

A Condensed Gas-Phase Chemical Model and Its Application

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ABSTRACT

Using the "lumped mechanism" and "counting species" methods, we developed a condensed gas-phase chemical model based on a simplified one. The modified quasi-steady-state approximation (QSSA) scheme and the error redistribution mass conservation technique are adopted to solve the atmospheric chemistry kinetic equations. Results show that the condensed model can well simulate concentration variations of gas species such as SO_2 , NO_x , O_3 , H_2O_2 and conversion rates of SO_2 and NO_x transformation to H_2SO_4 and HNO_3 . These results are in good agreement with those from the simplified model. The conversion rates of SO_2 and NO_x under different initial concentrations and meteorological conditions are computed, and the results can be directly applied to regional acid deposition model.

Key words: Gas-phase chemistry, Conversion rate

1. Introduction

The gas-phase chemistry is one of the most important components in regional air quality model, which can quantitatively illustrate the temporal variation of species concentration due to gas-phase chemical transformation and supply concentration fields for cloud-rain chemical model. Especially, for simulation of regional acid deposition, gas-phase chemistry cannot be simply parameterized but be described by chemical kinetic model. On the other hand, coupling a complex chemical submodel in a 3D Eulerian model will lead to large computation expense. Odman's (1992) study has showed that the numerical treatment of chemical kinetics takes approximately 80%–90% of the total computation time in current photochemical air quality models, therefore, if higher computation efficiency is needed, the chemical model should be designed in such a way as that condensed reaction mechanism and more accurate and efficient computation algorithm are adopted.

In this paper, the "lumped mechanism" and "counting species" schemes are used to construct a condensed gas-phase chemical model on the basis of a simplified one, which can be directly applied to the regional acid deposition model. The modified QSSA scheme with a mass conservation technique of error redistribution is used to solve atmospheric chemistry kinetic equations. The concentration variations of SO_2 , NO_x , O_3 , H_2O_2 etc. and the conversion rates of SO_2 , NO_x transformation to H_2SO_4 , HNO_3 are calculated, and the effects of SO_2 , NO_x , HC concentration, air temperature, relative humidity, solar zenith angle, clouds on conversion rates are investigated.

2. Gas-phase chemical mechanism

2.1 Simplified gas-phase chemical mechanism

There have been a lot of gas-phase chemical mechanisms, such as Carbon-Bond (Whitten, 1980), Explicit (Leone and Seinfeld, 1985), RADM (Chang, 1987), LCC (Lurmann et al, 1987), which can well illustrate transformation of SO_2 , NO_x to H_2SO_4 , HNO_3 . But most of these chemical mechanisms include so many reactions and species that if coupled with the regional model it will cost high computation expense. On the other hand, if the key transformation processes can be included in a gas-phase chemical mechanism, the model will not be too complex and less computation time will be cost. We have developed a simplified mechanism consisting of 20 chemical species and 36 reactions, which has been performed well in the simulation of regional acid deposition (Wang, 1996).

2.2 Condensed gas phase chemical mechanism

The above-mentioned gas-phase chemical model can well simulate the distributions of air pollutant concentration and acid deposition if coupled in the regional acid deposition model. The acid deposition model can only be used for case study other than long term simulations due to the fact that the chemical model is so complicated and very time-consuming to solve the nonlinear, stiff chemistry kinetic equations in thousands of grid meshes. Therefore, the simplified chemical mechanism needs to be further modified to form a so-called condensed chemical mechanism considering the three rules as follows:

(1) The organic compounds are represented by HC according to the lumped mechanism so that the number of species and reactions are reduced, while in the simplified mechanism, they are classed into four groups, such as PAR, OLE, ARO and CAR.

