30.3
2.50	1390	5.86	0.86	5.133	0.015	0.34	
2.50	1564	6.08	0.36	4.733	0.037	0.20	
2.50	1594	5.21	0.16	3.986	0.053	0.16	
2.50	1677	5.76	0.14	4.188	0.089	0.15	
2.50	1774	5.08	0.08	3.489	0.240	0.07	

Sensitivity Analysis

A sensitivity analysis (Green Function Method) for acetaldehyde oxidation was performed to study the previously developed mechanism[19]. The purpose of using the sensitivity analysis was to systematize the analysis of the present experimental results; in other words, to pinpoint the important reactions related to O-atom and CO- and OH- molecules and to obtain the proper rate constants for such reactions. Table 9 lists several reactions having sufficiently large sensitivity coefficients for the near-stoichiometric and rich $CH_3CHO/O_2/Ar$ mixtures. The hydrocarbon-related reactions such as

$$C2H5 = H + C2H4 \tag{72}$$

$$CH4 + M = CH3 + H + M \tag{41}$$

were seen to be more important for the reaction of rich mixtures than near-

Table 9. Sensitivity analysis for experimental data.

[O] Atom; T=1700 K, P=5 atm			
Equivalence Ratio			
$\phi=0.94$		$\phi=2.5$	
Reaction	Sensitivity Coefficient	Reaction	Sensitivity Coefficient
$CH_3CO \rightarrow CH_3 + CO$	12.25	$CH_3CO \rightarrow CH_3 + CO$	17.66
$CH_3CHO \rightarrow CH_3 + CHO$	5.86	$HCO + M \rightarrow H + CO + M$	12.42
$HCO + M \rightarrow H + CO + M$	5.86	$CH_3CHO \rightarrow CH_3 + CHO$	12.37
$CH_3 + CH_3 \rightarrow C_2H_6$	−4.07	$CH_3 + CH_3 \rightarrow C_2H_6$	−6.82
$H + CH_3CHO \rightarrow H_2 + CH_3CO$	−0.38	$H + CH_3CHO \rightarrow H_2 + CH_3CO$	−0.32
$H + O_2 \rightarrow OH + O$	0.27	$C_2H_5 \rightarrow H + C_2H_4$	0.23
$CH_3 + O \rightarrow CH_2O + H$	−0.21	$H + O_2 \rightarrow OH + O$	0.22
$O + CH_3CHO \rightarrow OH + CH_3CO$	−0.11	$CH_3 + O \rightarrow CH_2O + H$	−0.19
		$CH_4 + M \rightarrow CH_3 + H + M$	−0.17

[OH] Molecule; T=1700K, P=5 atm			
Equivalence Ratio			
$\phi=0.94$		$\phi=2.5$	
Reaction	Sensitivity Coefficient	Reaction	Sensitivity Coefficient
$CH_3CO \rightarrow CH_3 + CO$	8.44	$CH_3CO \rightarrow CH_3 + CO$	25.80
$CH_3CHO \rightarrow CH_3 + CHO$	4.57	$CH_3CHO \rightarrow CH_3 + CHO$	18.29
$HCO + M \rightarrow H + CO + M$	4.36	$HCO + M \rightarrow H + CO + M$	18.25
$CH_3 + CH_3 \rightarrow C_2H_6$	−2.53	$CH_3 + CH_3 \rightarrow C_2H_6$	−10.00
$OH + CH_3CHO \rightarrow H_2O + CH_3CO$	−1.46	$OH + CH_3CHO \rightarrow H_2O + CH_3CO$	−0.57
$H + O_2 \rightarrow OH + O$	0.80	$H + O_2 \rightarrow OH + O$	0.38
$H + CH_3CHO \rightarrow H_2 + CH_3CO$	−0.31	$C_2H_5 \rightarrow H + C_2H_4$	0.32
$O + CH_3CHO \rightarrow OH + CH_2CO$	0.21	$H + CH_3CHO \rightarrow H_2 + CH_3CO$	−0.28
$HO_2 + H \rightarrow OH + OH$	0.14	$CH_4 + M \rightarrow CH_3 + H + M$	−0.25
		$HCO + OH \rightarrow CH_2O + O$	0.12

stoichiometric ones.

The calculated time to the maximum concentrations of O-atom and OH-molecule was found to agree with that of experimental results without adjusting any rates except that of H_2O_2-related reactions. The present acetaldehyde oxidation mechanism contained 87 elementary reactions excluding ketene-related reactions. It was found out that H_2/O_2 reactions were important for the hydrocarbon combustion and the same H_2/O_2 rate constants could not be used for different temperature ranges if those reactions were strongly temperature dependent. The maximum concentrations of O-atom and OH- molecule were calculated using the results of sensitivity analysis. Basically, the following four elementary reactions were adjusted to fit the maximum values O-atom and CO- and OH-molecules concentrations;

$$HCO + M = H + CO + M \tag{35}$$

$$OH + CH3CHO = H2O + CH3CO \tag{173}$$

$$CH3 + O = CH2O + H \tag{51}$$

$$O + CH3CHO = OH + CH3CO \tag{174}$$
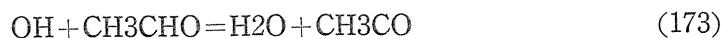
The rates of these reactions were obtained using typical experimental results on induction time,

$$K_{35} = 1 \times 10^{13} \exp(-19000/RT) \text{ cc/mole.sec}$$

$$K_{173} = 1.0 \times 10^{14} \exp(-4240/RT) \text{ cc/mole.sec}$$

$$K_{51} = 1.0 \times 10^{14} \exp(-2000/RT) \text{ cc/mole.sec}$$

$$K_{174} = 2.0 \times 10^{13} \exp(-2300/RT) \text{ cc/mole.sec}$$

where the published values on activation energy were used to determine the frequency factors. The above four reactions were chosen by setting up a criterion that well established reactions and their rates were fixed. It should be noted that the important reactions obtained using sensitivity analysis were essentially valid only within the temperature where the sensitivity analysis was applied. It is absolutely necessary to check the sensitivity at different temperatures as well as for different mixtures in order to establish a general reaction mechanism and associated reaction rates.

Discussions

The sensitivity analysis is powerful to determine the rates of unknown reactions when the rates of well established reactions can be fixed, as it proved in the present paper.

Reaction 35 is one of the most important reactions in acetaldehyde chemistry. This one and $CH_3CO \rightarrow CH_3 + CO$ compete each other for CO production. As Warnatz describes that further rate measurment is necessary for this reaction[23], it still has uncertainties. The presently obtained rates are rather close to that of Browne et al.[24] and Dean et al.[25] than that by Bowman.

Reaction 173 becomes more important to lean mixtures than to rich mixtures. The rates of this reaction at high temperatures are obtained only by Colket[26] with uncertainties. The normal sensitivity coefficient of Reaction 173 is one order smaller than the largest sensitivity coefficient in the same system. In other words, the obtained rate has a large uncertainty since a large frequency factor to adjust its rate does not affect the OH concentration.
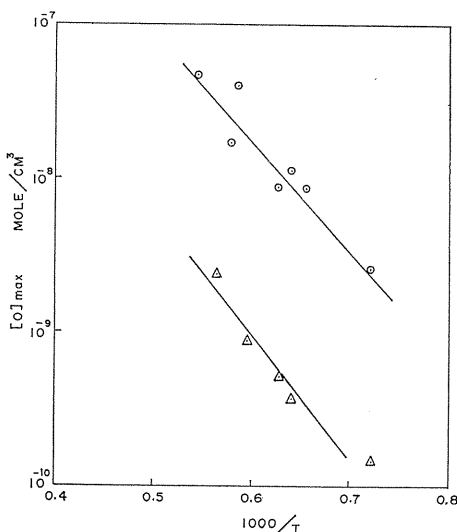

