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A tool model for predicting atmospheric chemical kinetics with sensitivity analysis

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Abstract: A package (a tool model) for program of predicting atmospheric chemical kinetics with sensitivity analysis is presented. The new direct method of calculating the first order sensitivity coefficients using sparse matrix technology to chemical kinetics is included in the tool model, it is only necessary to triangularize the matrix related to the Jacobian matrix of the model equation. The Gear type procedure is used to integrate a model equation and its coupled auxiliary sensitivity coefficient equations. The FORTRAN subroutines of the model equation, the sensitivity coefficient equations, and their Jacobian analytical expressions are generated automatically from a chemical mechanism. The kinetic representation for the model equation and its sensitivity coefficient equations, and their Jacobian matrix is presented. Various FORTRAN subroutines in packages, such as SLODE, modified MA28, Gear package, with which the program runs in conjunction are recommended. The photo-oxidation of dimethyl disulfide is used for illustration.

Key words: atmospheric chemical model; chemical kinetics; sensitivity analysis

A problem which frequently arises in the study of kinetics is the high degree of coupling of the reaction system. For example, in many realistic chemical processes, particularly those related to atmospheric chemistry, combustion phenomena, petrochemistry, industrial process, the number of reactions can often exceed hundreds. Modeling the processes is a computer program that predicts the time-dependent chemical behavior. In nearly all models, the solutions depend both on initial and boundary conditions, and on certain parameters that go into defining the model itself. Sensitivity analysis is a formal procedure to determine quantitatively how the solution to a model depends on certain parameters in the model formulation (Lutz, 1988). In the case considered here, the parameters are the reaction rate constants and initial concentrations. The sensitivity analysis allows one to understand how the model will respond to changes in the parameters. It also provides in sight about how important certain reaction pathways are to the model's predictions. Writing computer program, especially with sensitivity analysis, from a particular chemical mechanism is a tedious and consuming job if by hands.

Prior research clearly suggests the need for a user-oriented computer code which accepts a list of reactions and rate constants; and given operating conditions, calculates the model solution and sensitivities (Kee, 1980). Some codes can generate FORTRAN subroutines automatically from a chemical mechanism (Shi, 1996; Ruiz, 1993; Jacobian, 1994). Sandia researchers developed a series version of computer codes (CHEMKIN, CHEMSEN...) to calculate the model solution and sensitivity analysis (Lutz, 1988; Kramer, 1982; Kee, 1980).

In this paper we present a tool model for predicting atmospheric chemical behavior with sensitivity analysis. The recently developed direct methods of sensitivity analysis is included in the tool model (Shen, 1999a; 1999b). The FORTRAN subroutines of modeling and sensitivity analysis can be automatically generated from a chemical mechanism. Various FORTRAN subroutines related to modeling and sensitivity analysis are also included.

1 Government equations

1.1 General equations

The coupled first order ordinary differential equations (DOEs) describing chemical kinetic

systems are of the following general form:

$$\frac{dy}{dt} = f(y, \alpha, t), y(t_0) = y_0, \quad (1)$$

where y is the length n species concentration vector, and α the length m input parameter vector (taken here as rate constants k_j and initial species concentrations $y_i(t_0)$). y_0 is the initial value of y . This paper is primarily concerned with the first order sensitivity coefficient vector. Assume that y has continuous partial derivatives with respect to α_q , $q = 1, 2, \dots, m$. The sensitivity coefficient with respect to α_q is given by:

$$y_{\alpha_q}(t) \equiv \frac{\partial y(t)}{\partial \alpha_q}. \quad (2)$$

From Eq. (1)

$$\frac{\partial y_{\alpha_q}}{\partial t} = J(y, \alpha, t)y_{\alpha_q} + f_{\alpha_q}(y, \alpha, t), y_{\alpha_q}(0) = \frac{\partial y_0}{\partial \alpha_q}. \quad (3)$$

