Reaction Rate Analysis of Complex Kinetic Systems

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Abstract

Using the elementary sensitivity densities, a reaction rate sensitivity gradient is obtained which is the derivative of the rate of species concentration change with respect to the rate coefficient. The dimensionless (log-normalized) form of the reaction rate sensitivity gradient is the ratio of the rate of concentration change of species i due to elementary reaction j and the net rate of concentration change of species i. This result provides a mathematical basis for the use of various forms of reaction rate analyses in the study of complex reaction mechanisms. The kinetic information inherent in the relative reaction rate matrix is extracted by principal component analysis. The method is used to analyze the mechanism of high-temperature formaldehyde oxidation and high-temperature propane pyrolysis. Ranking of the elementary reactions allowed us to reduce significantly the original mechanisms and a detailed study of the results revealed the reaction structures and the major reaction paths of the species.

Introduction

Mathematical models of reaction mechanisms are used more and more widely in the investigation of complex chemical systems. The results derived from such models depend considerably on the appropriate selection of the elementary steps comprising the reaction mechanism and on the input data, first of all on the accuracy of the rate coefficients of the elementary reactions. Thus, it is of essential importance to establish the relationship between the model predictions and the values of kinetic parameters for given experimental conditions. A rigorous ranking of the elementary reactions provides a basis for mechanism reduction, that is for selecting the reactions which are

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unimportant under the given circumstances and may be eliminated from the scheme without significant loss of information.

Comparison of rates of competing reactions was and is often used as a means of selecting important reactions for reactive species. Furthermore, analysis of the "rate spectrum," i.e., the set of the logarithmic rates of all elementary reactions, was suggested as a possible method for constructing a reduced reaction mechanism. However, the role of the various elementary reactions of a complex process may be very different in influencing the overall kinetics or in determining certain kinetic features of the reaction system. Therefore, a simple comparison of the rates of different types of reactions is naturally inadequate.

Progress has been made by comparing rates only within selected groups of reactions. Thus Edelson and Allara [1] carried out preliminary screening of a 500-step model of "low-temperature" alkane pyrolysis by analyzing reactions in seven categories: initiation, radical decomposition and isomerization, hydrogen transfer, radical addition, recombination and disproportionation. Any reaction which did not contribute at least 0.1% of the flux within its category was removed from the scheme. Disadvantages occur in the mechanism reduction as a result of disintegration of the kinetic scheme into separated reaction categories. This may cause loss of information if categorization separates elementary reactions which belong to a certain kinetic structure. (The competitions between chain propagation and termination steps or between propagation and inhibition reactions constitute for instance such structures.)

A study of the mechanism of high-temperature propane pyrolysis by Lifshitz and Frenklach [2] considered the reactions of five free radicals. For each of these radicals, the rates of decomposition, atom transfer, and recombination were compared and the reactions were omitted which had small contributions to the net disappearance rate of the given free radical.

More sophisticated treatments of reaction rate analysis consider the contributions from each individual elementary reaction to the rate of production or to the rate of loss of the appropriate species. Such treatments, referred to as rate-of-production analysis [3], reaction path analysis, or screening analysis [4] were used expeditiously in analyzing reaction mechanisms and in revealing the pathways by which the various species are formed or consumed.

A different approach to mechanism reduction may be based on the relationship between model predictions and values of the kinetic parameters. Such relationships are detected by sensitivity analysis. The concentration sensitivity gradient defined [5] as the partial derivative of species concentration with respect to the kinetic parameter is often introduced in sensitivity analysis. This $s_{ij} = \partial c_i/\partial k_j$ quantity, which will be referred to hereafter as the concentration sensitivity coefficient, is a measure of the response of the species concentration to

the perturbation in the parameter. Thus, the s_{ij} coefficients are connected by definition to a time interval. However, the study of mechanistic problems should be based rather on local sensitivity analysis using instantaneous sensitivity coefficients. In this article we use the functional analysis approach and the so called "elementary sensitivity densities" [6] to show that a sensitivity analysis which meets these requirements is based on the analysis of the reaction rates. Principal component analysis [7] is then applied to extract the kinetic information from the relative reaction rate matrix.

Concentration Sensitivity Analysis

Consider a spatially homogeneous isothermal chemical system represented by a set of ordinary kinetic differential equations,

$$\frac{d\underline{c}}{dt} = f(\underline{k}, \underline{c}), \tag{1}$$

where $\underline{c}(t)$ is the n-vector of species concentrations with $\underline{c}(t = 0) = \underline{c}^\circ$ and $\underline{k}$ is the m-vector of kinetic parameters. In a usual kinetic system, the concentration vector $\underline{c}$ at a given time t_2 can be obtained as the solution of the system of kinetic differential equations (1) for a set of kinetic parameters $\underline{k}^\circ$. When the kinetic parameters are changed from $\underline{k}^\circ$ to $\underline{k}$ at time t_1, this perturbation causes a change in the solution at t_2 (where $t_1 < t_2$). The basic quantity used in local concentration sensitivity analysis to express the effect of parameter perturbation is the sensitivity coefficient:

$$s_{ij}\,(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2) = \frac{\partial c_i(t_2)}{\partial k_j} \tag{2}$$

In the first order approximation, the concentration sensitivity defined by eq. (2) represents the magnitude of the deviation in the concentration of species i at time t_2 caused by the variation of the parameter of reaction j at time t_1 from value k_j° to k_j.

The sensitivity coefficient in the log-normalized form,

$$\bar{s}_{ij}(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2) = \frac{k_j^\circ}{c_i(t_2)} \frac{\partial c_i(t_2)}{\partial k_j} = \frac{\partial \ell n\, c_i(t_2)}{\partial \ell n\, k_j} \tag{3}$$

is shown [5] to measure the relative importance of reaction j in influencing the concentration of species i.