Fig. 15. Comparison of measured and calculated maximum O-atm concentrations; circles show the acetaldehyde/oxygen/argon mixture at the equivalence ratio 0.94 and triangles at the equivalence ratio 2.5. Solid lines are calculated maximum O atom concentrations.
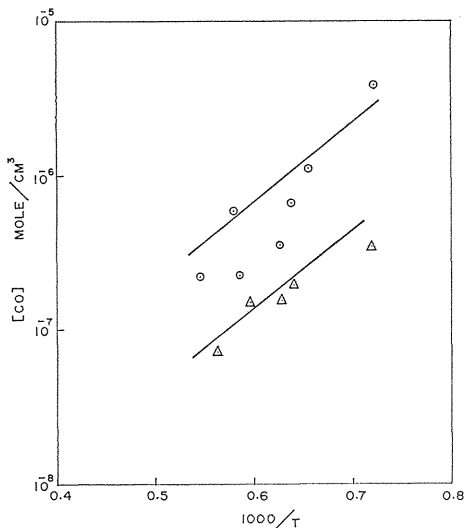
Fig. 16. Comparison of measured and calculated CO-molecule concentrations; circles show the acetaldehyde/oxygen/argon mixture at the equivalence ratio 0.94 and triangles at the equivalence ratio 2.5. Solid lines are calculated CO-molecule concentrations.
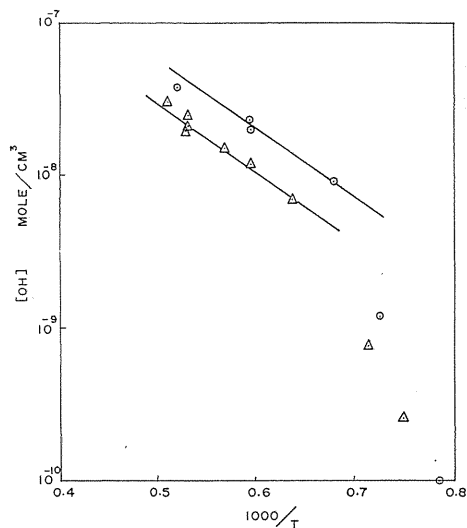
Fig. 17. Comparison of measure d and calculated OH-molecule concentrations; circles show the acetaldehyde/oxygen/argon mixture at the equivalence ratio 0.94 and triangles at the equivalence ratio 2.5. Solid lines are calculated OH-molecule concentrations.

The importance of Reaction 51 is dramatic in contrast with the statement of Bowman that the $CH_3+O_2 \rightarrow CH_2O+OH$ reaction is more important than Reaction 51. Instead, the sensitivity analysis on O-atom clearly discloses higher importance of Reaction 51. The rate presently obtained is the same as obtained by other shock tube researches.

Reaction 174 has also a large uncertainty in its rate, but the present result must be important since such a datum decreases the uncertainty at high temperatures. As seen in Table 9, this reaction becomes less important for richer mixtures, but still important for lean mixtures regarding both O-atom and OH-molecule.

The calculated values of O, CO, and OH concentrations using the newly obtained mechanism agree with the experimental data shown in Figs. 15, 16 and 17. The O-atom concentrations are explained well by the computed values. Fig. 15 shows an order of magnitude difference in O-atom concentrations between the stoichiometric and rich mixtures. The measured results for CO- molecules scatter a little, but the computational results agree with the experimental data.

Fig. 17 shows the OH ultraviolet emission data. The computational results agree at high temperatures, but not at low temperatures since the pressure effects become large.

It is concluded that the proposed mechanism can predict acetaldehyde/oxygen mixtures combustion at high temperatures.

4. 2. 3. Calculation of Green Function Coefficient

Sample calculations of the Green function coefficients in the 0.5 % acetaldehyde/99.5 % Ar pyrolysis at the temperature 1312 K and pressure 3.62 atm are

performed. Since $[CH_2CHO]$ and $[CH_2CO]$ perturbations to $[CH_3CHO]$ concentration are interested, their Green function coefficients are calculated and shown in Figs. 18, 19 and 20. The $[CH_3CHO]$ concentration responds immediately from $t=0$ and attenuates along t against all the three species $[CH_2CHO]$, $[CH_2CO]$ and $[CH_3]$. It is difficult to recognize the sign of sensitivity from these graphs, but $[CH_2CHO]$ reacts positive to the perturbation of $[CH_2CO]$ concentration. $[CH_2CHO]$ affects $[CH_3CHO]$ more than the other two species as far as the maximum value of the Green function coefficient is concerned.

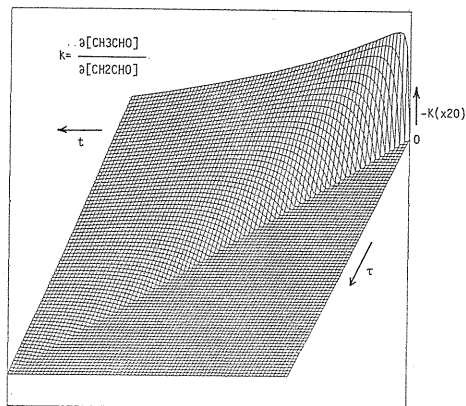Fig. 18. Green function coefficient, $\partial[CH_3CHO]/\partial[CH_2CHO]$.
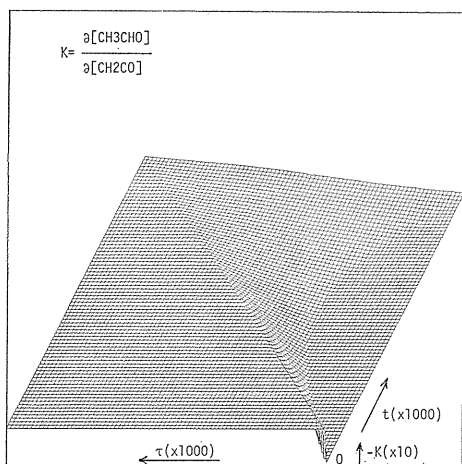

Fig. 19. Green function coefficient, $\partial[CH_3CHO]/\partial[CH_2CO]$.
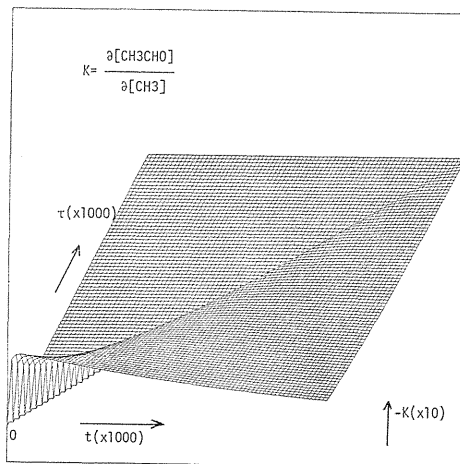

Fig. 20. Green function coefficient, $\partial[CH_3CHO]/\partial[CH_3]$.

4. 3. Methane Oxidation Mechanism

Fig. 21 shows the chemical kinetics run for the present case. Methane disappears at $t=1.4 \times 10^{-4}$ sec and the equilibrium is reached quickly. The normalized sensitivity coefficients of methane for various times are plotted in Fig. 22. The sensitivity for Reaction 1 increases drastically to the negative direction with the start of oxidation reaction, while the sensitivity for the chain-branching Reaction 3 increases positively. This is an interesting result in observing the differences among these reactions. The sensitivity calculation could not be extended to reach an equilibrium where the sensitivity coefficients become constant.

