KINETICS OF REACTIONS OCCURRING IN THE UNPOLLUTED TROPOSPHERE, II. SENSITIVITY ANALYSIS

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A reaction mechanism suggested for the description of
the kinetics in the unpolluted troposphere was inves-
tigated by rate sensitivity and concentration sensitiv-
ity analyses. The study resulted in a 50-step reduced
model and revealed the change of the importance of re-
actions during a diurnal cycle.

Механизм, описывающий кинетику реакций в незагрязненной
тропосфере, был исследован, анализируя чувствительно-
сти на скорости и на концентрации. В результате была
получена модель из 50 ступеней, которая подтверждает
изменение важности отдельных реакций в течение днев-
ного цикла.

INTRODUCTION

In Part I [1] a reaction mechanism of the photochemistry
of unpolluted troposphere had been suggested, which consisted
of 48 chemical reactions, including 12 photochemical steps. In
addition, emission and deposition processes were taken into
account, which were handled in the same way as the chemical re-
actions. Hydrocarbons were represented by methane, the most
abundant hydrocarbon in the unpolluted troposphere. The selec-
ted 60-step model — called the background model of the tropo-
sphere — was used in the computation of the diurnal concentra-

tion profiles for the trace pollutants. The calculated concentrations are characteristic values for a typical summer day (temperature 298 K) at mid-lattitudes of 45° N and at ground level.

In this paper the background model is investigated by sensitivity analysis. The objective of this study is to reveal the reactions which play an important role in the photooxidation processes and to identify the redundant reactions of the model.

SENSITIVITY ANALYSIS OF VARIABLE-PARAMETER MODELS

The coefficients of photochemical reactions show up a diurnal variation as a result of change in the intensity of sunshine. Most methods of sensitivity analysis can be used only in the study of constant-parameter systems [2]. Variable-parameter models may be investigated either by numerical calculation of the Gâteaux differentials (see e.g. [3]) or by the computation of functional derivatives (see e.g. [4, 5]).

Calculation of functional sensitivities is definitely required if the effect of the change of parameter functions on the solution is studied. Variable-parameter models may be investigated in the same way as the constant-parameter models if the sensitivity method assigns kinetic information to definite concentration sets and not to time intervals. However, in this case only the importance of the parameters can be established.

The background mechanism has been investigated previously by the method of quasi-stationary sensitivities [6]. This method is based on an approximation of the concentration sensitivities utilizing the singular perturbation theory. Here the method of rate sensitivities [7] will be used to gain information about the mechanism.

An element of the log-normalized rate sensitivity matrix $\tilde{F} = \{\partial \ln f_i / \partial \ln k_j\}$ expresses the percentage change of the rate of formation of species i caused by the percentage change of rate coefficient of reaction j. The matrix can be calculated easily [7]:

$$\tilde{F} = \{ \nu_{ij} \, f_i / R_j \}$$

where ν_{ij} is an element of the stoichiometric matrix, f_i is the rate of formation of species i and R_j is the rate of reaction j.

ANALYSIS OF THE BACKGROUND MODEL

Species concentrations belonging to each hour of a diurnal cycle were calculated by the procedure described in [1]. With these concentrations, the log-normalized rate sensitivity matrices were computed according to the equation given above. The matrices were interpreted by using principal component analysis [7]. A reaction was considered important if it belonged to an eigenvector element greater than 0.1 and the eigenvector corresponded to an eigenvalue greater then 0.0001. The results of the analysis are presented in Fig. 1. Shaded intervals indicate time periods where the particular reaction proved to be important. Reaction numbers conform to the numbering of the mechanism published in [1].

The figure shows the deposition processes (steps 49-55) and the emission processes (steps 56-60) to be important both during day time and at night. The only exception is the deposition of HONO (step 50) which is important only at night. A number of the chemical reactions appear to be important either during daytime or at night. There are ten reaction steps which are never important during a diurnal cycle. These are reactions 11, 12, 18, 19, 20, 23, 26, 41, 47 and 48. Elimination of these reactions results in a 50-step reduced model. The concentrations computed with the reduced model were compared with those derived from the full model after 24 hours simulation time, starting the simulations at noon with the same concentration set. The deviations were below 1% for species NO_2, O_3, HCHO, CH_4, CO, SO_2, SO_4^{2-}, HONO, CH_3O, O, and O*. For species NO, H_2O_2, HNO_3, HO_2NO_2, CH_3O_2, HO_2, N_2O_5, NO_3, OH and CH_3 the deviation was around 2%. The agreement is the worst in case of CH_3O_2H, where the reduction resulted in 7% deviation.