Both s_{ij} and $\bar{s}_{ij}$ depend on the species concentrations; they change in an usual kinetic experiment as reaction proceeds, thus sensitivity coefficients are functions of reaction time. However, another time dependence is also inherent in the concentration sensitivities by virtue of their derivation, since sensitivity coefficients are obtained by integration of the sensitivity equations from t_1 to t_2 (or by equivalent pro-

cedures). Thus, the results depend on the choice of time limits t_1 and t_2 (where $t_1 < t_2$, and $t_1 = 0$ or $t_1 \neq 0$). Consequently, the concentration sensitivity matrix $\bar{S}$ carries information on the relative importance of elementary reactions for a time period $[t_1, t_2]$ rather than for a single reaction time.

Reaction Rate Analysis

The kinetics of a complex chemical reaction at a given stage of the process is determined unequivocally by the kinetic standard parameters of the state (i.e., by the rate coefficients and the actual species concentrations). This fact should be taken into account when selecting a quantity for use in the investigation of mechanistic problems. It appears that a quantity which meets this requirement can be obtained by adopting the functional analysis approach to sensitivity theory [8] and using the concept of elementary sensitivity density [6]. The latter is given for the spatially homogeneous system described by eq. (1), as

$$d_{ij}(\underline{k}^\circ, \underline{c}^\circ, t', t_2) = \frac{\delta c_i(t_2)}{\delta k_j(t')} \tag{4}$$

where $\delta c_i(t_2)$ represents a change in concentration at time t_2 as a result of a small parameter perturbation $\delta k_j(t')$ at time $t'(t' < t_2)$. The concentration sensitivity coefficient is related to d_{ij} by the relation

$$s_{ij}(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2) = \int_{t_1}^{t_2} d_{ij}(\underline{k}^\circ, \underline{c}^\circ, t', t_2)\, dt' \tag{5}$$

Using the matrix notation

$$S(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2) = \int_{t_1}^{t_2} D(\underline{k}^\circ, \underline{c}^\circ, t', t_2)\, dt \tag{6}$$

Differentiation of the kinetic equations (1) with respect to the kinetic parameters yields the sensitivity equations

$$\frac{ds_{ij}(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2)}{dt} = \sum_{\ell=1}^{n} \frac{\partial f_i(t_2)}{\partial c_\ell} s_{\ell j}(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2) + \frac{\partial f_i(t_2)}{\partial k_j} \tag{7}$$

with the initial conditions $s_{ij} = 0$ if $t_1 = t_2$. Introducing the matrices

$$[J(\underline{k}^\circ, \underline{c}^\circ, t_2)]_{ij} = \frac{\partial f_i(t_2)}{\partial c_j} \tag{8}$$

and

$$[F(\underline{k}^\circ, \underline{c}^\circ, t_2)]_{ij} = \frac{\partial f_i(t_2)}{\partial k_j} \tag{9}$$

one can write eq. (7) in the concise form,

$$\frac{dS(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2)}{dt} = J(\underline{k}^\circ, \underline{c}^\circ, t_2)S(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2) + F(\underline{k}^\circ, \underline{c}^\circ, t_2) \tag{10}$$

with the initial condition $S = 0$ if $t_1 = t_2$.

Along a $\underline{c}(\underline{k}^\circ, \underline{c}^\circ, t)$ trajectory eq. (10) is a time variable linear system and its solution is given by

$$S(\underline{k}^\circ, \underline{c}^\circ, t_1, t_2) = \int_{t_1}^{t_2} G(t', t_2)F(\underline{k}^\circ, \underline{c}^\circ, t')\,dt' \tag{11}$$

where $G(t', t_2)$ is the Green's function [9]. For $t_2 < t'$ $G(t', t_2) = \underline{0}$, whereas for $t_2 \geqq t'$ $\underline{G}$ satisfies the equation

$$\frac{\mathrm{d}G(t', t_2)}{dt} = J(\underline{k}^\circ, \underline{c}^\circ, t_2)G(t', t_2) \tag{12}$$

with the initial condition

$$G(t', t') = I \tag{13}$$

Comparison of eq. (6) and (11) shows that the sensitivity densities are given by

$$D(\underline{k}^\circ, \underline{c}^\circ, t', t_2) = G(t', t_2)F(\underline{k}^\circ, \underline{c}^\circ, t') \tag{14}$$

The matrix $D(\underline{k}, \underline{c}, t', t_2)$ provides a measure of reaction significances over an interval $[t', t_2]$, where $t' \leqq t_2$. Since we are looking for a local measure of sensitivity, it seems to be obvious to consider the limiting value of D corresponding to $t' \to t_2$. Thus from eq. (13) and (14) it follows that

$$\lim_{t' \to t_2} D(\underline{k}^\circ, \underline{c}^\circ, t', t_2) = D(\underline{k}^\circ, \underline{c}^\circ) = F(\underline{k}^\circ, \underline{c}^\circ) \tag{15}$$

The final result formulated in eq. (15) indicates that the $F(\underline{k}^\circ, \underline{c}^\circ, t_2)$ matrix defined by eq. (9) carries information on the relative importance of the elementary reactions constituting the reaction system.

In order to reformulate our conclusion in a dimensionless form, the log-normalized matrix F will be applied:

$$[\tilde{F}(\underline{k}^\circ, \underline{c}^\circ, t_2)]_{ij} = \frac{k_j^\circ}{f_i(t_2)} \frac{\partial f_i(t_2)}{\partial k_j} \tag{16}$$

In this definition, the right hand sides of the kinetic differential equations occur which are given by

$$f_i(\underline{k}, \underline{c}) = \sum_{j=1}^{p} \nu_{ij} R_j = \sum_{j=1}^{p} \nu_{ij} k_j r_j(\underline{c})\,, \tag{17}$$

where $R_j = k_j r_j(\underline{c})$ and $r_j(\underline{c})$ are the reaction rate and the product of reactant concentrations for reaction j, respectively, and ν_{ij} designates

the stoichiometric coefficient for species i in reaction j. Therefore, the $\tilde{F}$ matrix elements, $\tilde{\phi}_{ij}$, may be expressed as

$$\tilde{\phi}_{ij}(\underline{k},\underline{c}) = [\tilde{F}(\underline{k},\underline{c})]_{ij} = \frac{k_j}{f_i(k,c)}\frac{\partial f_i(\underline{k},\underline{c})}{\partial k_j} = \frac{\nu_{ij}R_j(\underline{k},\underline{c})}{\sum_{j=1}^{p}\nu_{ij}R_j(\underline{k},\underline{c})} = \frac{\nu_{ij}R_j}{f_i} \tag{18}$$

