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An asymptotic model for the ozone production in the lower atmosphere

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The transient ozone generation process in the lower atmosphere is studied in this work, using a simplified set of chemical reactions for the NO_x and hydrocarbon photolysis. We obtained a reduced kinetic mechanism and solved the resulting governing equations using the boundary layer theory due to the appearance of two time scales in the problem. We obtained in closed form, the temporal evolution of the ozone concentration as a function of the physico-chemical parameters.

Keywords: Ozone generation; photolysis

En este trabajo se estudia el proceso transitorio de la generación de ozono en la baja atmósfera, empleando un conjunto simplificado de la cinética química para la fotólisis de los NO_x y de un simple hidrocarburo. Se obtuvo un esquema cinético reducido y se encontró la solución del sistema de ecuaciones diferenciales con la técnica de la capa límite debido a la existencia de dos escalas de tiempo bien diferenciadas. Se obtuvo en forma cerrada la evolución temporal de la concentración de ozono como una función de los parámetros físico-químicos.

Descriptores: Generación de ozono; fotólisis

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1. Introduction

The understanding of the physical and chemical mechanisms for the generation of the ozone molecules in the lower atmosphere is actually a very important multi-disciplinary research area. This field is associated with several aspects, fundamentally related with the human health, photochemical air pollution and acid deposition in large cities, the destructive environmental effects, like changes in the stratospheric ozone layer, control of emissions in industries, etc. [1, 2]. Recently, Atkinson [3] has published a review article, where the current knowledge of the main gas-phase reactions occurring in the troposphere are established and well documented. This is extremely important, because in the past, the models and evaluations to improve the chemical mechanisms have been concentrated with stratospheric modeling. Therefore, the study of the chemical mechanisms in the troposphere, in particular in polluted urban atmosphere, is fundamental due to the large variety of organic species production of much larger complexity compared with that originated in the upper atmosphere (DeMore *et al.*, [4], Baulch *et al.*, [5] and Atkinson *et al.*, [6]). In a recent article, Ruiz-Suárez *et al.* [7] has clearly shown that the different well-known numerical and experimental approaches are not sufficient to explain the generation of polluting agents in urban areas. They show that it is necessary to develop specific models to understand the dynamic of particular sites. They take as one example the well-recognized air pollution in Mexico City. In this sense, more realistic models are needed to improve the general control strategies in polluted urban areas and the predictions of global weather modifications. Over the past 30 years a vast amount of experimental work, involving laboratory, environmental chamber and ambient atmospheric studies, has been carried out concerning the chemical and physical processes occurring in the atmosphere. Because of the complexity of the processes, the systematized and sophisticated use of computers models are developed to elucidate the anthropogenic and biogenic emissions in the atmosphere. The majority of the published studies are numerical or experimental simulations using environmental chambers. Although it has been significant improvement in our knowledge of the chemistry of polluted atmosphere and in the level of detail of chemical mechanisms in recent years, the usefulness can be improved notably, if we develope complementarily analytical approaches, where the explicit influence of the physical and chemical parameters involved in the actual mathematical models, are revealed.

The main objective of this paper is to analyze analytically the generation of ozone in the lower atmosphere, using a reduced set of chemical reactions. This set of reactions is the simplest possible, where the effect of the photodecomposition of a simple fuel is included. The resulting mathematical modelling represented by a dynamical system of ordinary differential equations, can be solved in closed form with the aid of conventional boundary layer theory. In this formalism, it can be shown that two time scales are involved to describe the evolution of the ozone concentration. The short time scale is associated with the photo-chemical reaction of the nitrogen oxides while the long time scale is related to the photo-decomposition of the hydrocarbon in the lower atmosphere. We obtain a three step global reduced kinetic mechanism using the CSP (Computational Singular Perturbation) technique developed in Ref. 8. Here, the chemical reactions are reordered in reaction groups associated to the same order of magnitude of the characteristic times. These reaction groups can be active, dead or dormant depending on the relation of their characteristic times to the actual relevant characteristic time of the studied process. The dead groups are related to fast chemical reactions from which the appropriate quasi-steady and partial equilibrium assumptions can be derived. The dormant groups are related to slow chemical reactions playing no role at that moment. From the active and dormant groups the global mechanism can be obtained.