Table 1. Condensed gas-phase chemistry mechanism

Reaction equations	K_T (298K)*	E / R
(G1) $\text{NO}_2 + (h\nu) \rightarrow \text{NO} + \text{O}$	$2.199 \times 10^{-1} \text{J}^{**}$	
(G2) $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	4.386×10^6	-650
(G3) $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	2.7×10^1	1370
(G4) $\text{HC} + \text{O} (+\text{O}_2) \rightarrow (\text{RO}_2 + \text{OH} + \text{HCHO})$	5.1×10^3	
(G5) $\text{HC} + \text{O}_3 (+\text{O}_2) \rightarrow (\text{RO}_2 + \text{OH} + \text{HCHO})$	1.2×10^{-2}	
(G6) $\text{HC} + \text{OH} (+\text{O}_2) \rightarrow \text{RO}_2$	2.5×10^4	
(G7) $\text{HO}_2 + \text{NO} \rightarrow (\text{OH} + \text{NO}_2)$	2.0×10^3	-240
(G8) $\text{RO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{R}'\text{CHO} + \text{HO}_2$	3.0×10^3	
(G9) $\text{NO} + \text{OH} \rightarrow \text{HNO}_2$	3.0×10^3	-610
(G10) $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	5.0×10^3	-560
(G11) $\text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_3 + \text{O}_2$	3.0×10^0	
(G12) $\text{RO}_2 + \text{NO}_2 \rightarrow \text{PAN}$	1.0×10^1	
(G13) $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	0.4×10^4	-800
(G14) $\text{SO}_2 + \text{OH} \rightarrow \text{SO}_4^{2-}$	$0.1 \times 10^4 \text{RH}^{***}$	
(G15) $\text{SO}_2 + \text{HO}_2 \rightarrow \text{SO}_4^{2-}$	1.33RH	

* $K_T = K_{298} \text{Exp}\{(1/298 - 1/T)E/R\}$ (Unit: min^{-1} for the first order reaction, 10^6min^{-1} for the second order reaction, 10^{12}min^{-1} for the third order reaction)

** is photodissociation coefficient

*** RH is relative humidity

(2) In the simplified mechanism, SO_2 is oxidized by OH, HO_2 radicals described by several transitional reactions which are merged into two reactions (G14) and (G15).

(3) Several "counting species" are added to some reactions in order to judge which reaction are more important, therefore, some unimportant reactions are abandoned.

On the basis of rules mentioned above, a condensed gas-phase chemistry mechanism is formed, which includes 12 species and 15 reactions. The new mechanism is listed in Table 1.

3. Numerical scheme

A large stiff system of nonlinear equations describing how the pollutants react chemically can be written as:

$$\frac{dC_i}{dt} = P_i - L_i C_i, \quad (1)$$

where i stands for different species, C_i is concentration of species i , P_i and $L_i C_i$ are production term and lost term respectively.

There are many ways to solve equation (1). At present, scientists are engaging in finding new numerical algorithm with high accuracy and efficiency.

The simplified mechanism uses Hybrid scheme of Young and Boris (1977). Following Odman et al. (1992), the Hybrid scheme has high efficiency compared with the Gear method. Hesstvedt et al. (1978) put forward the (QSSA) method with about 2-4 times higher efficiency than the Hybrid scheme. Hybrid is more accurate but less efficient than QSSA, while QSSA is more efficient but less accurate compared to Hybrid. In this paper, an improved QSSA method is posed on the basis of QSSA with a correction step and convergence check. First, the predicted concentration $C_i^p(t + \Delta t; \Delta t)$ at $t + \Delta t$ is calculated using the QSSA scheme, where Δt is the time step. Then, $P_i(C^p)$, $L_i(C^p)$, dC_i^p / dt are computed to obtain the corrected concentration C_i^c .