According to eq. (18), the matrix element $\tilde{\phi}_{ij}$, which can be considered as a certain kind of a rate sensitivity coefficient* is the ratio of the rate of formation or consumption of species i in reaction j and the net rate of concentration change of species i. $\tilde{\phi}_{ij}$ may have a positive or negative value less than or greater than unity. The value of $\tilde{\phi}_{ij}$ is 0 if species i is neither a reactant nor a product of reaction j. $\tilde{\phi}_{ij}$ is to some extent similar to the quantity used in other treatments of reaction rate analysis as for instance in rate-of-production analysis [3], reaction path analysis, or screening analysis [4], which consider the contribution of reaction j to the net rate of production or net rate of consumption of species i. However, this contribution is by definition always positive and ≤ 1.

Derivation of Kinetic Information

Kinetic information will be obtained from matrix $\tilde{F}$ by principal component analysis [7,11]. The basic concept in principal component analysis is a response function which is formulated here in our reaction rate considerations as

$$Q(\underline{\alpha},\underline{c}) = \sum_{i=1}^{n}\left[\frac{f_i(\underline{\alpha},\underline{c}) - f_i(\underline{\alpha}^\circ,\underline{c})}{f_i(\underline{\alpha}^\circ,\underline{c})}\right]^2 \tag{19}$$

where $Q(\underline{\alpha},\underline{c})$ is a measure of the change in reaction rates brought about by a parameter perturbation, $\alpha_j = \ell n k_j$ and $\alpha_j^\circ = \ell n k_j^\circ$. In a way analogeous to that used before [7], the objective function Q can be approximated by the simple quadratic expression

$$\hat{Q}(\alpha) = (\Delta\alpha)^T\tilde{F}^T\tilde{F}(\Delta\alpha), \tag{20}$$

where $\hat{Q}(\alpha) = Q(\underline{\alpha},\underline{c})$ in the neighborhood of $\underline{\alpha}^\circ$. Information on reaction significances and reaction structures is obtained by performing eigenvalue-eigenvector decomposition of the matrix $\tilde{F}^T\tilde{F}$.

Let U denote the matrix of normalized eigenvectors $\underline{u}_j$ of $\tilde{F}^T\tilde{F}$ such that $\underline{u}_j^T\underline{u}_j = 1$ for each j ($j = 1, 2, \ldots, p$). Introduction of a new set of parameters, $\underline{\Psi} = U^T\underline{\alpha}$, called principal components, reduces eq. (20) to the canonical form

$$\hat{Q}(\underline{\Psi}) = \sum_{j=1}^{p}\lambda_j(\Delta\Psi_j)^2 \tag{21}$$

* Hwang [10] has introduced the term "rate sensitivity coefficient," however, he used it in a wider sense.

where $\Delta\underline{\Psi} = \underline{U}^T\Delta\underline{\alpha}$ and $\lambda_1 > \lambda_2 > \ldots > \lambda_p$ denote the eigenvalues of $\tilde{F}^T\tilde{F}$. If we move from $\underline{\alpha}^\circ$ along an eigenvector $\underline{u}_i$ in the space of the transformed coordinates $\underline{\Psi}$, then $\Delta\Psi_j = 0$ for $i \neq j$. Thus, $\hat{Q}(\underline{\Psi}) = \lambda_i(\Delta\Psi_i)^2$ and hence λ_i measures the significance of reactions occurring in the principal component Ψ_i. Thus, important reactions can be identified as the significant eigenvector elements of reaction subgroups characterized by large eigenvalues.

Naturally, what is important or unimportant in a study depends on the aims of the investigation. Consequently, one should formulate the response function Q in accordance with the objectives in order to obtain the appropriate ranking of the reactions considered in the mechanism. In the definition of the objective function by eq. (19), the responses for all species were taken into account and the same practice has been obeyed in the discussions of the reactions presented in this article. Such a definition comprises the requirement that our model should describe equally well the concentration changes of all species present in the system. However, the objective function may be formulated by considering only selected species (for instance those measured in an experiment). Definitely, the analysis of such objective functions can provide useful kinetic information, but the procedure may indicate some basic reactions as insignificant ones. (This occurs when the change of the rate coefficient of a fundamental reaction, e.g., a chain propagation step, does not directly influence the rates of concentration changes of the selected species.)

Another method of deriving kinetic information from the sensitivity matrix is provided by the use of overall sensitivities [7]. These can be defined in reaction rate analysis by

$$B_j = \sum_{i=1}^{n} [\tilde{\phi}_{ij}(\underline{k}, \underline{c})]^2 = \sum_{i=1}^{n} \left[\frac{k_j}{f_i(\underline{k}, \underline{c})} \frac{\partial f_i(\underline{k}, \underline{c})}{\partial k_j}\right]^2. \tag{22}$$

According to this definition, $B_j = \tilde{F}_j^T\tilde{F}_j$, where $\tilde{F}_j$ is the j-th column of the matrix of normalized rate sensitivities. Since $\|\tilde{F}_j\| = (\tilde{F}_j^T\tilde{F}_j)^{1/2}$ designates the Euclidean norm of the $\tilde{F}_j$ vector, the overall sensitivity B_j is the square of $\|\tilde{F}_j\|$. The overall sensitivity B_j is a convenient and simple measure of the significance of reaction j. Ranking of elementary reactions based on B_j may be somewhat different from that derived by principal component analysis, however, the reactions identified as definitely unimportant ones by the two methods are the same.

Comparison of Rate Analysis and Concentration Sensitivity Analysis

Below we compare the conclusions on reaction importances which can be derived from $\tilde{F}$ matrix and from $\tilde{S}$ matrix analysis. For simplicity we use the overall sensitivities or the Euclidean norm of the

column vector of the sensitivity matrix as a measure of the reaction importance.