2. Governing equations

The zero-dimensional reacting governing equations of an homogeneous mixture assuming an isothermal atmosphere are given by

$$\frac{dC_i}{dt} = \sum_{j=1}^{M} \nu_{ij} r_j, \quad i = 1, \ldots, N; \quad j = 1, \ldots, M, \qquad (1)$$

where t corresponds to the time; C_i corresponds to the molar concentration (mol/volume) of the specie i. N corresponds to the total number of species taking part in the process. M is the total number of elementary chemical reactions. ν_{ij} correspond to the stoichiometric coefficients of the species i in the chemical reaction j. ν_{ij} is negative for reactants and positive for products. r_j corresponds to the reaction rate of the elementary chemical reaction j, and is given generally in the Arrhenius form, $r_j = AT^n \exp(-E_j/RT)\Pi C_i$. A is the pre-exponential factor, E_j corresponds to the activation energy of the elementary chemical reaction j and the product function is assumed only with the reactant species of the reaction j. R is the universal gas constant, $R = 8314$ KJ/mol. T is the atmospheric temperature assumed to be constant in this model. The photo-chemical reactions are assumed with an averaged light intensity. All the elementary chemical reactions assumed in this work are displayed in Table I.

The solution of the governing Eq. (1), together with the corresponding initial conditions, $C_i = C_{i0}$ at $t = 0$, is obtained using the stiff differential equations code "FlameMaster", developed in Aachen, Germany [9]. Parallel to this numerical code, a CSP (computational singular perturbations) routine has been built. The procedure employed in order to obtain the reduced kinetic mechanism is by drooping out that reactions with a participation index [8] lower than a critical value in the whole event. This critical value is the maximum value obtained when no appreciable change in the maximum ozone concentration at a given time (4 hours), after dropping these chemical reactions. The resulting set of chemical reactions can be reduced after the introduction of steady-state behavior of several species. In the present study we took 9 elementary chemical reactions, which represents the simplest ozone production mechanism with the simplest reactive hydrocarbon, CH_2O.

TABLE I. Kinetic mechanism (units: mol, cm, s, Kj).

No.	Reaction	A	n	E
1	$NO_2 + h\nu \longrightarrow NO + O$	8.883×10^{-3}	0.00	0
2	$O_3 + NO \longrightarrow NO_2 + O_2$	1.325×10^{12}	0.00	11.9
3	$O_2 + O + M' \longrightarrow O_3 + M'$	1.084×10^{20}	−2.30	0
4	$CH_2O + h\nu \longrightarrow H + HCO$	2.667×10^{-5}	0.00	0
5	$HO_2 + NO \longrightarrow NO_2 + OH$	3.000×10^{12}	0.50	10.2
6	$CH_2O + h\nu \longrightarrow H_2 + CO$	3.517×10^{-5}	0.00	0
7	$H + O_2 + M' \longrightarrow HO_2 + M'$	2.300×10^{18}	−0.80	0
8	$HCO + O_2 \longrightarrow HO_2 + CO$	3.000×10^{12}	0.00	0
9	$OH + NO_2 \longrightarrow HNO_3$	6.625×10^{12}	0.00	0

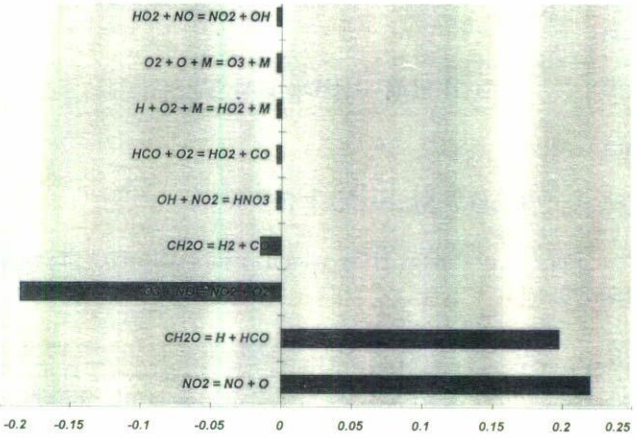

FIGURE 1. Sensitivity coefficients of the elementary reactions in the production of ozone molecules.

3. Asymptotic analysis

Two time scales are associated to the photo-chemical decay of NO_2 and the characteristic fuel assumed in this paper CH_2O. The first one is of the order of a couple of minutes, while the second one is of the order of hours. This strong difference between the two scales will permit to develope an asymptotic analysis for the ozone production described below. Figure 1 shows the sensitivity analysis obtained by increasing artificially ten times each individual reaction and looking at the generation of the ozone concentration at a given time which in our case is 60 minutes.

Ozone O_3 is produced in this scheme only through reaction

(3) $\mathrm{O_2 + O + M \to O_3 + M}$,

with free oxygen atoms liberated by the photo-chemical reaction

(1) $\mathrm{NO_2 + h\nu \to NO + O}$.