When $L_i(C^p)\Delta t < 0.01$,

$$C_i^c(t + \Delta t; \Delta t) = C_i(t) + \left(\frac{dC_i}{dt} + \frac{dC_i^p}{dt} \right) \frac{\Delta t}{2}. \quad (2)$$

When $0.01 < L_i(C^p)\Delta t < 10$,

$$C_i^c(t + \Delta t; \Delta t) = \varphi_i + [C_i(t) - \varphi_i] \exp[-(L_i(c) + L_i(c^p))\frac{\Delta t}{2}]. \quad (3)$$

when, $L_i(C^p)\Delta t > 10$,

$$C_i^c(t + \Delta t; \Delta t) = \varphi_i, \quad (4)$$

where,

$$\varphi_i = \frac{1}{4} [P_i(c) + P_i(c^p)] \frac{1}{L_i(c)} + \frac{1}{L_i(c^p)}.$$

The third step is convergence check. If $|C_i^p - C_i^c| / C_i^c < \varepsilon$ ($\varepsilon = 10^{-6}$), the concentration is convergent, otherwise, it should be recalculated with a smaller time step.

In addition, a mass conservation technique of redistributing errors proportionally among

various species (Odman, 1992) is used to solve equation (1) in order to keep chemical balance.

4. Model comparison and analyses

Many studies show that the simplified model performs well in many aspects (Wang et al., 1996), so, the condensed model is compared with the simplified one in order to understand its performance. The two models were integrated for 24 hours with time-varied temperature and photodissociation coefficient under the clear sky. The initial concentrations of each species are listed in Table 2. The simplified model uses the Hybrid scheme with a time step of 1 minute, while the condensed model applies the improved QSSA method with a time step of 30 seconds.

Table 2(a). Initial concentrations of simplified model ($\times 10^{-6}$)

species	NO	NO ₂	CO	HNO ₂	PAR	OLE	ARO	CAR	SO ₂
concentration	0.075	0.025	1.0	0.005	0.1368	0.0978	0.057	0.086	0.01

Table 2(b). Initial concentrations of condensed model ($\times 10^{-6}$)

species	NO	NO ₂	HC	SO ₂
concentration	0.075	0.025	0.30	0.01

4.1 Concentration of gas species

The time-dependent concentrations of SO₂, NO_x etc. species are computed and the results are shown in Fig. 1. The SO₂ and SO₄²⁻ concentrations calculated by the condensed model agree well with that by the simplified model. NO concentration calculated by the condensed model is also generally in agreement with that from the simplified model, while NO₂ concentration is relatively lower due to the fact that reactions of NO₃+NO→2NO₂ and PAN→NO₂+CH₃COO₂ are not considered. The peak values of O₃, PAN concentrations are lower and the equilibrium time is shorter for the condensed model. There is not remarkable difference for OH concentration calculated by the two models, concentration of HO₂ radical is a little lower in the condensed model.

4.2 Conversion rate

Figure. 2 shows the mean rates of SO₂, NO_x transformation to H₂SO₄, HNO₃. Average conversion rate is defined in the formula as follows:

$$R_{Ai} = \frac{C_i(t_0) - C_i(t)}{C_i(t_0)(t - t_0)}, \quad (5)$$

where i stands for SO₂ or NO_x; $C_i(t_0)$ and $C_i(t)$ is the concentration of species i at t_0 and t respectively.

Figure. 2 shows that the average conversion rates of SO₂ and NO_x are 0.69% / h and 4.6% / h, the maxima 0.85% / h and 7.4% / h appear at 3:00 pm and 11:00 am. Many studies show that the average conversion rates of SO₂ and NO_x are 1.0% / h and 6.0% / h, respectively (Sang et al., 1992). It shows that SO₂ conversion rates of the two models are very