The initial condition $y_{\alpha_q}(0)$ is a zero vector, unless α_q is the initial concentration of the i th species, in which case $y_{\alpha_q}(0) = \delta_i$. The symbol δ_i is a vector whose components are all zero except the i th component being 1. The matrix elements of the $n \times n$ Jacobian matrix J of model Equation(1) are given by:

$$J_{ij} = \left[\frac{\partial f_i}{\partial y_j} \right]_{\alpha_q}, \quad i, j = 1, 2, \dots, n; \quad (4)$$

$$\text{and } f_{\alpha_q}(y, \alpha, t) = \left[\frac{\partial f}{\partial \alpha_q} \right]_y. \quad (5)$$

where, $f_{\alpha_q}(y, \alpha, t)$ accounts for any explicit dependence of f on α_q , $q = 1, 2, \dots, m$. The Equation (3) has been obtained by many researchers (Dougherty, 1979; Hwang, 1978; Lutz, 1988; Ducker, 1984; Kramer, 1984). Many different methods for calculating sensitivity coefficients start from these equations. If there are n species and m input parameters α_q , $q = 1, 2, \dots, m$, the n model equations in (1) generally couple with $m \times n$ auxiliary sensitivity coefficient equations in (3).

The coupled equations are assumed to be stiff and to require a Gear type algorithm to solve (Gear, 1971). Gear sets up a prediction matrix.

$$P \approx I_0 = h\beta_0 G, \quad (6)$$

where, I_0 is an identity matrix, h the time step, β_0 a scalar multiplier that depends on the order of the approximation. The matrix elements of the $n(m+1) \times n(m+1)$ Jacobian matrix G_{ij} are given by

$$G_{ij} = \frac{\partial F_i}{\partial Y_j}. \quad (7)$$

$$\text{For } i = 1, 2, \dots, n: \quad F = f(y, \alpha, t) \quad (8)$$

$$\text{and } i = n+1, n+2, \dots, n(m+1): \quad F = J(y, \alpha, t)y_{\alpha_q} + f_{\alpha_q}(y, \alpha, t). \quad (9)$$

$$\text{For } j = 1, 2, \dots, n: \quad Y = y, \quad (10)$$

$$\text{and } j = n+1, n+2, \dots, n(m+1): \quad Y = y_{\alpha_q}(t). \quad (11)$$

With the prediction matrix, the code interactively solves the equation

$$Px = B, \quad (12)$$

where x is a vector used to correct y , y_{α_q} and its derivatives, and B is a continuously changing vector determined by valuating Eqs. (1) and (3) with the corrected values of y and y_{α_q} . The original Gear code (the classical Gear algorithm (Gear, 1971)) is elegant and accurate, if a user provides subroutines for F and G , and some parameters, such as error tolerance, maximum time-step, minimum time-step.

It has been shown that the prediction matrix \mathbf{P} is a block lower matrix, and the Equation(12) has the form (Shen, 1999a; 1999b):

$$\begin{bmatrix} \mathbf{P}_{11} & & & \\ \mathbf{P}_{21} & \mathbf{P}_{11} & & \\ \vdots & & \ddots & \\ \mathbf{P}_{(m+1)1} & & & \mathbf{P}_{11} \end{bmatrix} \begin{bmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \\ \vdots \\ \mathbf{x}_{m+1} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_1 \\ \mathbf{B}_2 \\ \vdots \\ \mathbf{B}_{m+1} \end{bmatrix}, \quad (12)$$

and

$$\mathbf{P}_{11} = \mathbf{I}_0 - h\beta_0 \mathbf{J}, \quad (13)$$

$$\mathbf{P}_{(q+1)1} = - \frac{h\beta_0 \partial [\mathbf{J}(\mathbf{y}, \boldsymbol{\alpha}, t) \mathbf{y}_{\alpha_q} + \mathbf{f}_{\alpha_q}(\mathbf{y}, \boldsymbol{\alpha}, t)]}{\partial \mathbf{y}}. \quad (14)$$