The sensitivity coefficients of a typical stable product CO2 and a radical CH3, are shown and compared with the results by Dougherty et al. in Fig. 23. Their results are always positive compared with ours, which change their signs and become
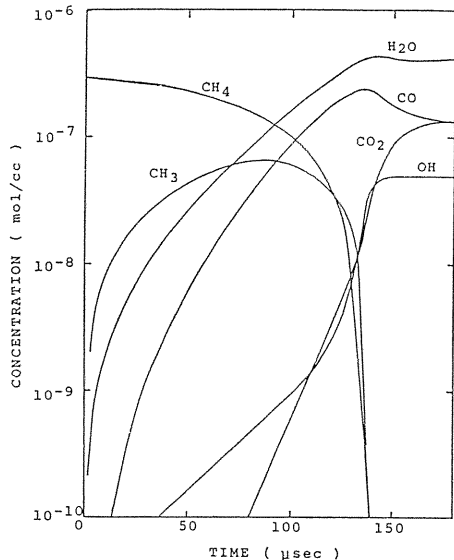
Fig. 21. Species concentration for the CH_4 /O_2/Ar system at $2000K$ and 9.746 atm. Initial concentrations are $[CH_4]/[O_2]/[Ar]=0.01/0.02/0.97$.
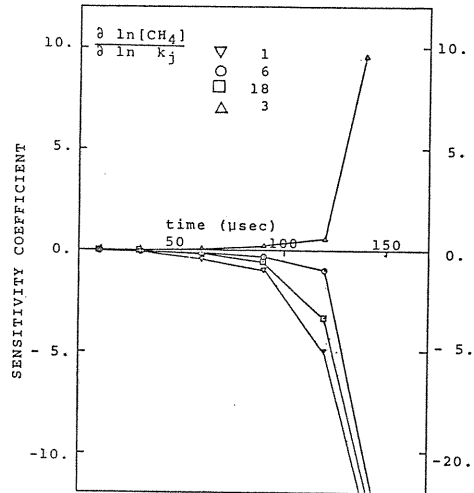

Fig. 22. Selected normalized sensitivity coefficients for the *GFM* methane combustion model. Sensitivity coefficients of methane for Reactions 1, 3, 6, and 18 in Table 1 are picked up as important reactions. Results did not reach the equilibrium state of this system.
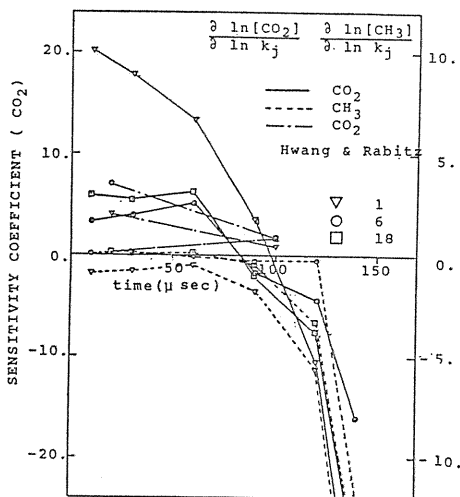

Fig. 23. Selected normalized sensitivity coefficients for the *GFM* methane combustion model. Sensitivity coefficients of carbon dioxide and methyl radical for Reactions 1, 6 and 18 in Table 1 are plotted. Sensitivity coefficients of CO_2 are specifically compared with the results obtained by Hwang and Rabitz.

negative rapidly near the reaction zone. These coefficients are the most sensitive ones.

5. Conclusions

The Green function method, one of the most useful methods in sensitivity analysis, was applied to hydrocarbon chemistry. The detailed interpretation of sensitivity coefficients has been discussed by Yetter et al.[5] and the present study confirmed some of their interpretation on wet CO oxidation. The local sensitivity coefficients and Green function coefficients of wet CO oxidation in the present analysis agreed with that obtained by Yetter et al., when all the conditions in CO oxidation were the same, using a different method of integrating nonlinear ordinary differential equations.

The application of sensitivity analysis to finding unknown parameters through experiments is very important and useful to develop a new mechanism.

It is noted that there is a limit in the conditions which can be fixed by the mechanism considered; the sensitivity analysis can not be applied beyond the limit. Furthermore, if the mechanism is not complete by losing important reactions, its sensitivity analysis does not have any meanings.

Further detailed interpretations have to be conducted for the use of the sensitivity analysis to chemical kinetics modeling.

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6. Appendix

No.	Reaction	Forward rate			Reference
		A	n	Ea	
1.	$H + O_2 = O + OH$	0.513E+17	−0.816	0.165E+05	Miller (1981)
2.	$O + H_2 = H + OH$	0.182E+11	1.00	0.890E+04	Baulch et al. (1973)
3.	$H_2 + OH = H_2O + H$	0.219E+14	0.000	0.515E+04	Baulch et al. (1973)
4.	$O + H_2O = OH + OH$	0.339E+14	0.000	0.184E+05	Baulch et al. (1973)
5.	$H + H + M = H_2 + M$	0.302E+16	0.000	0.000E+00	Baulch et al. (1973)
6.	$O + O + M = O_2 + M$	0.302E+16	−0.280	0.000E+00	Baulch et al. (1976)
7.	$O + H + M = OH + M$	0.100E+17	0.000	0.000E+00	Moretti (1965)
8.	$H + OH + M = H_2O + M$	0.141E+24	−2.00	0.000E+00	Baulch et al. (1973)
9.	$H + O_2 + M = HO_2 + M$	0.151E+16	0.000	−0.100E+04	Baulch et al. (1973)
10.	$H + HO_2 = H_2 + O_2$	0.251E+14	0.000	700.	Baulch et al. (1973)
11.	$H + HO_2 = OH + OH$	0.251E+15	0.000	0.190E+04	Baulch et al. (1973)
12.	$H + HO_2 = H_2O + O$	0.501E+14	0.000	0.100E+04	Lloyd (1974)
13.	$HO_2 + OH = H_2O + O_2$	0.501E+14	0.000	0.100E+04	Lloyd (1974)
14.	$HO_2 + O = O_2 + OH$	0.501E+14	0.000	0.100E+04	Lloyd (1974)
15.	$HO_2 + HO_2 = H_2O_2 + O_2$	0.100E+14	0.000	0.100E+04	Lloyd (1974)
16.	$H_2O_2 + OH = H_2O + HO_2$	0.100E+14	0.000	0.180E+04	Baulch et al. (1973)
17.	$H_2O_2 + H = H_2O + OH$	0.316E+15	0.000	0.894E+04	Baulch et al. (1969)
18.	$H_2O_2 + H = HO_2 + H_2$	0.170E+13	0.000	0.375E+04	Baulch et al. (1973)
19.	$H_2O_2 + M = OH + OH + M$	0.120E+18	0.000	0.455E+05	Baulch et al. (1973)
20.	$O + OH + M = HO_2 + M$	0.100E+18	0.000	0.000E+00	Bahn (1965)
21.	$H_2 + O_2 = OH + OH$	0.251E+13	0.000	0.390E+05	Baldwin et al. (1967)
22.	$O_3 + M = O_2 + O + M$	0.427E+15	0.000	0.222E+05	Heimerl & Coffee (1979)
23.	$O_3 + O = O_2 + O_2$	0.115E+14	0.000	0.457E+04	Hampson (1973)
24.	$H + O_3 = O_2 + OH$	0.794E+14	0.000	890.	Lee et al. (1978)
25.	$OH + O_3 = HO_2 + O_2$	0.110E+13	0.000	0.185E+05	Ravishankara et al. (1979)
26.	$CO + O + M = CO_2 + M$	0.589E+16	0.000	0.410E+04	Simonaitis & Heicklen (1972)
27.	$CO + O_2 = CO_2 + O$	0.316E+12	0.000	0.376E+05	Baulch et al. (1976)
28.	$CO + OH = CO_2 + H$	0.151E+08	1.30	−0.770	Baulch & Drysdale (1974)
29.	$CO + HO_2 = CO_2 + OH$	0.151E+15	0.000	0.237E+05	Atri et al. (1977)
30.	$CH_2O + M = HCO + H + M$	0.331E+17	0.000	0.810E+05	Dean et al. (1980)
31.	$CH_2O + OH = HCO + H_2O$	0.759E+13	0.000	170.	Atkinson & Pitts (1978)
32.	$CH_2O + H = HCO + H_2$	0.331E+15	0.000	0.105E+05	Dean et al. (1980)
33.	$CH_2O + O = HCO + OH$	0.501E+14	0.000	0.460E+04	Bowman (1975)
34.	$CH_2O + HO_2 = HCO + H_2O_2$	0.200E+12	0.000	0.800E+04	Lloyd (1974)
35.	$HCO + M = H + CO + M$	0.145E+15	0.000	0.190E+05	Westbrook et al. (1977)
36.	$HCO + O_2 = CO + HO_2$	0.302E+13	0.000	0.000E+00	Westbrook et al. (1977)
37.	$HCO + OH = CO + H_2O$	0.100E+15	0.000	0.000E+00	Bowman (1970)
38.	$HCO + H = CO + H_2$	0.200E+15	0.000	0.000E+00	Bowman (1975)
39.	$HCO + O = CO + OH$	0.100E+15	0.000	0.000E+00	Westenberg (1972)
40.	$HCO + HO_2 = CH_2O + O_2$	0.100E+15	0.000	0.300E+04	Baldwin & Walker (1973)
41.	$CH_4 + M = CH_3 + H + M$	0.141E+18	0.000	0.884E+05	Hartig et al. (1971)
42.	$CH_4 + O_2 = CH_3 + HO_2$	0.794E+14	0.000	0.560E+05	Skinner et al. (1972)
43.	$CH_4 + H = CH_3 + H_2$	0.224E+05	3.00	0.875E+04	Clark & Dove (1973)
44.	$CH_4 + OH = CH_3 + H_2O$	0.347E+04	3.08	0.200E+04	Zellner & Steinert (1976)
45.	$CH_4 + O = CH_3 + OH$	0.214E+08	2.21	0.648E+04	Roth & Just (1977)
46.	$CH_4 + HO_2 = CH_3 + H_2O_2$	0.200E+14	0.000	0.180E+05	Skinner et al. (1972)
47.	$CH_3 + O_2 = CH_3O + O$	0.479E+14	0.000	0.290E+05	Brabbs & Brokaw (1975)
48.	$CH_3 + CH_3 = C_2H_6$	0.891E+13	0.000	0.000E+00	Baulch & Duxbury (1980)
49.	$CH_3 + CH_3 = C_2H_5 + H$	0.794E+15	0.000	0.265E+05	Warnatz (1981)
50.	$CH_3 + CH_3 = C_2H_4 + H_2$	0.100E+17	0.000	0.320E+05	Warnatz (1981)