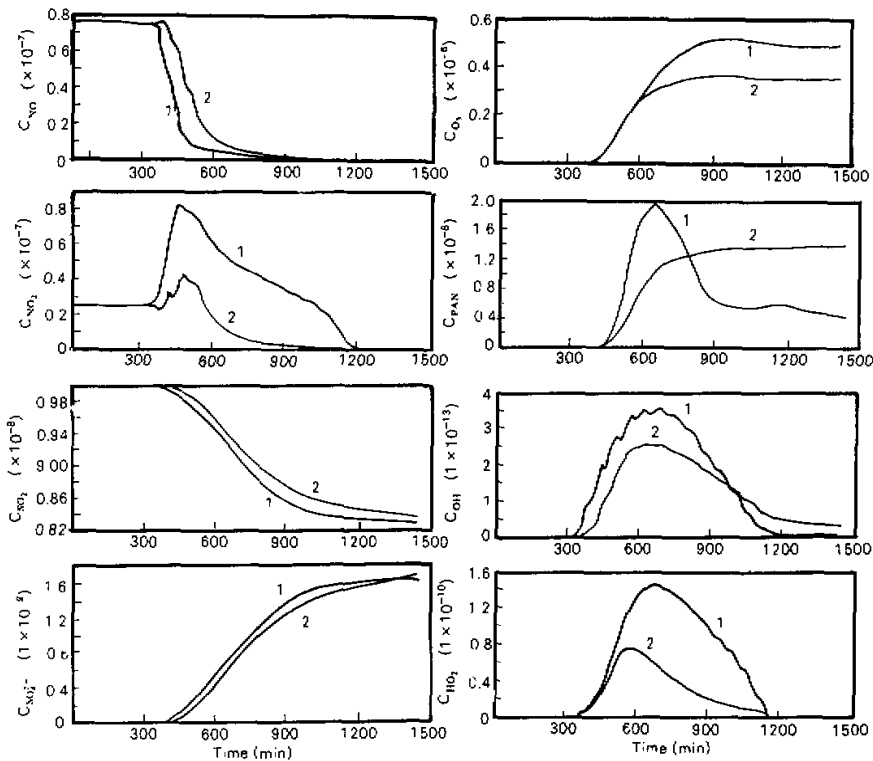


Fig. 1. Gas species concentrations as a function of time. 1 simplified model, 2 condensed model.

consistent, NO_x conversion rate of the condensed model is higher than that of the simplified model and more approximate to the common value.

In general, the condensed model agrees well with the simplified one in SO_2 , SO_4^{2-} , NO_x , OH etc. concentrations and SO_2 conversion rate, and has relatively lower O_3 , PAN, HO_2 concentrations and NO_x conversion rate. Since the main composition of acid deposition in China is sulphate, chemical transformation of SO_2 is more important than that of NO_x . As the condensed model succeeds in simulating SO_2 concentration and conversion rate, which includes fewer species and reactions than the simplified model but has higher efficiency, it will be useful for the gas-phase chemistry simulation in the regional acid deposition model.

5. Model application

As mentioned above, in a regional acid deposition model, the parameterization scheme cannot be used for atmospheric chemistry, while the complicated chemical model needs much computation time. Actually, SO_2 , NO_x conversion rates under different combined conditions can be calculated using the independent gas-phase chemical model and can be applied by the acid deposition model directly.

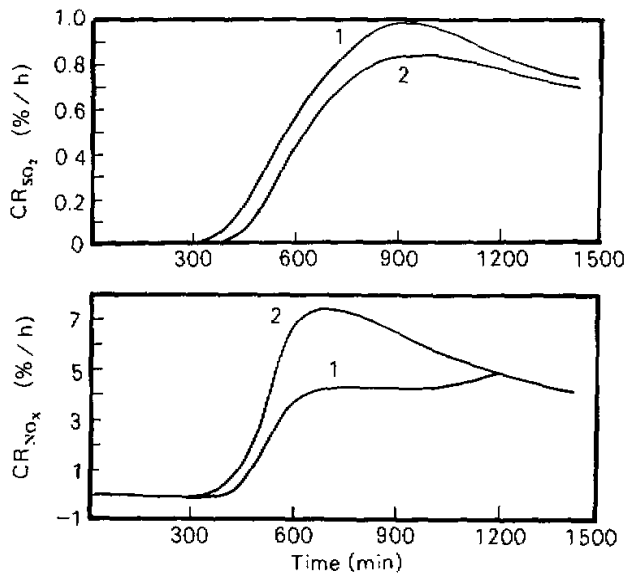


Fig. 2. Conversion rates as a function of time. 1 simplified model, 2 condensed model.