The results summarized in Fig. 1 are very similar to those given in Fig. 1 of paper [6], which represent the reaction importances derived from the quasi-stationary sensitivities. The
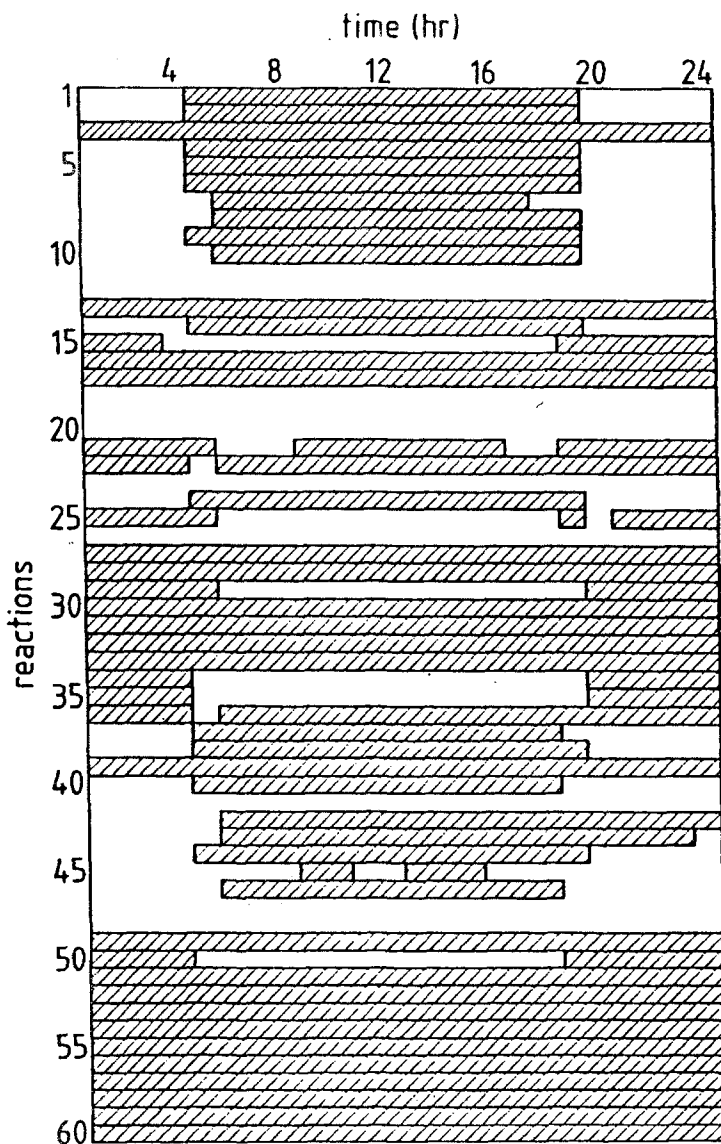
Fig. 1. Diurnal changes of reaction importances

latter method gave a 49-step reduced mechanism, which was iden-
tical to the reduced mechanism presented here, except for one
reaction which was step 45. Elimination of reaction 45 from the

50-step reduced model caused a slight increase of the concentration of H_2O_2 (cf. Table 1 in article [6]).

The results summarized in Fig. 1 were also compared with local concentration sensitivity outcomes. Local concentration sensitivity analysis should not be applied for the study of variable-parameter models. However, the photochemical parameters of the background model are zero at night and they change very slowly around noon. This permits us to make an approximate test. The local concentration sensitivity matrices were calculated from 12^{OO} to 13^{OO} and from 0^{OO} to 1^{OO} by the Decomposed Direct Method encoded in program ROW4S [8]. In the first calculation the rate coefficients were fixed at the noon values. The matrices obtained were interpreted by principal component analysis [9]. Threshold values were 0.0001 for the eigenvalues and 0.1 for the eigenvector elements. The analysis showed the following reactions to be important at noon: 1-10, 13-14, 16-17, 22, 24, 27-28, 30-33, 36-40, 42-46, 49, 51-57, 60. From the results of the other calculation the important steps at midnight are: 3, 13, 15-17, 21-22, 25, 27-35, 39, 42, 49-57, 60. This list is in reasonably accordance with Fig. 1. The main deviation is that the concentration sensitivity analysis showed steps 58 and 59, the emission of CH_4 and CO, respectively, to be negligible. Although these steps are important in the long-term material balance of the atmosphere, however, their elimination does not cause significant concentration changes in a short time as for instance in one hour, which was the time interval of our concentration sensitivity calculations.

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