It is easy to triangularize this class of block matrices using sparse matrix technology (Pissanetsky, 1984). The procedure is as follows: (1) Do LU decomposition of the prediction matrix \mathbf{P}_{11} for model Equation(1). Solve the first subsystem $\mathbf{P}_{11} \mathbf{x}_1 = \mathbf{B}_1$ and obtain the vector \mathbf{x}_1 of order n . (2) Subtract the products $\mathbf{P}_{(q+1)1} \mathbf{x}_1$ from the right-hand side $\mathbf{B}_{(q+1)}$ for $q = 1, 2, \dots, m$. (3) Compute the vector $\mathbf{x}_{(q+1)}$ of order n from the equation $\mathbf{P}_{11} \mathbf{x}_{(q+1)} = \mathbf{B}_{(q+1)} - \mathbf{P}_{(q+1)1} \mathbf{x}_1$ for $q = 1, 2, \dots, m$.

1.2 Kinetic equations

For modeling of a kinetic process, two FORTRAN subroutines are necessary in Gear type procedure(Gear, 1971). One is DIFFUN subroutine another PEDERV subroutine for \mathbf{F} and \mathbf{G} respectively. The vector \mathbf{f} in Equation(1) is generally a nonlinear function of $y_i, i = 1, 2, \dots, n$. As it involves linear combinations of the reaction rates $r_l, l = 1, 2, \dots, N$ where N is number of reactions, that are represented by generalized polynomials:

$$r_l = k_l \prod_{k=1}^n y_k^{\gamma_{lk}}, \quad (15)$$

where k_l is the rate constant of l th reaction, and γ_{lk} is the coefficient of k th species as a reactant in l th reaction. If k th species is a reactant in l th reaction $r_{lk} \geq 0$ and $\sum_{k=1}^n \gamma_{lk} \leq 3$, otherwise $\gamma_{lk} = 0$.

Then:

$$f_i(\mathbf{y}, \boldsymbol{\alpha}, t) = \sum_{l=1}^N \sum_{i=1}^n \text{sign}_i c_i k_l \prod_{k=1}^n y_k^{\gamma_{lk}}. \quad (16)$$

If i th species is a reactant in l th reaction, $\text{sign}_i = -1$, or a product $\text{sign}_i = 1$, otherwise $\text{sign}_i = 0$, c_i is the coefficient of i th species in l th reaction. The element J_{ij} of Jacobian \mathbf{J} is:

$$J_{ij} = \frac{\partial f_i}{\partial y_j} = \sum_{l=1}^N \sum_{i=1}^n \text{sign}_i c_i k_l \gamma_{lj} y_j^{(\gamma_{lj}-1)} \prod_{\substack{k=1 \\ k \neq j}}^n y_k^{\gamma_{lk}}, \quad (17)$$

if j th species is a reactant in l th reaction.

If the direct method is employed to sensitivity analysis(Shen, 1999a; 1999b), the DIFFUN subroutine is from modeling Equation(1) coupled with its sensitivity coefficient Equation(3). The kinetic representation of model equation has been given in Equation(16). The sensitivity coefficient Equation(3) have two parts. One is a product of the matrix Jacobian of model Equation(1) and the vector of sensitivity coefficients. The kinetic representation of the element of Jacobian of model equation has been given in Equation(17). Another part is $\mathbf{f}_{\alpha_q}(\mathbf{y}, \boldsymbol{\alpha}, t)$. For sensitivity analysis of initial concentrations the term $\mathbf{f}_{\alpha_q}(\mathbf{y}, \boldsymbol{\alpha}, t)$ vanishes, for sensitivity analysis of rate constants only a few terms $\mathbf{f}_{\alpha_q}(\mathbf{y}, \boldsymbol{\alpha}, t) \neq 0$. If $\alpha_q = k_l$:

$$\mathbf{f}_{\alpha_q}(\mathbf{y}, \boldsymbol{\alpha}, t) = \sum_{i=1}^n \text{sign}_i c_i \prod_{k=1}^n y_k^{\gamma_{ik}}. \quad (18)$$

For calculation of prediction matrix of sensitivity analysis only \mathbf{P}_{11} and $\mathbf{P}_{(q+1)1}$ are needed evaluated and stored. The kinetic representation of \mathbf{P}_{11} can be calculated from Jacobian of model