The conversion rates of SO_2 and NO_x under different initial concentrations and meteorological conditions are computed, where the effect of cloud cover on the conversion rate is considered following the scheme of Chang (1989).

5.1 Conversion rate at various meteorological situation

In this section, the SO_2 and NO_x conversion rates as functions of solar zenith angle (SZA), air temperature and relative humidity are computed and the cloud effect on the conversion rate is investigated, which are shown in Fig. 3. The initial concentrations of SO_2 , NO_x , HC are listed in Table 2(b). If cloud is considered, total cloud amount is set to be 0.5, altitude 1000 m, liquid water content 1 g/m^3 . The base values of solar zenith angle, air temperature and relative humidity are 45° , 298 K and 100%. When one parameter is changed, the other two keep constant.

Figure 3 shows that the SO_2 , NO_x conversion rates decrease if SZA increases. The conversion rates reduce sharply when $\text{SZA} > 60^\circ$ because the solar radiation is weak and the photodissociation rate of NO_2 is low.

When cloud appears, the conversion rates of SO_2 and NO_x enhance above cloud, and reduce below cloud. In cloud, the conversion rates increase when $\text{SZA} < 45^\circ$ and decrease when $\text{SZA} > 45^\circ$. The reason is that, above cloud, the photodissociation rates increase compared to a clear-sky situation due to reflection from the cloud. Below cloud, where only diffuse radiation will penetrate, photodissociation rates are much lower than corresponding clear-sky rates. The radiation is reduced and efficiently scattered in cloud, the net effect is that the photolysis rate can either enhance or reduce, depending on solar zenith angle (Jonson et al., 1993). The variations of photodissociation lead to the changes of conversion rates.

The SO_2 conversion rate increases while the NO_x conversion rate decreases with the enhancement of temperature because the reaction rates are influenced by temperature. For

the heat-absorbed reactions, the rates increase with temperature, while for the heat-released reactions are on the contrary.

Relative humidity has little effect on the NO_x conversion rate, while the SO_2 conversion rate increases linearly with the enhancement of relative humidity. It shows that SO_2 transformation to SO_4^{2-} has good relation to relative humidity.