Assume that $\|\tilde{F}_j(\underline{k}^\circ, \underline{c}^\circ, t_2)\| \leqq \epsilon$ for all $0 \leqq t \leqq t_2$. For the linear system (12) there exist constant M and β such that $\|\tilde{G}(t', t_2)\| \leqq M \exp(\beta t)$ for all $t' \leqq t$. If the trajectory $\underline{c}(\underline{k}^\circ, \underline{c}^\circ, t)$ leads to an assymptotically stable equilibrium state, then $\beta < 0$ and

$$\|\tilde{S}_j(\underline{k}^\circ, \underline{c}^\circ, t_2)\| \leqq \frac{M\epsilon}{\beta}[\exp(\beta t) - 1] \tag{23}$$

If the trajectory $\underline{c}(\underline{k}^\circ, \underline{c}^\circ, t)$ is stable, but does not converge to an assymptotically stable equilibrium state, then $\beta = 0$ and

$$\|\tilde{S}_j(\underline{k}^\circ, \underline{c}^\circ, t_2)\| \leqq M\epsilon t \tag{24}$$

for all $0 \leqq t \leqq t_2$. We can conclude that any reaction which is unimportant according to reaction rate considerations proves to be unimportant also in concentration sensitivity analysis.

On the other hand, it appears that a reaction shown to be important by the $\tilde{F}$ matrix analysis may still prove to be unimportant in considerations based on the $\tilde{S}$ matrix. In fact, $\|\tilde{S}_j(\underline{k}^\circ, \underline{c}^\circ, t_2)\| = 0$ implies $\|\tilde{F}_j(\underline{k}^\circ, \underline{c}^\circ, t_2)\| = 0$ only under the special condition called the invertibility of the system (11) [12]. Furthermore, eq. (12) is an integral equation of the first kind for a small $\|\tilde{S}_j(\underline{k}^\circ, \underline{c}^\circ, t_2)\| < \epsilon$.

There may exist a large $\tilde{F}_j(\underline{k}^\circ, \underline{c}^\circ, t_2)$ that satisfies the equation even for invertible systems [13]. However, this conclusion is only valid for a limited range of reaction time. Since [in accordance with eq. (10)]

$$\frac{d}{dt}\tilde{S}_j = \tilde{J}\tilde{S}_j + \tilde{F}_j \tag{25}$$

indicates that a large $\|\tilde{F}_j\|$ imples a fast change of $\|\tilde{S}_j\|$ with time which results soon at another t_2' reaction time in a large $\|\tilde{S}_j\|$ value. Thus, taking into account $\|\tilde{S}_j\|$ at various t_2, t_2', t_2'', etc. reaction times around t_2, we identify the same reactions as unimportant steps in the $\tilde{S}$ matrix analysis which were found unimportant in the $\tilde{F}$ matrix considerations.

Further comparisons of concentration and rate sensitivities can be made by transforming eq. (25) into the equivalent integral equation:

$$\tilde{S}_j(\underline{k}, \underline{c}^\circ, t_1, t_2) = \int_{t_1}^{t_2} \tilde{J}(\underline{k}, \underline{c}^\circ, t')\tilde{S}_j(\underline{k}, \underline{c}^\circ, t')\,dt + \int_{t_1}^{t_2} \tilde{F}_j(\underline{k}, \underline{c}^\circ, t')\,dt \tag{26}$$

The two terms in eq. (26) represent the direct and indirect effects of parameter perturbation. The second term gives the direct change in species concentration as a result of parameter perturbation, while the first term expresses the additional concentration change induced by the primary change in component concentrations. This complex nature of $\tilde{S}_j$ clearly shows why the concentration sensitivities are not

completely adequate for the study of local mechanistic or kinetic problems. Assume that step j is important over the interval $[0, t_p]$, but does practically not contribute to concentration changes at $t > t_p$. Nevertheless, $\bar{S}(\underline{k}^\circ, \underline{c}^\circ, t)$ may be large at $t > t_p$ as a result of the contribution of the first term in eq. (26). As it has been pointed out in ref. [11], this "memory effect" in concentration sensitivity analysis is a definitive drawback when studying mechanisms, for instance the reaction mechanism of an oscillating reaction. On the other hand, ϕ_{ij} and relative reaction rate matrix $\bar{F}$ depend only on the kinetic standard parameters of the state, i.e., on $\underline{k}$ and $\underline{c}$, and are hereby especially suitable for obtaining local reaction importances attached to a particular point of the parameter-concentration space.

Matrix $\bar{\underline{S}}$ belongs to a time interval $[t_1, t_2]$, hence an implicit assumption of time-independent principal component structure is inherent in the derivation of kinetic information. No similar approximation is used in the principal component analysis of the $\bar{\underline{F}}^T\bar{\underline{F}}$ matrix, since the reaction rate sensitivities depend only on the kinetic standard parameters of the state corresponding to a certain reaction time.

Both the $\bar{S}$ and the $\bar{F}$ matrices can supply information on quasi-steady-state and fast equilibrium relations. In the S matrix analysis such reaction structures are identified by principal components belonging to relatively small eigenvalues [7], while in $\bar{F}$ matrix analysis these appear in eigenvectors related to the largest eigenvalues. Thus, principal components characterized by small eigenvalues play only minor or no role at all in the derivation of kinetic information from cross-product matrix $\bar{F}^T\bar{F}$ and therefore possible numerical uncertainties do not significantly influence the conclusions.

Kinetic Analysis of Two Complex Reaction Mechanisms

Hereinafter we investigate the mechanisms of high-temperature formaldehyde oxidation and high-temperature propane pyrolysis. Principal component analysis of the relative reaction rate matrices will be shown to allow a significant reduction of the original schemes and to reveal the major reaction paths for the species.