Equation(17). The general form of $\mathbf{P}_{(q+1)1}$ is given:

$$\mathbf{P}_{(q+1)1} = -h\beta_0 y_q \frac{\partial \mathbf{J}}{\partial \mathbf{y}} - h\beta_0 \frac{\partial f_q(\mathbf{y}, \boldsymbol{\alpha}, t)}{\partial \mathbf{y}}. \quad (19)$$

If p th species is a reactant in l th reaction and $p \neq j$, the element of kinetic representation of $\frac{\partial \mathbf{J}}{\partial \mathbf{y}}$ for $\gamma_{ij} > 0$ and $\gamma_{lp} > 0$ is given.

$$\frac{\partial J_{ij}}{\partial y_p} = \sum_{l=1}^N \sum_{i=1}^n \text{sig } n_{ci} k_l \gamma_{lj} \gamma_{lp} y_j^{(\gamma_{lj}-1)} y_p^{(\gamma_{lp}-1)} \prod_{\substack{k=1 \\ k \neq j \\ k \neq p}}^N y_k^{\gamma_{lk}}. \quad (20)$$

If $p = j$ and $\gamma_{ij} > 0$:

$$\frac{\partial J_{ij}}{\partial y_j} = \sum_{l=1}^N \sum_{i=1}^n \text{sig } n_{ci} k_l \gamma_{lj} (\gamma_{lj} - 1) y_j^{(\gamma_{lj}-2)} \prod_{\substack{k=1 \\ k \neq j}}^N y_k^{\gamma_{lk}}. \quad (21)$$

Most of elementary reactions in atmosphere are the first or second order reactions, the Equation (21) can be simplified:

$$\text{If } \gamma_{lj} = 1, \quad \frac{\partial J_{ij}}{\partial y_j} = 0, \quad (22)$$

$$\text{if } \gamma_{lj} = 2, \quad \frac{\partial J_{ij}}{\partial y_j} = 2 \sum_{l=1}^N \sum_{i=1}^n \text{sig } n_{ci} k_l \prod_{\substack{k=1 \\ k \neq j}}^N y_k^{\gamma_{lk}}. \quad (23)$$

If $\alpha_q = k_l$ and j th species is a reactant in l th reaction, the kinetic representation of $\frac{\partial f_q(\mathbf{y}, \boldsymbol{\alpha}, t)}{\partial \mathbf{y}}$ for $\gamma_{ij} > 0$ is given:

$$\frac{\partial f_q(\mathbf{y}, \boldsymbol{\alpha}, t)}{\partial y_j} = \sum_{l=1}^n \text{sig } n_{ci} \gamma_{lj} y_j^{(\gamma_{lj}-1)} \prod_{\substack{k=1 \\ k \neq j}}^N y_k^{\gamma_{lk}}. \quad (24)$$

2 Program structure

The tool model is not a stand-alone code, it must be run in conjunction with various FORTRAN subroutines. To solve model Equation (1) and its coupled sensitivity coefficient Equation(3) many FORTRAN subroutines are necessary, such as subroutines from SLODE (Hindmarsh, 1980), MA28 (Duff, 1977) or Gear (Gear, 1971), in addition to subroutines generated by the tool model. Fig.1 shows the relationship among these components.

A package written with C language is developed to generate the FORTRAN subroutines of DIFFUN and PEDERV in Gear type procedure automatically from a particular chemical mechanism. It is noted KINTOOL. The KINTOOL reads user-supplied information about the chemical reactions for a particular reaction mechanism in text file. A structure of array in C language is used to recognize the reaction number, reactants, products and their coefficients. Two files are output.