No.	Reaction	Forward rate			Reference
		A	n	Ea	
51.	$CH_3 + O = CH_2O + H$	0.129E+15	0.000	0.200E+04	Peeters & Mahnen (1973)
52.	$CH_3 + OH = CH_2O + H_2$	0.398E+13	0.000	0.000E+00	Fenimore (1969)
53.	$CH_3 + OH = CH_3O + H$	0.200E+17	0.000	0.274E+05	Bhaskaran et al. (1979)
54.	$CH_3 + CH_2O = CH_4 + HCO$	0.100D+11	0.500	0.600E+04	Tunder et al. (1981)
55.	$CH_3 + HCO = CH_4 + CO$	0.302E+12	0.500	0.000E+00	Tunder et al. (1981)
56.	$CH_3 + HO_2 = CH_3O + OH$	0.200E+14	0.000	0.000E+00	Colket et al. (1977)
57.	$CH_3 + M = CH_2 + H + M$	0.195E+17	0.000	0.916E+05	Roth et al. (1979)
58.	$CH_3O + M = CH_2O + H + M$	0.501E+14	0.000	0.210E+05	Brabbs & Brokaw (1975)
59.	$CH_3O + O_2 = CH_2O + HO_2$	0.100E+13	0.000	0.600E+04	Engleman (1976)
60.	$CH_3O + H = CH_2O + H_2$	0.200E+14	0.000	0.000E+00	Hoyermann et al. (1981)
61.	$CH_3O + CH_2O = CH_3OH + HCO$	0.603E+12	0.000	0.330E+04	Pitz et al. (1984)
62.	$CH_3O + CH_4 = CH_3OH + CH_3$	0.200E+12	0.000	0.700E+04	Pitz et al. (1984)
63.	$CH_3O + C_2H_6 = CH_3OH + C_2H_5$	0.302E+12	0.000	0.700E+04	Pitz et al. (1984)
64.	$CH_3O + C_3H_8 = CH_3OH + C_2H_5CH_2$	0.302E+12	0.000	0.700E+04	Pitz et al. (1984)
65.	$CH_3O + C_3H_8 = CH_3OH + C_2H_4CH_3$	0.302E+12	0.000	0.700E+04	Pitz et al. (1984)
66.	$C_2H_6 + O_2 = C_2H_5 + HO_2$	0.100E+14	0.000	0.510E+05	Taylor & Kulich (1973)
67.	$C_2H_6 + CH_3 = C_2H_5 + CH_4$	0.550E+00	4.00	0.828E+04	Clark & Dove (1973)
68.	$C_2H_6 + H = C_2H_5 + H_2$	0.537E+03	3.50	0.520E+04	Clark & Dove (1973)
69.	$C_2H_6 + O = C_2H_5 + OH$	0.110E+15	0.000	0.785E+04	Herron & Huie (1973)
70.	$C_2H_6 + OH = C_2H_5 + H_2O$	0.871E+10	1.05	0.181E+04	Tully et al. (1985)
71.	$C_2H_6 + HO_2 = C_2H_5 + H_2O_2$	0.302E+12	0.000	0.115E+05	Pitz et al. (1984)
72.	$C_2H_5 + M = C_2H_4 + H + M$	0.200E+16	0.000	0.300E+05	Olson et al. (1979)
73.	$C_2H_5 + O_2 = C_2H_4 + HO_2$	0.100E+13	0.000	0.500E+04	Westbrook et al. (1983)
74.	$C_2H_5 + O = CH_3CHO + H$	0.501E+14	0.000	0.000E+00	Warnatz (1981)
75.	$C_2H_5 + O = CH_2O + CH_3$	0.100E+14	0.000	0.000E+00	Hoyermann & Sievert (1979)
76.	$C_2H_5 + C_2H_5 = C_2H_6 + C_2H_4$	0.398E+13	0.000	0.000E+00	Pitz et al. (1984)
77.	$C_2H_5 + C_3H_5 = C_3H_6 + C_2H_4$	0.126E+13	0.000	0.000E+00	Pitz et al. (1984)
78.	$C_2H_5 + CH_3 = C_2H_4 + CH_4$	0.794E+12	0.000	0.000E+00	Pitz et al. (1984)
79.	$C_2H_4 + M = C_2H_2 + H_2 + M$	0.933E+17	0.000	0.772E+05	Franck (1985)
80.	$C_2H_4 + M = C_2H_3 + H + M$	0.631E+19	0.000	0.109E+06	Westbrook et al. (1983)
81.	$C_2H_4 + C_2H_4 = C_2H_3 + C_2H_5$	0.501E+15	0.000	0.647E+05	Benson & Haugen (1967)
82.	$C_2H_3 + M = C_2H_2 + H + M$	0.794E+15	0.000	0.315E+05	Benson & Haugen (1967)
83.	$C_2H_3 + O_2 = C_2H_2 + HO_2$	0.100E+13	0.000	0.100E+05	Westbrook et al. (1983)
84.	$C_2H_3 + CH_3 = C_2H_2 + CH_4$	0.100E+13	0.000	0.000E+00	Pitz et al. (1984)
85.	$C_2H_4 + H = C_2H_3 + H_2$	0.151E+08	2.00	0.600E+04	Westbrook et al. (1983)
86.	$C_2H_4 + OH = C_2H_3 + H_2O$	0.479E+13	0.000	0.123E+04	Westbrook et al. (1983)
87.	$C_2H_4 + O = CH_3 + HCO$	0.331E+13	0.000	0.113E+04	Herron & Huie (1973)
88.	$C_2H_4 + O = CH_2O + CH_2$	0.251E+14	0.000	0.500E+04	Westbrook et al. (1983)
89.	$C_2H_4 + OH = CH_3 + CH_2O$	0.200E+13	0.000	960.	Westbrook et al. (1983)
90.	$C_2H_3 + H = C_2H_2 + H_2$	0.200E+14	0.000	0.250E+04	Tanzawa & Gardiner (1980)
91.	$C_2H_3 + O = CH_2CO + H$	0.331E+14	0.000	0.000E+00	Hoyermann
92.	$C_2H_3 + OH = C_2H_2 + H_2O$	0.501E+13	0.000	0.000E+00	Miller et al. (1983)
93.	$C_2H_3 + C_2H_4 + C_4H_6 + H$	0.100E+13	0.000	0.730E+04	Benson & Haugen (1967)
94.	$C_2H_2 + M = C_2H + H + M$	0.100E+15	0.000	0.114E+06	Tanzawa & Gardiner (1980)
95.	$C_2H_2 + C_2H_2 = C_4H_3 + H$	0.100E+14	0.000	0.450E+05	Tanzawa & Gardiner (1979)
96.	$C_2H_2 + O_2 = HCCO + OH$	0.501E+13	0.000	0.235E+05	Miller et al. (1983)
97.	$C_2H_2 + O_2 = HCO + HCO$	0.398E+13	0.000	0.280E+05	Gardiner & Walker (1968)
98.	$C_2H_2 + H = C_2H + H_2$	0.200E+15	0.000	0.190E+05	Browne et al. (1969)
99.	$C_2H_2 + O = C_2H + OH$	0.316E+16	-0.600	0.170E+05	Browne et al. (1969)
100.	$C_2H_2 + O = CH_2 + CO$	0.676E+14	0.000	0.400E+04	Lohr & Roth (1981)
101.	$C_2H_2 + O = HCCO + H$	0.355E+05	2.70	0.139E+04	Lohr & Roth (1981)
102.	$C_2H_2 + OH = CH_2CO = H$	0.324E+12	0.000	200.	Vandooren & Tiggelen (1977)