Analysis of High-temperature Formaldehyde Oxidation Mechanism

The mechanism of high-temperature formaldehyde oxidation in the presence of carbon monoxyde reported by Vardanyan et al. [14] and eproduced in Table I, has been analyzed at the following reaction conditions: 952 K, $[CH_2O]_o = 1.128 \times 10^{-4}$ mol dm^{-3}, $[O_2]_o = 2.117 \times 10^{-3}$ mol dm^{-3}, $[CO]_o = 4.717 \times 10^{-3}$ mol dm^{-3}, and $[M] = 1.182 \times 10^{-2}$ mol dm^{-3}. The $\bar{F}$ matrix has been constructed at seven

TABLE I. Mechanism of high-temperature oxidation of formaldehyde in the presence of CO.

No.	Reaction	k (952 K)
1.	$HCO + O_2 \longrightarrow HO_2 + CO$	1.00 E-13
2.	$HO_2 + CH_2O \longrightarrow H_2O_2 + HCO$	5.70 E-14
3.	$H_2O_2 + M \longrightarrow 2OH + M$	6.66 E-18
4.	$OH + CH_2O \longrightarrow H_2O + HCO$	1.60 E-10
5.	$OH + H_2O_2 \longrightarrow H_2O + HO_2$	5.10 E-12
6.	$H_2O_2 \xrightarrow{wall}$ products	1.05 E 02
7.	$HO_2 \xrightarrow{wall}$ products	1.05 E 01
8.	$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	3.00 E-12
9.	$OH + CO \longrightarrow CO_2 + H$	3.30 E-13
10.	$HO_2 + CO \longrightarrow CO_2 + OH$	1.20 E-15
11.	$H + CH_2O \longrightarrow H_2 + HCO$	2.70 E-12
12.	$H + O_2 \longrightarrow OH + O$	5.51 E-14
13.	$H + O_2 + M \longrightarrow HO_2 + M$	1.00 E-32
14.	$HO_2 + M \longrightarrow H + O_2 + M$	4.70 E-19
15.	$O + H_2 \longrightarrow OH + H$	3.02 E-13
16.	$O + CH_2O \longrightarrow OH + HCO$	1.00 E-10
17.	$H + H_2O_2 \longrightarrow HO_2 + H_2$	1.30 E-12
18.	$H + H_2O_2 \longrightarrow H_2O + OH$	5.90 E-12
19.	$O + H_2O_2 \longrightarrow OH + HO_2$	1.00 E-13
20.	$HCO \longrightarrow H + CO$	4.60 E-12
21.	$OH + H_2 \longrightarrow H_2O + H$	1.00 E-11
22.	$CH_2O + O_2 \longrightarrow HCO + HO_2$	2.90 E-20
23.	$H + HO_2 \longrightarrow 2OH$	5.00 E-12
24.	$H + HO_2 \longrightarrow H_2O + O$	5.00 E-11
25.	$H + HO_2 \longrightarrow H_2 + O_2$	4.50 E-11

reaction times between 1×10^{-5} s (0.01% CH_2O conversion) and 5×10^{-3} s (1.23% CH_2O conversion). Eigenvalue-eigenvector decomposition of the cross-product matrix $\tilde{F}^T\tilde{F}$ has been performed at each time. As an example, the largest eigenvalues* together with the significant elements* of the corresponding eigenvectors for reaction time 1×10^{-5} s are given in Table II.

Selecting the important reactions (as the significant eigenvector elements of the principal components characterized by larger eigenvalues) at the very early stage of 0.01% conversion, we can reduce the original 25-step scheme to a 10-step mechanism.

Analysis at a somewhat latter stage (i.e., at 1.23% conversion) reveals that three further reactions (reactions (3), (6), and (8) of hydrogen peroxide) become increasingly important as the oxidation proceeds. Thus, one can suggest on the basis of reaction rate analysis a simple 13-step reaction scheme for formaldehyde oxidation in the presence of

* Eigenvalues $\geq 10^{-4}$ and eigenvector elements ≥ 0.1 are considered to be significant. This choice of the limits is arbitrary, but it is well supported by experience.

TABLE II. Eigenvalues and eigenvector elements from the analysis of formaldehyde oxidation at 1×10^{-5} s (0.01% conversion).

No.	Eigenvalue	Significant (≥0.1) eigenvector elements[a]
1.	1.75 E+4	10(−0.73), 4(0.68)
2.	3.65 E+3	12(−0.72), 16(0.70)
3.	1.47 E+1	22(0.80), 1(−0.60)
4.	1.17 E+1	9(0.91), 11(−0.37), 13(−0.17)
5.	2.04 E 0	1(0.80), 22(0.60)
6.	1.00 E 0	2(1.00)
7.	9.37 E-1	4(−0.71), 10(−0.66), 11(−0.23), 9(−0.09)
8.	8.72 E-1	11(−0.90), 9(−0.35), 4(0.19), 10(0.15)
9.	4.10 E-4	13(0.98), 9(0.18)

[a] Figures before the brackets refer to the reaction numbering as indicated in Table I, while the eigenvector elements are given in the brackets.

TABLE III. Comparison of product concentrations calculated from the original and reduced model of high-temperature formaldehyde oxidation.

Products	CH_2O	H_2O_2	H_2O	CO_2	H_2
Full model concentration mol dm^{-3}	1.115 E-4	5.701 E-7	6.450 E-7	6.556 E-7	2.988 E-8
Reduced model %deviation	−0.002	1.9	1.6	1.7	1.0

CO which consists of reactions: (1), (2), (3), (4), (6), (8), (9), (10), (11), (12), (13), (16), and (22). Kinetic differential equations of the 13-step and the original 25-step model were solved for the above given initial conditions. The concentrations calculated at 5×10^{-3} s for CH_2O and the stable reaction products from the reduced and the full model agree within 2 percent (see Table III). The good agreement indicates that the reaction kinetics is very well described by the reduced reaction scheme.

Apart from ranking the elementary reactions according to their kinetic significance, the present method of rate analysis can supply additional mechanistic information, too.