One is FORTRAN subroutines of DIFFUN and PEDERV in Gear type procedure. Another is a text file which provides a record of the chemical reaction mechanism. It includes a summary of labeling of species, a list of species which appear in what reactions and a list of reactions with reactants, products and their coefficients. The text file is useful for the user to check the information of the chemical mechanism and to understand the FORTRAN subroutines. The process

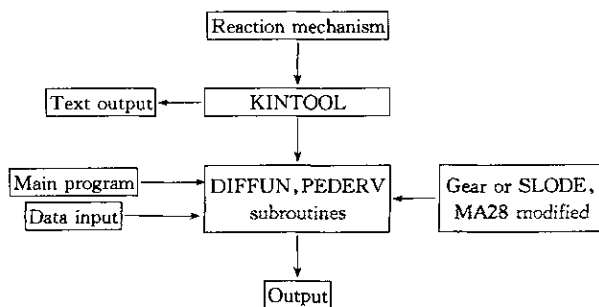


Fig.1 Relationship of KINTOOL and SLODE, modified MA28, and Gear subroutines in the tool model

of generating FORTRAN subroutine code is a procedure of manipulation of string according to Equation(1), (3), (4) and (7) and their kinetic representation Equation(16)-(22). The FORTRAN subroutines can be optimized by taking advantage of the sparse structure of the prediction matrix and the similarity of $J(y, \alpha, t)y_{\alpha_q}$ and their derivatives with respect to y_i for $q = 1, 2, \dots, m$ and $i = 1, 2, \dots, n$. Note that in the prediction matrix P , only submatrix P_{11} and $P_{(q+1)1, q} = 1, 2, \dots, m$ need to be evaluated and stored (Shen, 1999a; 1999b). The FORTRAN subroutines generated is very compact. It is also very flexible in that it can generate FORTRAN subroutines for any number of first order sensitivity coefficients with respect to just one or two etc. up to the total number of rate constants or of initial concentrations.

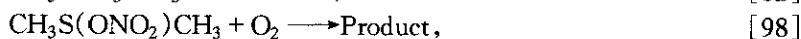
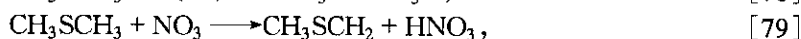
If a user likes to use the tool model developed in this paper, the first thing for the user is to prepare a chemical mechanism in text file. The first 6 column is the reaction number, then the reaction, and rate constant. If one reaction occurs more than one line, the reaction number is not listed in the second and next lines. So, the formatted mechanism is much easily understood by chemists. Then, the user executes the KINTOOL to generate DIFFUN and PEDERV subroutines for model equation, or sensitivity analysis of rate constants or initial concentrations. The user should write a short main program (there is a sample) to call SLODE (Hindmarsh, 1980) subroutine or Gear subroutine (Gear, 1971). If a user likes to run model equation, the classical Gear subroutine (Gear, 1971) or SLODE (Hindmarsh, 1980) subroutine can be chosen optionally. It is dependent on which subroutines are in user's hands. If a user likes to do sensitivity analysis, SLODE (Hindmarsh, 1980) and modified MA28 (Duff, 1977) subroutines are suggested, because the classical Gear procedure (Gear, 1971) is not efficient in this circumstance (Shen, 1999a; 1999b), although the KINTOOL can generate the DIFFUN and PEDERV subroutine for classical Gear procedure. The KINTOOL and other FORTRAN subroutines together are in noted the tool model.

3 Miscellaneous

The KINTOOL has some special functions. If a user inputs a chemical mechanism into the KINTOOL, it will show in the output file that which reaction rate constant is equal to zero; which reactions have the same reactants; which species concentration does not change in the reaction system. With this information the user may modify the mechanism more efficiently.

3.1 Test of rate constant

After the tool model reads a input file of chemical mechanism, the tool model automatically tests that which rate constant is equal to or less than zero. If there is a reaction with rate constant less than zero, a warning will show "There is a negative rate constant in x th reaction, could you check the mechanism?" on the screen and on the output file. For example, Yin (Yin, 1990a) investigated the mechanism of photooxidation of dimethyl sulfide and dimehyl disulfide. They discussed all available kinetic and mechanistic information. There are some reactions with rate constants very close to zero. Follows Yin (Yin, 1990a) to number the reaction, these reactions are:



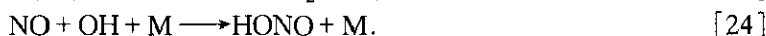
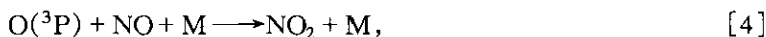
If these reactions are included in model equation, the rates are approximately equal to zero. If these reactions are included in sensitivity analysis, the sensitivity coefficients with respect to these reaction rate constants are approximately equal to zero. That is, nothing happened with these reactions. From chemistry these reactions are too slow in our present understanding, therefore, from the point of view of modeling or sensitivity analysis we do not need to include these reactions. With this informaton the user can delete the reactions with rate constants very close to zero for modeling and/or sensitivity analysis.