The extremely low sensitivity of reaction (3), in the ozone production indicates that this reaction is fast enough with the rate limited by the photo reaction (1). Therefore, atomic oxygen can be assumed to be in steady state. The second important limiting chemical reaction is the photo-chemical reaction

(4) $\mathrm{CH_2O + h\nu \to HCO + H}$.

This reaction consumes the fuel, producing both HCO and atomic hydrogen. Both are consumed very rapidly by reactions

(7) $\mathrm{O_2 + H + M \to HO_2 + M}$

and

(8) $\mathrm{HCO + M \to CO + H + M}$.

Reaction (7) produces HO_2 which reacts with NO through reaction

(5) $\mathrm{HO_2 + NO \to NO_2 + OH}$,

generating NO_2 to be converted to ozone with the aid of reactions (1) and (3). OH is rapidly consumed by reaction (9)

(9) $\mathrm{OH + NO_2 \to HNO_3}$

Ozone reacts with NO through reaction

(2) $\mathrm{O_3 + NO \to O_2 + NO_2}$

Therefore O, H, HCO, HO_2 and also OH are rapidly consumed and then can be assumed to be in steady state. Therefore is possible to reduce the number of global reactions and species. Reaction

(6) $\mathrm{CH_2O + h\nu \to H_2 + CO}$

consumes the fuel producing only relatively stable chemical species. The influence of this reaction is to reduce the fuel concentration (ozone precursor) and then has a negative sensitivity. Using the steady state for the atomic oxygen, the limiting reaction (1) then transforms to the global step

(*I*) $\mathrm{NO_2 + O_2 \rightleftharpoons NO + O_3}$,

which is the backward of the elementary reaction (2). The global reaction rate is then given by $r_{\mathrm{I}} = k_1 C_{\mathrm{NO_2}} - k_2 C_{\mathrm{NO}} C_{\mathrm{O_3}}$. The characteristic time of this global reaction is of order of a couple minutes and then is too fast compared with the photo-chemical reactions associated to the fuel consumption. The elementary chemical reaction (4) transforms to

(*II*) $\mathrm{CH_2O + 2O_2 + 2NO \to CO + 2HNO_3}$,

with the rate given by $r_{\mathrm{II}} = k_4 C_{\mathrm{CH_2O}}$. The consumption of NO through the global reaction increases the concentration of O_3 through the forward reaction (*I*). The last global step is exactly the elementary reaction (6)

(*III*) $\mathrm{CH_2O \to CO + H_2}$,

with the rate given by $r_{\mathrm{III}} = k_6 C_{\mathrm{CH_2O}}$.

The governing equations assuming these three global reactions are given by

$$\frac{dC_{\mathrm{NO_2}}}{dt} = -k_1 C_{\mathrm{NO_2}} + k_2 C_{\mathrm{NO}} C_{\mathrm{O_3}}, \tag{2}$$

$$\frac{dC_{\mathrm{NO}}}{dt} = k_1 C_{\mathrm{NO_2}} - k_2 C_{\mathrm{NO}} C_{\mathrm{O_3}} - 2k_4 C_{\mathrm{CH_2O}}, \tag{3}$$

$$\frac{dC_{\mathrm{O_3}}}{dt} = k_1 C_{\mathrm{NO_2}} - k_2 C_{\mathrm{NO}} C_{\mathrm{O_3}}, \tag{4}$$

$$\frac{dC_{\mathrm{CH_2O}}}{dt} = -(k_4 + k_6) C_{\mathrm{CH_2O}}. \tag{5}$$

These equations are to be solved with the following initial conditions

$$C_{\mathrm{NO_2}} = (C_{\mathrm{NO_2}})_0, \qquad C_{\mathrm{NO}} = (C_{\mathrm{NO}})_0,$$
$$C_{\mathrm{CH_2O}} = (C_{\mathrm{CH_2O}})_0, \qquad C_{\mathrm{O_3}} = 0. \tag{6}$$