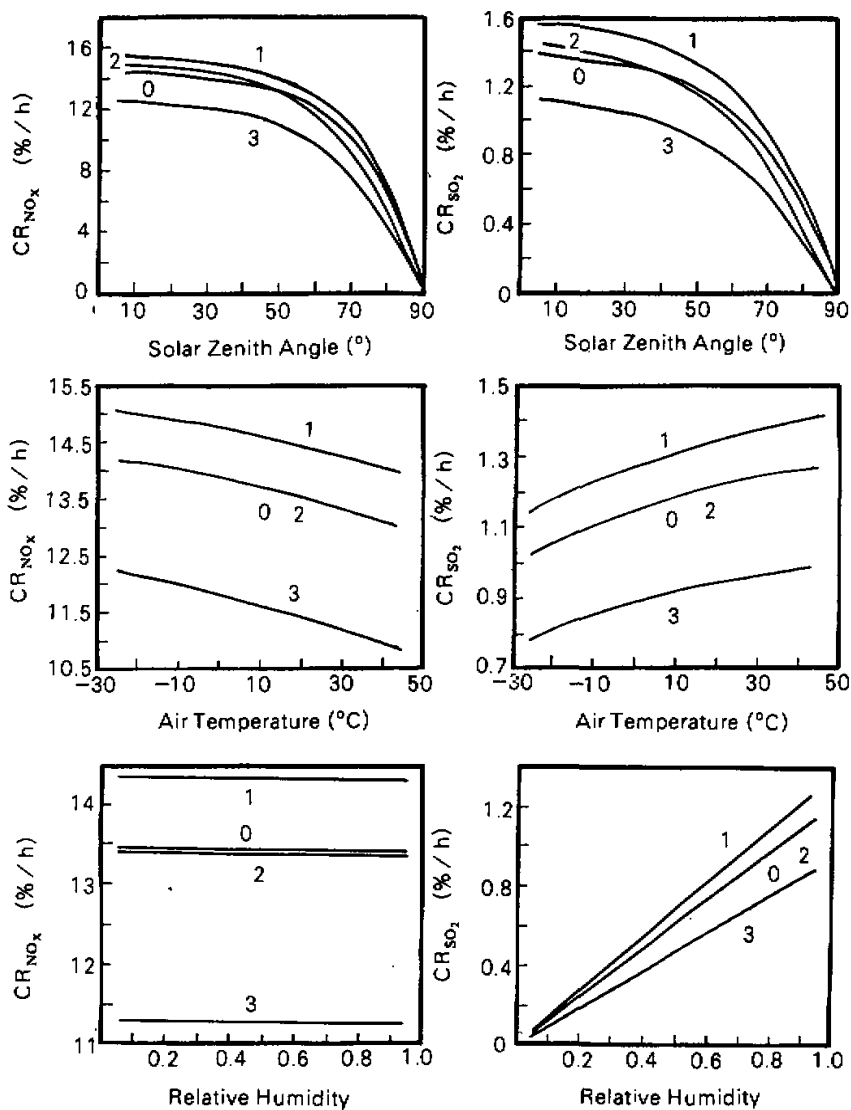


Fig. 3. Effect of meteorological conditions on SO_2 and NO_x conversion rates (a) solar zenith angle (b) air temperature (c) relative humidity. 0 no cloud, 1 above cloud, 2 in cloud, 3 below cloud.