Principal component Ψ_1 in Table II contains two entries which refer to reactions (10) and (4). These are the major routes of OH radical formation and consumption, respectively, at very low conversion. However, as the process proceeds, reaction (3) increasingly contributes to OH radical formation as indicated by the appearance of reaction (3) in the principal component Ψ_1 at higher conversion. Furthermore it

can be seen easily that principal components Ψ_2, Ψ_3, Ψ_4, Ψ_5, and Ψ_6 identify the major formation and consumption reactions of the highly reactive species O, HCO, HO_2, and H_2O_2, respectively. Finally, principal components Ψ_7 and Ψ_8 contain the dominant reactions of two reactive species, those of OH (steps (4) and (10)) and H (steps (11) and (9)). These two species are closely coupled by reaction (9) which converts OH radicals into H atoms. Thus, it is not surprising that the reaction of two species appear in the same principal component.

Sensitivity analysis based on the $\tilde{S}$ matrix has been carried out recently [7] for the same formaldehyde oxidation mechanism investigated in the present study. The reduced mechanisms of 13 important elementary reactions derived from the $\tilde{S}$ and $\tilde{F}$ matrices were the same, though the ranking of reaction importance slightly differed. More characteristic differences were found between the $\tilde{F}$ and $\tilde{S}$ matrix results in the study of reaction structures and characteristic reaction groups. The physical meaning and interpretation of the reaction groups identified by the significant eigenvector elements belonging to larger eigenvalues are not so straightforward in case of concentration sensitivities then in the analysis of the rate matrix. Furthermore, the distinction between "small" and "large" eigenvalues, which follows naturally in case of rate sensitivity considerations, is less clear for the analysis of concentration sensitivities.

Analysis of High-temperature Propane Pyrolysis Mechanism

The mechanism selected for analysis was based on the scheme published by Hautman et al. [15] which involved 13 chemical species and consisted of 32 reversible elementary reactions. This mechanism was supplemented by two further reactions [steps (65) and (66)] claimed to be important by J. N. Bradley [16]. The investigated 66-step mechanism and the kinetic parameters taken from the cited literature are shown in Table IV. Reaction rate analysis has been carried out at the following reaction conditions: 1250 K temperature, $[C_3H_8]_0 = 3.849 \times 10^{-5}$ mol dm^{-3} concentration, and at four different reaction times corresponding to propane consumption from 0.0005% up to 38% conversion. The results of the eigenvalue-eigenvector decomposition of $\tilde{F}^T\tilde{F}$ for an early stage of the reaction (1×10^{-5} s, 0.11% conversion) are presented in Table V. Analysis revealed only 11 principal components characterized by large eigenvalues. Eigenvalue λ_{12} was almost eight orders of magnitude smaller than λ_{11}. In Table VI, we have indicated the elementary steps which proved to be important in the analyses carried out at different conversions.

At the early stage and at medium conversion, initiation by propane decomposition [step (1)] and reaction chains involving propyl radicals are of importance. These chains consist of propyl radical formation by

TABLE IV. Mechanism of high-temperature propane pyrolysis.

No.	Reaction	k(1250 K)
1.	$C_3H_8 \longrightarrow CH_3 + C_2H_5$	5.85 E 01
2.	$CH_3 + C_2H_5 \longrightarrow C_3H_8$	9.11 E 09
3.	$CH_3 + C_3H_8 \longrightarrow CH_4 + i\text{-}C_3H_7$	2.86 E 07
4.	$CH_4 + i\text{-}C_3H_7 \longrightarrow CH_3 + C_3H_8$	4.56 E 05
5.	$CH_3 + C_3H_8 \longrightarrow CH_4 + n\text{-}C_3H_7$	4.01 E 07
6.	$CH_4 + n\text{-}C_3H_7 \longrightarrow CH_3 + C_3H_8$	1.76 E 05
7.	$H + C_3H_8 \longrightarrow H_2 + i\text{-}C_3H_7$	2.95 E 09
8.	$H_2 + i\text{-}C_3H_7 \longrightarrow H + C_3H_8$	2.17 E 06
9.	$H + C_3H_8 \longrightarrow H_2 + n\text{-}C_3H_7$	4.14 E 09
10.	$H_2 + n\text{-}C_3H_7 \longrightarrow H + C_3H_8$	4.56 E 06
11.	$C_2H_3 + C_3H_8 \longrightarrow C_2H_4 + i\text{-}C_3H_7$	1.26 E 06
12.	$C_2H_4 + i\text{-}C_3H_7 \longrightarrow C_2H_3 + C_3H_8$	5.65 E 03
13.	$C_2H_3 + C_3H_8 \longrightarrow C_2H_4 + n\text{-}C_3H_7$	1.77 E 06
14.	$C_2H_4 + n\text{-}C_3H_7 \longrightarrow C_2H_3 + C_3H_8$	1.86 E 04
15.	$C_2H_5 + C_3H_8 \longrightarrow C_2H_6 + i\text{-}C_3H_7$	1.26 E 06
16.	$C_2H_6 + i\text{-}C_3H_7 \longrightarrow C_2H_5 + C_3H_8$	2.01 E 05
17.	$C_2H_5 + C_3H_8 \longrightarrow C_2H_6 + n\text{-}C_3H_7$	1.77 E 06
18.	$C_2H_6 + n\text{-}C_3H_7 \longrightarrow C_2H_5 + C_3H_8$	4.21 E 05
19.	$C_3H_5 + C_3H_8 \longrightarrow C_3H_6 + i\text{-}C_3H_7$	4.86 E 05
20.	$C_3H_6 + i\text{-}C_3H_7 \longrightarrow C_3H_5 + C_3H_8$	3.06 E 05
21.	$C_3H_5 + C_3H_8 \longrightarrow C_3H_6 + n\text{-}C_3H_7$	6.83 E 05
22.	$C_3H_6 + n\text{-}C_3H_7 \longrightarrow C_3H_5 + C_3H_8$	1.63 E 06
23.	$i\text{-}C_3H_7 + C_3H_8 \longrightarrow n\text{-}C_3H_7 + C_3H_8$	1.76 E 05
24.	$n\text{-}C_3H_7 + C_3H_8 \longrightarrow i\text{-}C_3H_7 + C_3H_8$	2.62 E 05
25.	$i\text{-}C_3H_7 \longrightarrow H + C_3H_6$	2.23 E 07
26.	$H + C_3H_6 \longrightarrow i\text{-}C_3H_7$	4.20 E 10
27.	$i\text{-}C_3H_7 \longrightarrow CH_3 + C_2H_4$	1.39 E 05
28.	$CH_3 + C_2H_4 \longrightarrow i\text{-}C_3H_7$	1.52 E 05
29.	$n\text{-}C_3H_7 \longrightarrow H + C_3H_6$	4.23 E 07
30.	$H + C_3H_6 \longrightarrow n\text{-}C_3H_7$	1.73 E 10
31.	$n\text{-}C_3H_7 \longrightarrow CH_3 + C_2H_4$	3.02 E 08
32.	$CH_3 + C_2H_4 \longrightarrow n\text{-}C_3H_7$	2.22 E 08
33.	$C_2H_5 \longrightarrow C_2H_4 + H$	8.63 E 06
34.	$C_2H_4 + H \longrightarrow C_2H_5$	1.79 E 10
35.	$H + C_3H_6 \longrightarrow C_3H_5 + H_2$	1.61 E 09
36.	$C_3H_5 + H_2 \longrightarrow H + C_3H_6$	1.99 E 05
37.	$CH_3 + C_3H_6 \longrightarrow CH_4 + C_3H_5$	2.91 E 06
38.	$CH_4 + C_3H_5 \longrightarrow CH_3 + C_3H_6$	7.48 E 03
39.	$H + C_2H_6 \longrightarrow H_2 + C_2H_5$	4.27 E 09
40.	$H_2 + C_2H_5 \longrightarrow H + C_2H_6$	2.02 E 07
41.	$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$	4.33 E 07
42.	$CH_4 + C_2H_5 \longrightarrow CH_3 + C_2H_6$	4.34 E 06
43.	$CH_4 + H \longrightarrow CH_3 + H_2$	1.05 E 09
44.	$CH_3 + H_2 \longrightarrow CH_4 + H$	2.28 E 10
45.	$H_2 \longrightarrow 2H$	2.60 E-03
46.	$2H \longrightarrow H_2$	2.83 E-24
47.	$2CH_3 \longrightarrow C_2H_6$	1.15 E 10
48.	$C_2H_6 \longrightarrow 2CH_3$	1.30 E 01
49.	$H + CH_3 \longrightarrow CH_4$	1.00 E 08
50.	$CH_4 \longrightarrow H + CH_3$	3.50 E 0
51.	$C_2H_4 \longrightarrow C_2H_2 + H_2$	3.54 E 03