Introducing the following nondimensional variables

$$x = \frac{C_{\mathrm{NO_2}}}{(C_{\mathrm{NO_2}})_0}, \qquad y = \frac{C_{\mathrm{NO}}}{(C_{\mathrm{NO}})_0},$$
$$z = \frac{C_{\mathrm{O_3}}}{(C_{\mathrm{O_3}})_c}, \qquad u = \frac{C_{\mathrm{CH_2O}}}{(C_{\mathrm{CH_2O}})_0},$$
$$\tau = k_1 t \tag{7}$$

the governing equations transform in nondimensional form to

$$\frac{dx}{d\tau} = -x + yz, \tag{8}$$

$$\frac{dy}{d\tau} = \frac{1}{\alpha}\left(x - yz - 2K_4 \varepsilon \beta u\right), \tag{9}$$

$$\frac{dz}{d\tau} = K_2 \alpha \left(x - yz\right), \tag{10}$$

$$\frac{du}{d\tau} = -(K_4 + K_6)\varepsilon u, \tag{11}$$

where

$$K_2 = \frac{k_2 (C_{\mathrm{NO_2}})_0}{k_1}, \qquad K_4 = \frac{k_4}{k_1 \varepsilon}, \qquad K_6 = \frac{k_6}{k_1 \varepsilon} \tag{12}$$

are of order unity and $\varepsilon = 10^{-3}$ (showing the disparity in the characteristic time scales of the process). The resulting nondimensional parameters are defined by

$$\alpha = \frac{(C_{\mathrm{NO}})_0}{(C_{\mathrm{NO_2}})_0} \qquad \text{and} \qquad \beta = \frac{(C_{\mathrm{CH_2O}})_0}{(C_{\mathrm{NO_2}})_0}, \tag{13}$$

which determine the relative concentrations of the ozone precursor species. The characteristic ozone concentration is then defined by $(C_{\mathrm{O_3}})_c = k_1/(k_2\alpha)$. The nondimensional characteristic time of the photo-decomposition of $\mathrm{NO_2}$ is of order of unity while the characteristic time of the photo-decomposition of the fuel is of order ε^{-1}. In order to eliminate the non linear terms in two of the governing equations we define conservative scalars in the short time scale as $r = x + z/(K_2\alpha)$ and $s = \alpha y - z/(K_2\alpha)$, reducing the set of the governing equations to

$$\frac{dz}{d\tau} = K_2\alpha r - (1 + K_2 s)z - \frac{z^2}{\alpha}\,, \tag{14}$$

$$\frac{dr}{d\tau} = 0\,, \tag{15}$$

$$\frac{ds}{d\tau} = -2K_4\beta\varepsilon u\,, \tag{16}$$

$$\frac{du}{d\tau} = -(K_4 + K_6)\varepsilon u. \tag{17}$$

The solution to the last three equations considering the initial conditions are:

$$\begin{aligned} r &= 1\,,\\ u &= \exp\left[-(K_4 + K_6)\sigma\right]\,,\\ s &= \alpha - \frac{2K_4\beta}{(K_4 + K_6)}\left\{1 - \exp\left[-(K_4 + K_6)\sigma\right]\right\}\,, \end{aligned} \tag{18}$$

where σ is the large time scale, $\sigma = \varepsilon\tau$. Equation (14) can be rewritten as

$$\frac{dZ}{d\zeta} = 1 - F(\sigma)Z - Z^2, \tag{19}$$

where

$$Z = \frac{z}{\sqrt{K_2}\alpha}\,, \qquad \zeta = \sqrt{K_2}\tau$$

and

$$F = 1 + \frac{1}{K_2\alpha} - \frac{K_4\beta}{\alpha(K_4 + K_6)} \times \left\{1 - \exp\left[-(K_4 + K_6)\sigma\right]\right\}\sqrt{K_2}\alpha\,, \tag{20}$$

to be solved with the initial condition $Z(0) = 0$. The Ricatti Eq. (19), gives the nondimensional ozone concentration as a function of time. This equation has not a closed form solution. We use the boundary layer technique in order to have an approximate solution to this equation. The inner stage corresponds to the time scale $\zeta \sim 1$, $\sigma \to 0$, where the ozone concentration increases rapidly from 0 up to an equilibrium value dictated by the global step (I). A second or outer stage is followed where the ozone concentration increases slowly in times of order $\zeta \sim \bar{\varepsilon}^{-1}$, due to the slow photo-chemical reactions of the fuel decomposition. Here $\bar{\varepsilon} = \varepsilon/\sqrt{K_2} \ll 1$. In physical units, the inner zone corresponds to characteristic times of order of a couple of minutes, which is very fast for practical purposes. The outer zone is associated to time scales of several hours.