3.2 The third body

If there is an inert third body M in an atmospheric reaction mechanism, the concentration of M in the reaction system does not change at all.

$$\frac{d[M]}{dt} = 0.0, [M] = [M]_0.$$

For example, in the mechanism of photo-oxidation of dimethyl sulfide and dimethyl disulfide (Yin, 1990a) there are reactions:



The inert third body M appears as a reactant and product with the same coefficients in reactions. If the third body M is treated as a reactant and product explicitly the rate equation is given:

$$\begin{aligned} \frac{d[M]}{dt} = & k_4[O(^3P)][NO][M] - k_4[O(^3P)][NO][M] + k_{24}[NO][HO][M] - \\ & k_{24}[NO][HO][M] + \dots \end{aligned}$$

and its Jacobian:

$$\frac{\partial}{\partial [O(^3P)]} \left[\frac{d[M]}{dt} \right] = k_4[NO][M] - k_4[NO][M] + \dots$$

$$\frac{\partial}{\partial [NO]} \left[\frac{d[M]}{dt} \right] = k_4[O(^3P)][M] - k_4[O(^3P)][M] + k_{24}[HO][M] - k_{24}[HO][M] + \dots$$

$$\frac{\partial}{\partial [OH]} \left[\frac{d[M]}{dt} \right] = k_{24}[NO][M] - k_{24}[NO][M] + \dots$$

Two equal terms with different sign appear in model equations and Jacobian matrix. Subtracting of two big equal float numbers would produce a large roundoff error in computation. If the third body M is not treated as a reactant and product in rate equation explicitly, the numerical instability would be improved significantly. The tool model automatically checks whether species appear as a reactant and product with the same coefficient in a reaction, if does, it displays on the screen and on the output file. For the default version the third body does not appear in the rate equation. The FORTRAN program generated by the tool model is much more stable, fast and accurate. The third body concentrations should be included in rate constants, such as $k'_4 = k_4[M]$, the model equation and sensitivity analysis would be simplified.

4 Photo-oxidation of dimethyl disulfide in the presence of NOx

The tool model can be used to calculate the first order sensitivity coefficients for any stiff problem solved by Gear algorithm. For demonstration, we applied it to photo-oxidation of dimethyl disulfide. The mechanism of the atmospheric oxidation of dimethyl disulfide has been investigated (Yin, 1990a; 1990b) both in theory and in experiments. The predictions of the mechanism were found to be in substantial agreement with the measured concentrations from the smog chamber. This mechanism includes 198 reactions which are too long to list here, but they can be found in the original paper (Yin, 1990a). Simulation and sensitivity analysis of the outdoor smog chamber experiment of CH_3SSCH_3 -NO_x-air- $h\nu$ (experiment DDS7A) are described here to illustrate the application of the tool model developed in this paper. The initial concentrations of NO, NO₂ and CH_3SSCH_3 are 0.149, 0.055 and 0.526 ppm respectively. The profiles of temperature and intensity of irradiation were not reported in the literature (Yin, 1990b), thus we choose the average temperature as 304K, the relative humidity as 47% and an atmospheric pressure in our simulation. The rate constant k_1 in Reaction [1] is assumed to be 0.48 min^{-1} .



The simulated temporal profiles of NO, NO₂, O₃, CH_3SSCH_3 and SO₂ were almost the same as

those by Yin(Yin, 1990b) up to 260 min. Most of CH_3SSCH_3 is consumed in the first 40 min.