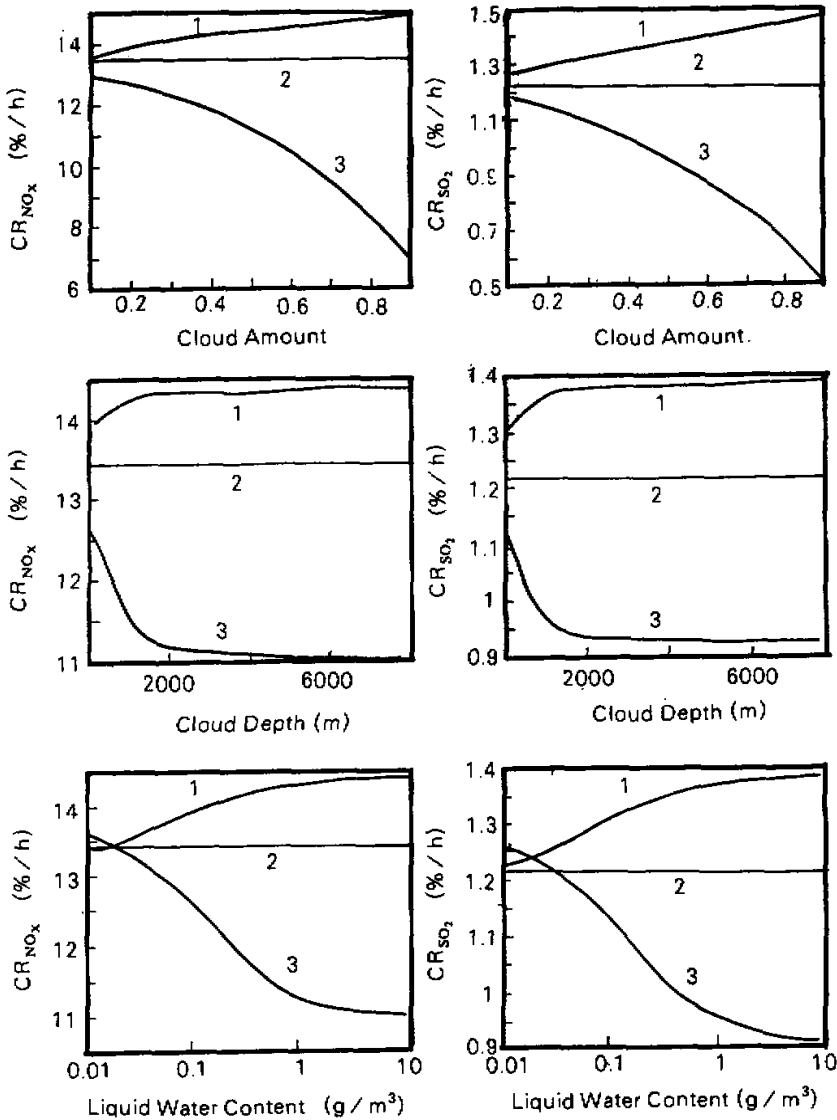


Fig. 4. Effect of cloud parameters on SO_2 and NO_x conversion rates (a) cloud amount (b) cloud depth (c) liquid water content. 1 above cloud, 2 in cloud, 3 below cloud.

Cloud parameters, such as cloud depth, cloud amount, condensed water content, have influence on the conversion rates of SO_2 and NO_x . Figure 4 shows that the conversion rates in cloud are hardly affected by the changes of cloud parameters. Generally, the conversion rates are enhanced above cloud, reduced below cloud with the enhancement of the cloud physical parameters. Cloud depth has little effect on the conversion rates. Obviously, the conversion