No.	Reaction	Forward rate			Reference
		A	n	Ea	
103.	$C_2H_2+OH=C_2H+H_2O$	0.631E+13	0.000	0.700E+04	Browne et al. (1969)
104.	$C_2H_2+OH=CH_3+CO$	0.120E+13	0.000	500.	Smith & Zellner (1973)
105.	$C_2H_2+OH=C_2H_2OH$	0.676E+12	0.000	230.	Miller et al. (1983)
106.	$C_2H_2OH+H=CH_2CO+H_2$	0.200E+14	0.000	0.400E+04	Miller et al. (1983)
107.	$C_2H_2OH+O=CH_2CO+OH$	0.200E+14	0.000	0.400E+04	Miller et al. (1983)
108.	$C_2H_2OH+OH=CH_2CO+H_2O$	0.100E+14	0.000	0.200E+04	Miller et al. (1983)
109.	$C_2H_2OH+O_2=CH_2CO+HO_2$	0.200E+13	0.000	0.100E+05	Miller et al. (1983)
110.	$C_2H_2OH+M=CH_2CO+H+M$	0.501E+16	0.000	0.280E+05	Miller et al. (1983)
111.	$CH_2CO+M=CH_2O+CO+M$	0.200E+17	0.000	0.600E+05	Miller et al. (1983)
112.	$CH_2CO+OH=CH_2O+HCO$	0.282E+14	0.000	0.000E+00	Vandooren & Tiggelen (1977)
113.	$CH_2CO+OH=HCCO+H_2O$	0.759E+13	0.000	0.300E+04	Miller et al. (1983)
114.	$CH_2CO+O=HCCO+OH$	0.501E+14	0.000	0.800E+04	Miller et al. (1983)
115.	$CH_2CO+O=HCO+HCO$	0.100E+14	0.000	0.240E+04	Warnatz (1981)
116.	$CH_2CO+H=HCCO+H_2$	0.759E+14	0.000	0.800E+04	Miller et al. (1983)
117.	$CH_2CO+H=CH_3+CO$	0.110E+14	0.000	0.340E+04	Warnatz (1981)
118.	$HCCO+O_2=CO+CO+OH$	0.631E+12	0.000	0.200E+04	Miller et al. (1983)
119.	$HCCO+O=CO+CO+H$	0.120E+13	0.000	0.000E+00	Jones & Bayes (1973)
120.	$HCCO+O=HCO+CO$	0.100E+14	0.000	0.000E+00	Pitz et al. (1984)
121.	$HCCO+H=CH_2+CO$	0.501E+14	0.000	0.000E+00	Miller et al. (1983)
122.	$HCCO+OH=HCO+H+CO$	0.200E+13	0.000	0.000E+00	Miller et al. (1983)
123.	$HCCO+OH=HCO+HCO$	0.339E+14	0.000	0.200E+04	Pitz et al. (1984)
124.	$HCCO+CH_2=C_2H_3+CO$	0.302E+14	0.000	0.000E+00	Miller et al. (1983)
125.	$CH_2+O_2=CO_2+H_2$	0.162E+13	0.000	0.100E+04	Miller et al. (1983)
126.	$CH_2+O_2=CO_2+H+H$	0.372E+13	0.000	0.150E+04	Miller et al. (1983)
127.	$CH_2+O_2=CO+H_2O$	0.100E+12	0.000	0.000E+00	Miller et al. (1983)
128.	$CH_2+O_2=CO+OH+H$	0.200E+12	0.000	0.000E+00	Miller et al. (1983)
129.	$CH_2+O_2=HCO+OH$	0.100E+15	0.000	0.370E+04	Benson & Haugen (1967)
130.	$CH_2+O=CH+OH$	0.200E+12	0.680	0.250E+05	Mayer et al. (1967)
131.	$CH_2+O=CO+H+H$	0.501E+13	0.000	0.000E+00	Miller et al. (1983)
132.	$CH_2+O=CO+H_2$	0.501E+13	0.000	0.000E+00	Miller et al. (1983)
133.	$CH_2+OH=CH+H_2O$	0.251E+12	0.670	0.257E+05	Peeters & Vinckier (1975)
134.	$CH_2+H=CH+H_2$	0.251E+12	0.670	0.257E+05	Mayer et al. (1967)
135.	$CH_2+CH_2=C_2H_3+H$	0.501E+13	0.000	0.000E+00	Miller et al. (1983)
136.	$CH_2+CH_2=C_2H_2+H_2$	0.316E+14	0.000	0.000E+00	Braun et al. (1970)
137.	$CH_2+C_2H_3=CH_3+C_2H_2$	0.302E+14	0.000	0.000E+00	Miller et al. (1983)
138.	$C_2H+O_2=HCCO+O$	0.331E+13	0.000	0.000E+00	Miller et al. (1983)
139.	$C_2H+O_2=HCO+CO$	0.100E+14	0.000	0.700E+04	Browne et al. (1969)
140.	$C_2H+O=CO+CH$	0.501E+14	0.000	0.000E+00	Browne et al. (1969)
141.	$C_2H+C_2H_3=C_2H_2+C_2H_2$	0.302E+14	0.000	0.000E+00	Miller et al. (1983)
142.	$CH+O_2=HCO+O$	0.100E+14	0.000	0.000E+00	Miller et al. (1983)
143.	$CH+O_2=CO+OH$	0.135E+12	0.670	0.257E+05	Peeters & Vinckier (1975)
144.	$CH+O=CO+H$	0.400E+14	0.000	0.000E+00	Warnatz (1984)
145.	$C_4H_3+M=C_4H_2+H+M$	0.100E+17	0.000	0.600E+05	Tanzawa & Gardiner (1979)
146.	$C_2H_2+C_2H=C_4H_2+H$	0.398E+14	0.000	0.000E+00	Lange & Wagner (1975)
147.	$C_4H_2+M=C_4H+H+M$	0.347E+18	0.000	0.800E+05	Tanzawa & Gardiner (1979)
148.	$CH_3OH+M=CH_3+OH+M$	0.302E+19	0.000	0.800E+05	Westbrook & Dryer (1979)
149.	$CH_3OH+O_2=CH_2OH+HO_2$	0.398E+11	0.000	0.509E+05	Aronowitz et al. (1979)
150.	$CH_3OH+H=CH_3+H_2O$	0.525E+13	0.000	0.534E+04	Westbrook & Dryer (1979)
151.	$CH_3OH+H=CH_2OH+H_2$	0.302E+14	0.000	0.700E+04	Westbrook & Dryer (1979)
152.	$CH_3OH+OH=CH_2OH+H_2O$	0.398E+13	0.000	0.200E+04	Westbrook & Dryer (1979)
153.	$CH_3OH+O=CH_2OH+OH$	0.170E+13	0.000	0.229E+04	LeFevre et al. (1972)
154.	$CH_3OH+CH_3=CH_2OH+CH_4$	0.182E+12	0.000	0.980E+04	Gray & Herod (1968)