To identify the important and unimportant reactions, the normalized first order sensitivity coefficients $S_{ia_q,t}$ of all species with respect to each reaction rate constant were calculated every 10 seconds for $i = 1, 2, \dots, n$; $q = 1, 2, \dots, m$; $t = 10, 20, \dots, 2400$, in the first 40 min.

$$S_{ia_q,t} = \frac{\alpha_q \partial y_i}{y_i \partial \alpha_q} = \frac{\partial \ln y_i}{\partial \ln \alpha_q}. \quad (25)$$

The maximum absolute normalized sensitivity coefficients were also calculated over the simulation period (2400 s) as

$$S_{ia_q,\max} = \text{MAX}(\text{ABS}(S_{ia_q,10}), \text{ABS}(S_{ia_q,20}), \dots, \text{ABS}(S_{ia_q,2400})).$$

The time at which the maximum absolute normalized sensitivity coefficients occur is denoted by

$$t_{ia_q,\max} = t, \text{ if } S_{ia_q,\max} = \text{ABS}(S_{ia_q,t}).$$

The main product of photo-oxidation of dimethyl disulfide is SO_2 . We list the maximum absolute normalized sensitivity coefficients $S_{ia_q,\max}$ larger than 0.4 for dimethyl disulfide and those larger than 0.1 for sulfur dioxide and the corresponding time $t_{ia_q,\max}$ in Table 1. The sequence in Table 1 is according to descending of the maximum absolute normalized sensitivity coefficients of dimethyl disulfide concentration with respect to rate constants. For photo-oxidation of CH_3SCH_3 to form SO_2 , the most important reactions are free radical OH, $\text{O}(^3\text{P})$ reactions(Shen,1999). But, for photo-oxidation of CH_3SSCH_3 to form SO_2 , in addition to free radical OH, $\text{O}(^3\text{P})$ reactions the photo-oxidation of CH_3SSCH_3 and the free radical reactions of its produced CH_3S , CH_3SOO and CH_3SOO play an important role. The important reactions for photo-oxidation of dimethyl disulfide and production of SO_2 have been discussed by Yin(Yin, 1990a; 1990b)

Table 1 The maximum absolute normalized sensitivity coefficients(with sign) and its occurred time(min) of dimethyl disulfide and sulfur dioxide