Table IV. *(continued)*

52.	$C_2H_2 + H_2 \longrightarrow C_2H_4$	2.36 E 06
53.	$C_2H_4 \longrightarrow C_2H_3 + H$	1.72 E 0
54.	$C_2H_3 + H \longrightarrow C_2H_4$	1.99 E 14
55.	$H + C_2H_4 \longrightarrow H_2 + C_2H_3$	1.10 E 09
56.	$H_2 + C_2H_3 \longrightarrow H + C_2H_4$	1.81 E 08
57.	$2C_2H_4 \longrightarrow C_2H_3 + C_2H_5$	1.00 E 10
58.	$C_2H_4 + C_2H_5 \longrightarrow 2C_2H_4$	3.63 E-01
59.	$C_2H_3 \longrightarrow H + C_2H_2$	2.47 E 09
60.	$H + C_2H_2 \longrightarrow C_2H_3$	9.96 E 12
61.	$C_2H_3 + C_2H_4 \longrightarrow C_2H_2 + C_2H_5$	3.99 E 06
62.	$C_2H_2 + C_2H_5 \longrightarrow C_2H_3 + C_2H_4$	2.67 E 06
63.	$C_2H_3 + H \longrightarrow C_2H_2 + H_2$	1.83 E 09
64.	$C_2H_2 + H_2 \longrightarrow C_2H_3 + H$	1.79 E-02
65.	$C_2H_5 \longrightarrow C_2H_3 + H_2$	3.61 E 03
66.	$CH_3 + C_3H_6 \longrightarrow C_2H_4 + C_2H_5$	2.14 E 06

TABLE V. Eigenvalues and eigenvector elements from the analysis of high-temperature propan pyrolysis at 1×10^{-5} s (0.11% conversion).

No.	Eigenvalue	Significant (≥0.1) eigenvector elements[a]
1.	7.65 E+7	9(0.74), 31(−0.67)
2.	6.84 E+7	33(−0.71), 1(0.71)
3.	7.47 E+6	59(−0.76), 60(0.65)
4.	3.53 E+5	25(−0.71), 7(0.70)
5.	1.15 E+1	1(0.55), 33(0.55), 31(−0.47), 9(−0.42)
6.	9.95 E-1	47(−1.00)
7.	9.91 E-1	35(1.00)
8.	8.32 E-1	51(−0.99), 57(0.10)
9.	8.17 E-1	31(0.53), 9(0.48), 1(0.41), 33(0.40), 7(0.29), 25(0.28)
10.	4.35 E-1	7(0.62), 25(0.61), 29(0.24), 31(−0.24), 9(−0.18), 1(−0.18), 33(−0.18), 33(−0.18), 5(0.10)
11.	3.93 E-1	5(−0.79), 3(−0.56), 44(−0.24), 7(0.10)

[a] Figures before the brackets refer to the reaction numbering as indicated in Table IV, while the eigenvector elements are given in the brackets.

H-atom abstraction from propane and propyl radical decompositions. Our analysis reveals that H-atom abstraction by i-C_3H_7 and n-C_3H_7 radicals in reactions (23) and (24) is not important at all and abstraction by C_2H_5 radicals through reactions (15) and (17) is only significant in the very early stage of the pyrolysis. Propyl radical formation in methyl radical reactions (3) and (5) is important at moderately low

TABLE VI. Important elementary reactions[a] of high-temperature propane pyrolysis at different conversion.