No.	Reaction	Forward rate			Reference
		A	n	Ea	
155.	$CH_3OH + HO_2 = CH_2OH + H_2O_2$	0.631E+13	0.000	0.194E+05	Aronowitz et al. (1979)
156.	$CH_2OH + M = CH_2O + H + M$	0.251E+14	0.000	0.290E+05	Westbrook & Dryer (1979)
157.	$CH_2OH + O_2 = CH_2O + HO_2$	0.100E+13	0.000	0.600E+04	Aronowitz et al. (1979)
158.	$CH_2OH + H = CH_2O + H_2$	0.302E+13	0.000	0.000E+00	Hoyermann et al. (1981)
159.	$C_2H_5OH + M = CH_3 + CH_2OH + M$	0.302E+19	0.000	0.755E+05	Natarajan & Bhaskaran (1981)
160.	$C_2H_5OH + O_2 = CH_3CHOH + HO_2$	0.398E+11	0.000	0.500E+05	Westbrook & Dryer (1984)
161.	$C_2H_5OH + OH = CH_3CHOH + H_2O$	0.302E+14	0.000	0.596E+04	Natarajan & Bhaskaran (1981)
162.	$C_2H_5OH + H = CH_3CHOH + H_2$	0.437E+13	0.000	0.457E+04	Aders & Wagner (1973)
163.	$C_2H_5OH + O = CH_3CHOH + OH$	0.676E+13	0.000	0.151E+04	Ayub & Roscoe (1979)
164.	$C_2H_5OH + HO_2 = CH_3CHOH + H_2O_2$	0.631E+13	0.000	0.150E+05	Westbrook & Dryer (1984)
165.	$C_2H_5OH + CH_3 = CH_3CHOH + CH_4$	0.398E+13	0.000	0.969E+04	Kerr & Parsonage (1976)
166.	$CH_3CHOH + M = CH_3CHO + H + M$	0.501E+14	0.000	0.219E+05	Natarajan & Bhaskaran (1981)
167.	$CH_3CHOH + O_2 = CH_3CHO + HO_2$	0.100E+14	0.000	0.556E+04	Natarajan & Bhaskaran (1981)
168.	$C_2H_5OH + H = C_2H_5 + H_2O$	0.525E+13	0.000	0.500E+04	Westbrook & Dryer (1984)
169.	$CH_3CHO = CH_3 + HCO$	0.708E+16	0.000	0.818E+05	Colket et al. (1977)
170.	$CH_3CHO = CH_3CO + H$	0.501E+15	0.000	0.879E+05	Kerr (1966)
171.	$CH_3CHO + O_2 = CH_3CO + HO_2$	0.200E+14	0.500	0.422E+05	Colket et al. (1977)
172.	$CH_3CHO + H = CH_3CO + H_2$	0.398E+14	0.000	0.420E+04	Warnatz (1981)
173.	$CH_3CHO + OH = CH_3CO + H_2O$	0.100E+14	0.000	0.000E+00	Warnatz (1981)
174.	$CH_3CHO + O = CH_3CO + OH$	0.501E+13	0.000	0.179E+04	Warnatz (1981)
175.	$CH_3CHO + CH_3 = CH_2CO + CH_4$	0.759E+13	0.000	0.800E+04	Ushimaru et al. (1985)
176.	$CH_3CHO + HO_2 = CH_3CO + H_2O_2$	0.851E+12	0.000	0.107E+05	Colket et al. (1977)
177.	$CH_3CHO + CH_3 = CH_2CHO + CH_4$	0.550E+00	4.00	0.828E+04	Colket (1975)
178.	$CH_3CO = CH_3 + CO$	0.302E+14	0.000	0.172E+05	Watkins & Word (1974)
179.	$C_3H_8 = C_2H_5 + CH_3$	0.170E+17	0.000	0.848E+05	Westbrook & Pitz (1985)
180.	$C_3H_8 + O_2 = C_2H_4CH_3 + HO_2$	0.398E+14	0.000	0.475E+05	Walker (1977)
181.	$C_3H_8 + O_2 = C_2H_5CH_2 + HO_2$	0.398E+14	0.000	0.475E+05	Walker (1977)
182.	$C_2H_4CH_3 + C_3H_8 = C_2H_5CH_2 + C_3H_8$	0.316E+11	0.000	0.129E+05	Pitz et al. (1984)
183.	$C_3H_8 + H = C_2H_4CH_3 + H_2$	0.871E+07	2.00	0.500E+04	Westbrook & Pitz (1985)
184.	$C_3H_8 + H = C_2H_5CH_2 + H_2$	0.562E+08	2.00	0.770E+04	Westbrook Pitz (1985)
185.	$C_3H_8 + CH_3 = C_2H_4CH_3 + CH_4$	0.110E+16	0.000	0.251E+05	Hautman et al. (1981)
186.	$C_3H_8 + CH_3 = C_2H_5CH_2 + CH_4$	0.110E+16	0.000	0.251E+05	Hautman et al. (1981)
187.	$C_3H_8 + C_2H_3 = C_2H_4CH_3 + C_2H_4$	0.100E+12	0.000	0.104E+05	Hautman et al. (1981)
188.	$C_3H_8 + C_2H_3 = C_2H_5CH_2 + C_2H_4$	0.100E+12	0.000	0.104E+05	Hautman et al. (1981)
189.	$C_3H_8 + C_2H_5 = C_2H_4CH_3 + C_2H_6$	0.100E+12	0.000	0.104E+05	Hautman et al. (1981)
190.	$C_3H_8 + C_2H_5 = C_2H_5CH_2 + C_2H_6$	0.100E+12	0.000	0.104E+05	Hautman et al. (1981)
191.	$C_3H_8 + C_3H_5 = C_2H_4CH_3 + C_3H_6$	0.794E+12	0.000	0.162E+05	Hautman et al. (1981)
192.	$C_3H_8 + C_3H_5 = C_2H_5CH_2 + C_3H_6$	0.794E+12	0.000	0.162E+05	Hautman et al. (1981)
193.	$C_3H_8 + O = C_2H_4CH_3 + OH$	0.282E+14	0.000	0.520E+04	Westbrook & Pitz (1985)
194.	$C_3H_8 + O = C_2H_5CH_2 + OH$	0.112E+15	0.000	0.785E+04	Westbrook & Pitz (1985)
195.	$C_3H_8 + OH = C_2H_4CH_3 + H_2O$	0.479E+09	1.40	850.	Tully et al. (1985)
196.	$C_3H_8 + OH = C_2H_5CH_2 + H_2O$	0.479E+09	1.40	850.	Tully et al. (1985)
197.	$C_3H_8 + HO_2 = C_2H_4CH_3 + H_2O_2$	0.339E+13	0.000	0.170E+05	Westbrook & Pitz (1985)
198.	$C_3H_8 + HO_2 = C_2H_5CH_2 + H_2O_2$	0.112E+14	0.000	0.194E+05	Westbrook & Pitz (1985)
199.	$C_2H_5CH_2 = C_2H_4 + CH_3$	0.955E+14	0.000	0.310E+05	Kerr & Trotman-Dickenson (1959)
200.	$C_2H_5CH_2 = C_3H_6 + H$	0.126E+15	0.000	0.370E+05	Kerr & Trotman-Dickenson (1959)
201.	$C_2H_4CH_3 = C_2H_4 + CH_3$	0.200E+11	0.000	0.295E+05	Westbrook & Pitz (1985)
202.	$C_2H_4CH_3 = C_3H_6 + H$	0.631E+14	0.000	0.369E+05	Jackson & McNesby (1961)
203.	$C_2H_5CH_2 + O_2 = C_3H_6 + HO_2$	0.100E+13	0.000	0.500E+04	Westbrook & Pitz (1985)
204.	$C_2H_4CH_3 + O_2 = C_3H_6 + HO_2$	0.100E+13	0.000	0.500E+04	Westbrook & Pitz (1985)
205.	$C_3H_6 = C_3H_5 + H$	0.100E+14	0.000	0.780E+05	Szwarc (1949)
206.	$C_3H_6 = C_2H_3 + CH_3$	0.631E+16	0.000	0.858E+05	Warnatz (1981)