No.	Reaction	CH_3SSCH_3		SO_2	
		Coeffi.	Time	Coeffi.	Time
255	$\text{CH}_3\text{S} + \text{NO} \longrightarrow \text{CH}_3\text{SNO}$	2.828	40.0	-0.856	6.1
256	$\text{CH}_3\text{SNO} + h\nu \longrightarrow \text{CH}_3\text{S} + \text{NO}$	-2.083	40.0	0.482	18.1
226	$\text{CH}_3\text{SSCH}_3 + h\nu \longrightarrow \text{CH}_3\text{S} + \text{CH}_3\text{S}$	-2.045	40.0	0.694	3.8
249	$\text{CH}_3\text{S} + \text{NO}_2 \longrightarrow \text{CH}_3\text{SO} + \text{NO}$	-1.879	40.0	0.609	3.4
2	$\text{O}(^3\text{P}) + \text{O}_2 \longrightarrow \text{O}_3$	1.566	40.0	-0.416	1.2
223	$\text{CH}_3\text{SSCH}_3 + \text{O}(^3\text{P}) \longrightarrow \text{CH}_3\text{SO} + \text{CH}_3\text{S}$	-1.505	40.0	0.416	1.2
1	$\text{NO}_2 + h\nu \longrightarrow \text{NO} + \text{O}(^3\text{P})$	-1.503	40.0	0.379	0.2
278	$\text{CH}_3\text{SO} + \text{CH}_3\text{SNO} \longrightarrow \text{CH}_3\text{S}(\text{O})\text{SCH}_3 + \text{NO}$	1.429	40.0	-0.285	25.0
247	$\text{CH}_3\text{S} + \text{O}_2 \longrightarrow \text{CH}_3\text{SOO}$	-1.168	40.0	0.315	16.9
248	$\text{CH}_3\text{SOO} \longrightarrow \text{CH}_3\text{S} + \text{O}_2$	1.098	40.0	-0.293	17.2
260	$\text{CH}_3\text{SOO} + \text{NO} \longrightarrow \text{CH}_3\text{SO} + \text{NO}_2$	-1.062	40.0	0.293	17.3
290	$\text{CH}_3\text{SO}_2 \longrightarrow \text{SO}_2 + \text{CH}_3$	-0.943	40.0	0.500	0.2
280	$\text{CH}_3\text{S}(\text{O})\text{OO} + \text{NO} \longrightarrow \text{CH}_3\text{SO}_2 + \text{NO}_2$	-0.863	40.0	0.225	21.6
270	$\text{CH}_3\text{SO} + \text{NO}_2 \longrightarrow \text{CH}_3\text{SO}_2 + \text{NO}$	-0.856	40.0	0.192	18.5
45	$\text{HCHO} + h\nu + \text{O}_2 \longrightarrow 2\text{HO}_2 + \text{CO}$	-0.853	40.0		
222	$\text{CH}_3\text{SSCH}_3 + \text{OH} \longrightarrow \text{CH}_3\text{SOH} + \text{CH}_3\text{S}$	-0.740	40.0		
28	$\text{NO}_2 + \text{OH} \longrightarrow \text{HNO}_3$	0.710	40.0		
311	$\text{CH}_3\text{S}(\text{O})_2\text{OO} + \text{NO}_2 \longrightarrow \text{CH}_3\text{S}(\text{O})_2\text{OONO}_2$	0.577	40.0		
304	$\text{CH}_3\text{S}(\text{O})_2\text{OO} + \text{NO} \longrightarrow \text{CH}_3\text{SO}_3 + \text{NO}_2$	-0.479	40.0		
312	$\text{CH}_3\text{S}(\text{O})_2\text{OONO}_2 \longrightarrow \text{CH}_3\text{S}(\text{O})_2\text{OO} + \text{NO}_2$	-0.478	40.0		
291	$\text{CH}_3\text{SO}_2 + \text{O}_2 \longrightarrow \text{CH}_3\text{S}(\text{O})_2\text{OO}$	0.472	40.0	-0.494	0.2
287	$\text{CH}_3\text{S}(\text{O})\text{OO} + \text{NO}_2 \longrightarrow \text{CH}_3\text{S}(\text{O})\text{OONO}_2$	0.465	40.0	-0.176	11.6
302	$\text{CH}_3\text{SO}_2 + \text{CH}_3\text{SNO} \longrightarrow \text{CH}_3\text{S}(\text{O})_2\text{SCH}_3 + \text{NO}$	0.456	40.0		
288	$\text{CH}_3\text{S}(\text{O})\text{OONO}_2 \longrightarrow \text{CH}_3\text{S}(\text{O})\text{OO} + \text{NO}_2$	-0.435	40.0	0.117	20.3
268	$\text{CH}_3\text{SO} + \text{O}_2 \longrightarrow \text{CH}_3\text{S}(\text{O})\text{OO}$	-0.429	40.0		
269	$\text{CH}_3\text{S}(\text{O})\text{OO} \longrightarrow \text{CH}_3\text{SO} + \text{O}_2$	0.418	40.0		

5 Conclusion

If a user would like to use the tool model for modeling of the atmospheric chemical kinetics with sensitivity analysis, the first thing is to prepare a chemical mechanism with rate constants in a simple formatted text file. Then, the user executes the KINTOOL in the tool model automatically to generate FORTRAN subroutines for modeling or sensitivity analysis of rate constants or initial concentrations from the chemical mechanism. Another list text file is provided for the user to understand the FORTRAN subroutines. The user would write a short main program (there is a sample) to call SLODE or Gear package. If a user likes to do sensitivity analysis, SLODE and modified MA28 package in the tool model are suggested. Because the Jacobian matrix of the model equation is the same as that of the sensitivity coefficient equation with respect to a parameter, it is only necessary to triangularize the matrix related to the Jacobian matrix of the model equation. It is much more efficient.

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