1×10^{-7} s 0.0005% conv.	1×10^{-5} s 0.11% conv.	1×10^{-4} s 3.1% conv.	3×10^{-4} s 37.0% conv.
(1)	(1)	(1)	
(3)	(3)		
(5)	(5)		
(7)	(7)	(7)	(7)
(9)	(9)	(9)	(9)
(15)			
(17)			
(25)	(25)	(25)	(25)
			(26)
(29)	(29)	(29)	
			(30)
(31)	(31)	(31)	(31)
(33)	(33)	(33)	(33)
(35)	(35)	(35)	(35)
			(39)
	(44)	(44)	(44)
	(47)	(47)	(47)
(51)	(51)	(51)	(51)
		(54)	(54)
	(57)	(57)	(57)
(59)	(59)	(59)	(59)
	(60)	(60)	(60)
(65)			

[a]The figures given in the Table refer to reaction numbering as indicated in Table IV.

conversion. Finally, H-abstraction by hydrogen atoms in reactions (7) and (9) is seen to be important under all conditions including high conversion. Regarding radical decomposition reactions (25), (29), and (33), and CH_3 elimination from *n*-propyl by step (31) are found to be important throughout the whole process.

In general reactions of products become significant only at higher conversion as products accumulate. This is the case for hydrogen atom addition to propylene [steps (26) and (30)] and H-abstraction from C_2H_6 [reaction (39)]. However, our analysis reveals that allyl radical formation in reaction (35) is important throughout the whole process.

A notable conclusion that can be formulated on the basis of the results summarized in Table VI is the significant role played by C_2H_4, C_2H_2 and especially by vinyl radical reactions in the high-temperature propane pyrolysis mechanism. The analysis shows these reactions to be important from the very beginning of the pyrolysis. Thus,

direct transformation of C_2H_4 to C_2H_2 in step (51) is seen to be significant throughout the whole process. Interconversion of the olefins via C_2H_3 radicals is also contributing in any stages of the reaction. Vinyl radicals are formed at very small conversion through ethyl radical decomposition according to step (65) which is gradually replaced by reactions (57) and (60) with increasing conversion. The major C_2H_3 consuming reaction is step (59) which is supplemented by step (54) at higher conversion.

On the basis of the results of the rate analysis a 23-step mechanism can be suggested for a wide range of conditions. This reduced mechanism consists of reactions (1), (3), (5), (7), (9), (15), (17), (25), (26), (30), (31), (33), (35), (39), (44), (47), (51), (54), (57), (59), (60), and (65). It can be seen from Table VII that the kinetics of pyrolysis may be well described by the 23-step scheme; the calculated product concentrations at about 3% propane conversion agree within 1% with the results derived from the full mechanism.

Our reduced mechanism has been compared with other mechanisms used to interpret high-temperature propane pyrolysis results. One of these is the well known mechanism reported by Lifshitz and Frenklach [2]. We find that this mechanism leads to serious underestimation of the rate of product formation as indicated by the data given in the last column of Table VII. Considering the steps of the Lifshitz-Frenklach (LF) scheme and of the reduced mechanism one finds that the inadequacy of the LF scheme comes from the neglect of some olefine reactions.

Note: A program package of reaction rate analysis and concentration sensitivity analysis is available for IBM PC and compatible computers. Those who are interested in receiving the programs are requested to send an empty 5 1/4" floppy disk to the first author.

TABLE VII. Comparison of product concentrations calculated from various models of high-temperature propane pyrolisis at 1250 K and 1×10^{-4} s.

Products	66-step model mol dm^{-3}	23-step model deviation, %	LF model deviation, %
$-\Delta C_3H_8$	1.175 E-6	0.47	−39.51
CH_4	2.304 E-7	0.38	−79.51
C_2H_4	5.711 E-7	0.30	−17.04
C_2H_2	1.528 E-7	−0.67	
C_2H_6	5.626 E-8	−0.05	−12.75
H_2	8.083 E-7	0.43	−45.48
C_3H_6	4.493 E-7	1.10	−47.29

Bibliography

[1] D. Edelson and D. L. Allara, *Int. J. Chem. Kinet.*, **12**, 605 (1980).
[2] A. Lifshitz and M. Frenklach, *J. Phys. Chem.*, **79**, 686 (1975).
[3] R. J. Kee, J. F. Grear, M. D. Smooke, and J. A. Miller, Sandia National Laboratories, SAND85-8240, 1985, cited in P. Glarborg, J. A. Miller, and R. J. Kee, *Combust. Flame*, **65**, 177 (1986).
[4] R. J. Gelinas, Science Application, Inc., Preprint No. SAI/PL/C279, December 1979, cited in T. P. Coffee, *Comb. Flame*, **65**, 53 (1986).
[5] H. Rabitz, M. Kramer, and D. Dacol, *Ann. Rev. Phys. Chem.*, **34**, 419 (1983).
[6] M. Demiralp and H. Rabitz, *J. Chem. Phys.*, **74**, 3362 (1981).
[7] S. Vajda, P. Valkó, and T. Turányi, *Int. J. Chem. Kinet.*, **17**, 55 (1985).
[8] D. G. Cacuci, *J. Math. Phys.*, **22**, 2794 (1981).
[9] J-T. Hwang, E. P. Dougherty, S. Rabitz, and H. Rabitz, *J. Chem. Phys.*, **69**, 5180 (1978).
[10] J-T. Hwang, Proc. Natl. Sci. Counc. B. ROC, **6**, 270 (1982).
[11] S. Vajda and T. Turányi, *J. Phys. Chem.*, **90**, 1664 (1986).
[12] L. M. Silverman, IEEE Trans. Automat. Control, **14**, 270 (1969).
[13] B. R. Hunt, *Math. Biosci.*, **10**, 215 (1971).
[14] I. A. Vardanyan, G. A. Sachyan, and A. B. Nalbandyan, *Int. J. Chem. Kinet.*, **7**, 23 (1975).
[15] D. J. Hautman, R. J. Santoro, F. L. Dryer, and I. Glassman, *Int. J. Chem. Kinet.*, **13**, 149 (1981).
[16] J. N. Bradley, *J.C.S. Faraday Trans. I.*, **75**, 2819 (1979).

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