No.	Reaction	Forward rate			Reference
		A	n	Ea	
207.	$C_3H_6+O=CH_2O+C_2H_4$	0.589E+14	0.000	0.500E+04	Westbrook & Pitz (1985)
208.	$C_3H_6+O=CH_3+CH_3CO$	0.118E+14	0.000	600.	Warnatz (1981)
209.	$C_3H_6+OH=CH_3+CH_3CHO$	0.347E+12	0.000	0.000E+00	Warnatz (1981)
210.	$C_3H_6+O=C_2H_5+HCO$	0.355E+13	0.000	0.000E+00	Huie & Herron (1978)
211.	$C_3H_6+OH=C_3H_5+H_2O$	0.398E+13	0.000	0.000E+00	Westbrook & Pitz (1985)
212.	$C_3H_6+OH=C_2H_5+CH_2O$	0.794E+13	0.000	0.000E+00	Cathonnet et al. (1981)
213.	$C_3H_6+H=C_3H_5+H_2$	0.501E+13	0.000	0.150E+04	Westbrook & Pitz (1985)
214.	$C_3H_6+CH_3=C_3H_5+CH_4$	0.891E+11	0.000	0.850E+04	Cvetanovic & Irwin (1967)
215.	$C_3H_6+C_2H_5=C_3H_5+C_2H_6$	0.100E+12	0.000	0.920E+04	Sundaram & Froment (1978)
216.	$C_2H_5C_2H_5=C_2H_5+C_2H_5$	0.200E+17	0.000	0.813E+05	Allara & Edelson (1975)
217.	$C_2H_5C_2H_5=C_2H_5CH_2+CH_3$	0.100E+18	0.000	0.854E+05	Allara & Edelson (1975)
218.	$C_2H_5C_2H_5+O_2=C_3H_6CH_3+HO_2$	0.398E+14	0.000	0.476E+05	Walker (1977)
219.	$C_2H_5C_2H_5+O_2=C_2H_5C_2H_4+HO_2$	0.251E+14	0.000	0.490E+05	Pitz et al. (1984)
220.	$C_2H_5C_2H_5+H=C_2H_5C_2H_4+H_2$	0.562E+08	2.00	0.770E+04	Walker (1977)
221.	$C_2H_5C_2H_5+H=C_3H_6CH_3+H_2$	0.174E+08	2.00	0.500E+04	Walker (1977)
222.	$C_2H_5C_2H_5+O=C_2H_5C_2H_4+OH$	0.112E+15	0.000	0.785E+04	Walker (1977)
223.	$C_2H_5C_2H_5+O=C_3H_6CH_3+OH$	0.562E+14	0.000	0.520E+04	Walker (1977)
224.	$C_2H_5C_2H_5+OH=C_2H_5C_2H_4+H_2O$	0.257E+10	1.05	0.181E+04	Walker (1977)
225.	$C_2H_5C_2H_5+OH=C_3H_6CH_3+H_2O$	0.257E+10	1.25	700.	Walker (1977)
226.	$C_2H_5C_2H_5+HO_2=C_2H_5C_2H_4+H_2O_2$	0.112E+14	0.000	0.194E+05	Walker (1977)
227.	$C_2H_5C_2H_5+HO_2=C_3H_6CH_3+H_2O_2$	0.676E+13	0.000	0.170E+05	Walker (1977)
228.	$C_2H_5C_2H_5+CH_3=C_2H_5C_2H_4+CH_4$	0.129E+13	0.000	0.116E+05	Walker (1977)
229.	$C_2H_5C_2H_5+CH_3=C_3H_6CH_3+CH_4$	0.794E+12	0.000	0.950E+04	Walker (1977)
230.	$C_2H_5C_2H_5+CH_3O=C_2H_5C_2H_4+CH_3OH$	0.302E+12	0.000	0.700E+04	Pitz et al. (1984)
231.	$C_2H_5C_2H_5+CH_3O=C_3H_6CH_3+CH_3OH$	0.603E+12	0.000	0.700E+04	Pitz et al. (1984)
232.	$C_2H_5C_2H_5+C_2H_3=C_2H_5C_2H_4+C_2H_4$	0.100E+13	0.000	0.180E+05	Sundaram & Froment (1978)
233.	$C_2H_5C_2H_5+C_2H_3=C_3H_6CH_3+C_2H_4$	0.794E+12	0.000	0.168E+05	Sundaram & Froment (1978)
234.	$C_2H_5C_2H_5+C_2H_5=C_2H_5C_2H_4+C_2H_6$	0.100E+12	0.000	0.134E+05	Cathonnet et al. (1981)
235.	$C_2H_5C_2H_5+C_2H_5=C_3H_6CH_3+C_2H_6$	0.100E+12	0.000	0.104E+05	Allara & Edelson (1975)
236.	$C_2H_5C_2H_5+C_3H_5=C_2H_5C_2H_4+C_3H_6$	0.398E+12	0.000	0.188E+05	Sundaram & Froment (1978)
237.	$C_2H_5C_2H_5+C_3H_5=C_3H_6CH_3+C_3H_6$	0.794E+12	0.000	0.168E+05	Sundaram & Froment (1978)
238.	$C_3H_7CH_3+H=C_3H_6CH_3+H_2$	0.210E+15	0.000	0.150E+05	Warnatz (1984)
239.	$C_3H_7CH_3+O=C_3H_6CH_3+OH$	0.470E+14	0.000	0.389E+04	Warnatz (1984)
240.	$C_3H_7CH_3+OH=C_3H_6CH_3+H_2O$	0.580E+13	0.000	620.	Warnatz (1984)
241.	$C_3H_7CH_3+HO_2=C_3H_6CH_3+H_2O_2$	0.440E+13	0.000	0.153E+05	Warnatz (1984)
242.	$C_3H_7CH_3+CH_3=C_3H_6CH_3+CH_4$	0.950E+11	0.000	0.790E+04	Warnatz (1984)
243.	$C_3H_7CH_3=C_2H_4CH_3+CH_3$	0.400E+17	0.000	0.828E+05	Warnatz (1984)
244.	$C_2H_5C_2H_4=C_2H_5+C_2H_4$	0.252E+14	0.000	0.288E+05	Warnatz (1984)
245.	$C_2H_5C_2H_4=C_3H_6CH_2+H$	0.126E+14	0.000	0.386E+05	Pitz et al. (1984)
246.	$C_3H_6CH_3=C_3H_6+CH_3$	0.200E+15	0.000	0.332E+05	Pitz et al. (1984)
247.	$C_3H_6CH_3=C_3H_6CH_2+H$	0.200E+14	0.000	0.404E+05	Sundaram & Froment (1978)
248.	$C_3H_6CH_3=C_2H_5C_2H_3+H$	0.200E+14	0.000	0.398E+05	Sundaram & Froment (1978)
249.	$C_2H_5C_2H_4+O_2=C_3H_6CH_2+HO_2$	0.100E+13	0.000	0.200E+04	Baker et al. (1975)
250.	$C_3H_6CH_3+O_2=C_3H_6CH_2+HO_2$	0.100E+13	0.000	0.450E+04	Baker et al. (1975)
251.	$C_3H_6CH_3+O_2=C_2H_5C_2H_3+HO_2$	0.200E+13	0.000	0.425E+04	Baker et al. (1975)
252.	$C_3H_6CH_2+H=C_4H_7+H2$	0.501E+14	0.000	0.390E+04	Sundaram & Froment (1978)
253.	$C_2H_5C_2H_3+H=C_4H_7+H_2$	0.501E+14	0.000	0.380E+04	Sundaram & Froment (1978)
254.	$C_3H_6CH_2+O=C_3H_6+CH_2O$	0.501E+13	0.000	0.000E+00	Huie & Herron (1978)
255.	$C_2H_5C_2H_3+O=C_2H_5CH_2+HCO$	0.603E+13	0.000	0.000E+00	Huie & Herron (1978)
256.	$C_3H_6CH_2+OH=C_2H_5CH_2+CH_2O$	0.182E+14	0.000	0.000E+00	Ravishankara et al. (1978)
257.	$C_2H_5C_2H_3+OH=C_2H_5+CH_3CHO$	0.257E+14	0.000	0.000E+00	Ravishankara et al. (1978)
258.	$C_3H_6CH_2+CH_3=C_4H_7+CH_4$	0.100E+12	0.000	0.000E+00	Sundaram & Froment (1978)