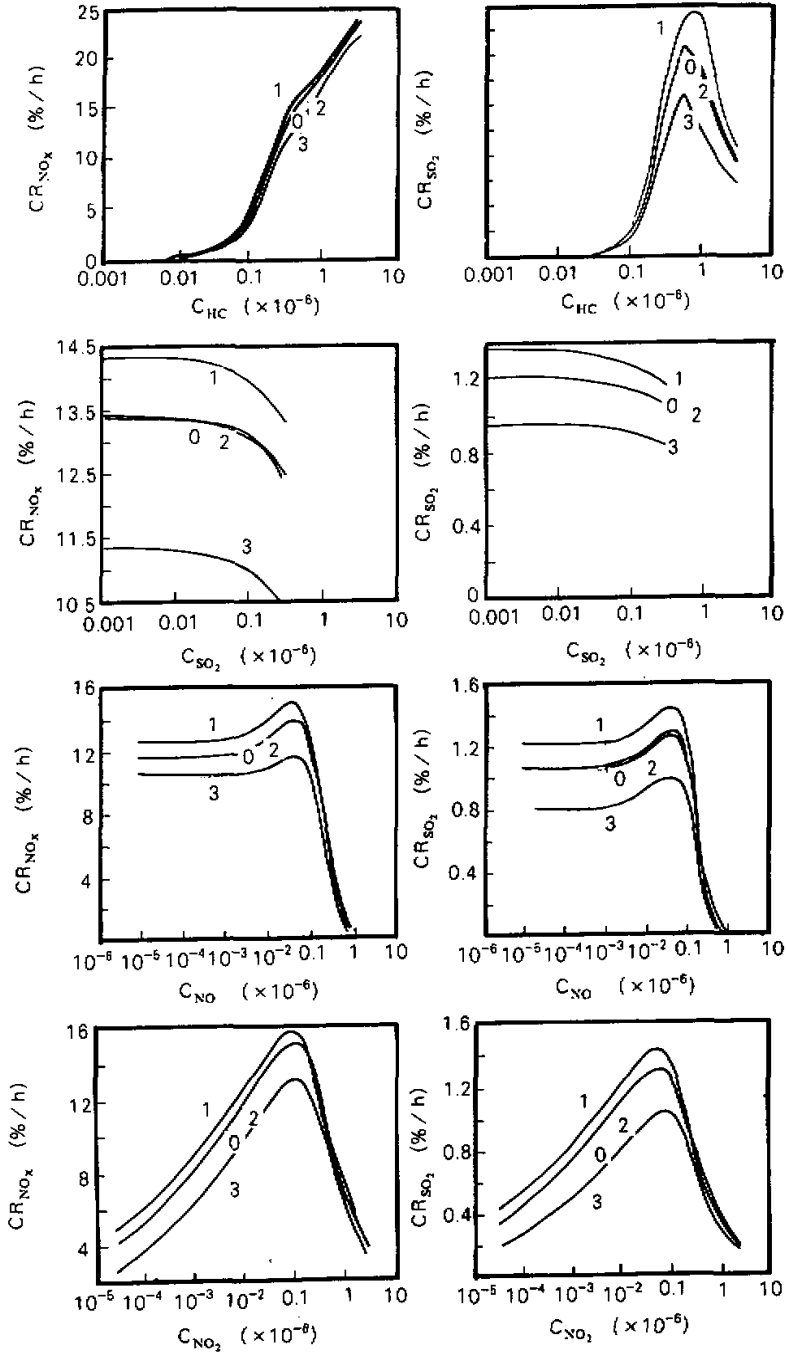


Fig. 5. Effect of initial concentration on SO₂ and NO_x conversion rate (a) HC (b) SO₂ (c) NO (d) NO₂ (a) solar zenith angle, (b) air temperature, (c) relative humidity. 0 no cloud, 1 above cloud, 2 in cloud, 3 below cloud.

rates of SO_2 and NO_x are influenced significantly by cloud amount and liquid water content which are the key factors affecting optical depth of the cloud and transmissivity of solar radiation.

5.2 Effect of initial concentration on conversion rate

On the basis of the condensed model, the SO_2 , NO_x transformation rates are presented under different SO_2 , NO_x , HC concentrations. The meteorological and cloud physical parameters are the same as those in Section 5.1. Figure. 5 shows the conversion rates as the function of initial concentration. When the HC concentration is smaller than 0.1×10^{-6} , the SO_2 , NO_x conversion rates are very small; When the HC concentration is greater than 0.1×10^{-6} , the SO_2 , NO_x conversion rates increase rapidly with the HC concentration and a peak value appears. Since SO_2 is mainly oxidized by OH radical, and OH is not only the product of HC oxidization by O, O_3 but also an oxidizer of HC, a peak value of OH is sure to appear leading to the maximum SO_2 conversion rate. The initial concentration of SO_2 has little effect on the conversion rate, especially when the SO_2 concentration is lower than 0.01×10^{-6} . While the SO_2 concentration increases, more OH radicals are lost in SO_2 oxidation and the NO_x conversion rate will decrease. Lower NO concentration almost affects the conversion rate. When the NO concentration is between 0.01×10^{-6} and 0.1×10^{-6} , the SO_2 , NO_x conversion rates increase with the NO concentration; when the NO concentration is greater than 0.1×10^{-6} , the conversion rates of SO_2 , NO_x decrease with the NO concentration. As reaction G9 competes with reaction G14 for OH, the OH concentration will decrease and conversion rates will be lower. NO_2 can be photodissociated and be oxidized by OH to form HNO_3 . When the NO_2 concentration is lower, photodissociation dominated and OH is accumulated through (G7); When the NO_2 concentration is larger, reaction between NO_2 and OH dominated consuming more OH. This is the reason for the variation of the SO_2 , NO_x conversion rates as functions of the NO_2 concentration.

6. Conclusion

In the context of the lumped mechanism and counting species schemes, a condensed gas-phase chemical model was constructed based on a simplified one. The modified QSSA scheme and the mass conservation technique of error redistribution are used to solve the atmospheric chemistry kinetic equations. Model comparisons and analyses suggest that the condensed model can well simulate the concentration variation of SO_2 , NO_x , O_3 , H_2O_2 and the transformation rates of SO_2 , NO_x to H_2SO_4 , HNO_3 . These results are in good agreement with those from the simplified model. Especially, by use of the condensed model, SO_2 , NO_x transformation rates under different SO_2 , NO_x , HC concentration, air temperature, relative humidity, solar zenith angle, clouds are computed. The condensed chemical model can be applied in the regional acid deposition model, including the nonlinear process of atmospheric chemistry instead of too simple parameterization or too complicated chemical mechanism, and can be run in a highly efficient way.

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