No.	Reaction	Forward rate			Reference
		A	n	Ea	
259.	$C_2H_5C_2H_3+CH_3=C_4H_7+CH_4$	0.100E+12	0.000	0.820E+04	Sundaram & Froment (1978)
260.	$C_2H_5C_2H_3+O=C_2H_5+CH_3CO$	0.129E+14	0.000	0.850E+04	Warnatz (1981)
261.	$C_4H_7+M=C_4H_6+H+M$	0.120E+15	0.000	0.493E+05	Sundaram & Froment (1978)
262.	$C_4H_7+M=C_2H_4+C_2H_3+M$	0.100E+12	0.000	0.370E+05	Sundaram & Froment (1978)
263.	$C_4H_7+C_4H_7=C_3H_6CH_2+C_4H_6$	0.158E+13	0.000	0.000E+00	Allara & Edelson (1975)
264.	$C_4H_7+C_4H_7=C_2H_5C_2H_3+C_4H_6$	0.158E+13	0.000	0.000E+00	Allara & Edelson (1975)
265.	$C_4H_7+CH_3=C_4H_6+CH_4$	0.794E+13	0.000	0.000E+00	Allara & Edelson (1975)
266.	$C_3H_6CH_2=C_3H_5+CH_3$	0.151E+20	−1.00	0.734E+05	Pitz et al. (1984)
267.	$C_3H_6CH_2=C_2H_3+C_2H_5$	0.100E+20	−1.00	0.968E+05	Pitz et al. (1984)
268.	$C_3H_6CH_2+O=C_2H_4+CH_3CHO$	0.129E+14	0.000	850.	Pitz et al. (1984)
269.	$C_3H_6CH_2+OH=C_2H_5+CH_3CHO$	0.100E+14	0.000	0.000E+00	Pitz et al. (1984)
270.	$C_3H_6CH_2+OH=CH_3CO+C_2H_6$	0.100E+14	0.000	0.000E+00	Pitz et al. (1984)
271.	$C_3H_6CH_2=C_4H_7+H$	0.407E+19	−1.00	0.974E+05	Pitz et al. (1984)
272.	$C_2H_5C_2H_3=C_4H_7+H$	0.407E+19	−1.00	0.974E+05	Pitz et al. (1984)
273.	$C_2H_5C_2H_3+O=C_2H_4+CH_3CHO$	0.100E+13	0.000	0.000E+00	Pitz et al. (1984)
274.	$C_3H_6CH_2+OH=C_4H_7+H_2O$	0.479E+13	0.000	0.123E+04	Pitz et al. (1984)
275.	$C_4H_7+O_2=C_4H_6+HO_2$	0.100E+12	0.000	0.000E+00	Pitz et al. (1984)
276.	$C_4H_7+H=C_4H_6+H_2$	0.316E+14	0.000	0.000E+00	Pitz et al. (1984)
277.	$C_4H_7+C_2H_3=C_4H_6+C_2H_4$	0.398E+13	0.000	0.000E+00	Pitz et al. (1984)
278.	$C_4H_7+C_2H_5=C_4H_6+C_2H_6$	0.398E+13	0.000	0.000E+00	Pitz et al. (1984)
279.	$C_4H_7+C_2H_5=C_3H_6CH_2+C_2H_4$	0.501E+12	0.000	0.000E+00	Pitz et al. (1984)
280.	$C_4H_7+C_2H_5=C_2H_5C_2H_3+C_2H_4$	0.501E+12	0.000	0.000E+00	Pitz et al. (1984)
281.	$C_4H_7+C_3H_5=C_4H_6+C_3H_6$	0.631E+13	0.000	0.000E+00	Pitz et al. (1984)
282.	$C_4H_6=C_2H_3+C_2H_3$	0.398E+14	−1.00	0.982E+05	Pitz et al. (1984)
283.	$C_4H_6+OH=C_2H_5+CH_2CO$	0.100E+13	0.000	0.000E+00	Pitz et al. (1984)
284.	$C_4H_6+OH=C_3H_5+CH_2O$ ·	0.100E+13	0.000	0.000E+00	Pitz et al. (1984)
285.	$C_4H_6+OH=C_2H_3+CH_3CHO$	0.100E+13	0.000	0.000E+00	Pitz et al. (1984)
286.	$C_4H_6+O=C_2H_4+CH_2CO$	0.100E+13	0.000	0.000E+00	Pitz et al. (1984)
287.	$C_4H_6+O=CH_2CCH_2+CH_2O$	0.100E+13	0.000	0.000E+00	Pitz et al. (1984)
288.	$C_4H_6+O=CH_3CCH+CH_2O$	0.100E+13	0.000	0.000E+00	Pitz et al. (1984)
289.	$C_3H_5+O_2=CH_3CCH+HO_2$	0.603E+12	0.000	0.100E+05	Westbrook & Pitz (1985)
290.	$C_3H_5+O_2=CH_2CCH_2+HO_2$	0.603E+12	0.000	0.100E+05	Westbrook & Pitz (1985)
291.	$C_3H_5+H=CH_3CCH+H_2$	0.100E+14	0.000	0.000E+00	Westbrook & Pitz (1985)
292.	$C_3H_5+H=CH_2CCH_2+H_2$	0.100E+14	0.000	0.000E+00	Westbrook & Pitz (1985)
293.	$C_3H_5+CH_3=CH_3CCH+CH_4$	0.100E+13	0.000	0.000E+00	Westbrook & Pitz (1985)
294.	$C_3H_5+CH_3=CH_2CCH_2+CH_4$	0.100E+13	0.000	0.000E+00	Westbrook & Pitz (1985)
295.	$CH_3CCH+H=C_3H_5$	0.200E+14	0.000	0.239E+04	Warnatz (1984)
296.	$CH_2CCH_2+H=C_3H_5$	0.120E+14	0.000	0.210E+04	Warnatz (1984)
297.	$CH_3CCH+O=CH_2O+C_2H_2$	0.150E+14	0.000	0.210E+04	Warnatz (1984)
298.	$CH_3CCH+O=HCO+C_2H_3$	0.150E+14	0.000	0.210E+04	Warnatz (1984)
299.	$CH_3CCH+OH=CH_2O+C_2H_3$	0.500E+13	0.000	0.129E+04	Warnatz (1984)
300.	$CH_3CCH+OH=HCO+C_2H_4$	0.500E+13	0.000	0.129E+04	Warnatz (1984)
301.	$CH_2CCH_2+OH=CH_2O+C_2H_3$	0.270E+12	0.000	0.000E+00	Warnatz (1984)
302.	$CH_2CCH_2+OH=HCO+C_2H_4$	0.270E+12	0.000	0.000E+00	Warnatz (1984)