3.1. Inner stage

For values of ζ of order unity, we assume a solution of the form $Z = \sum_{i=0}^{\infty} \bar{\varepsilon}^{\,i} Z_i$, resulting in the following set of equations

$$\frac{dZ_0}{d\zeta} = 1 - AZ_0 - Z_0^2\,, \tag{21}$$

$$\frac{dZ_1}{d\zeta} + Z_1\left(A + 2Z_0\right) = \gamma Z_0\zeta\,, \tag{22}$$

etc. Here $A = (1 + K_2\alpha)/\sqrt{K_2} \sim 1$ and $\gamma = 2\sqrt{K_2}K_4\beta \sim 1$. The initial conditions are then $Z_i(0) = 0$, for all i. The solution to the Ricatti Eq. (21) is

$$Z_0 = \frac{A_2\left[1 - \exp(-\sqrt{A^2 + 4}\zeta)\right]}{\dfrac{A_2}{A_1} + \exp(-\sqrt{A^2 + 4}\zeta)}, \tag{23}$$

where $A_1 = (\sqrt{A^2 + 4} - A)/2$ and $A_2 = (\sqrt{A^2 + 4} + A)/2$. The equilibrium ozone concentration in this initial stage is then $Z_0 \to A_1$ for $\zeta \to \infty$. The first order solution is given by

$$Z_1 = \frac{1}{\exp\left[\int_0^\zeta a(\xi)d\xi\right]}\int_0^\zeta b(\xi)\exp\left[\int_0^\xi a(\eta)d\eta\right]d\xi, \tag{24}$$

where

$$a(\zeta) = A + 2Z_0\,, \qquad b(\zeta) = \gamma Z_0\zeta. \tag{25}$$

3.2. Outer stage

For large values of ζ and values of σ of order unity, the governing Eq. (19) takes the form

$$\bar{\varepsilon}\frac{d\bar{Z}}{d\sigma} = 1 - F(\sigma)\bar{Z} - \bar{Z}^2 \quad \text{where} \quad \bar{Z} = Z(\sigma)\,. \tag{26}$$

Assuming a solution of the form $\bar{Z} = \sum_{i=0}^{\infty} \bar{\varepsilon}^{\,i}\bar{Z}_i$, we obtain the following set of equations

$$\bar{Z}_0^2 + F\bar{Z}_0 - 1 = 0\,, \tag{27}$$

$$\bar{Z}_1(F + 2\bar{Z}_0) = -\frac{d\bar{Z}_0}{d\sigma}\,, \tag{28}$$

etc. The solution to Eqs. (27) and (28) are

$$\bar{Z}_0 = \frac{\sqrt{F^2 + 4} - F}{2}$$

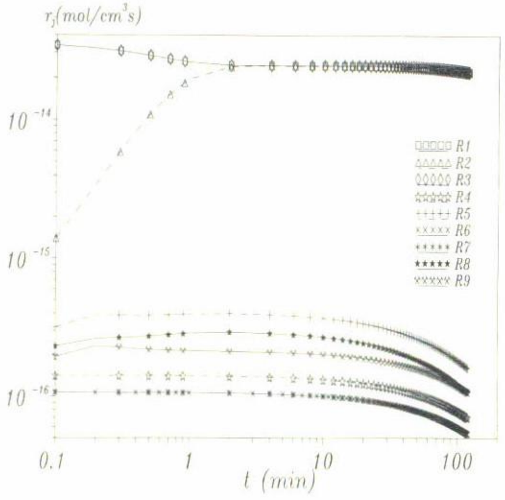

FIGURE 2. Reaction rates of the elementary chemical reactions as a function of time.

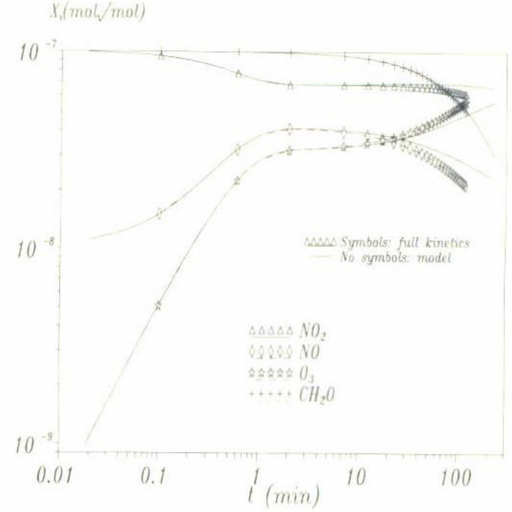

FIGURE 3. Temporal evolution of the main species obtained with numerical computations and using the analytical model.

and

$$\bar{Z}_1 = \frac{[\gamma \exp(-(K_4 + K_6)\sigma)]}{2\sqrt{F^2+4}} \left[\frac{F}{\sqrt{F^2+4}} - 1\right]. \tag{29}$$

4. Results and conclusions

To the leading order, the nondimensional ozone concentration is therefore given by

$$Z_0 = \frac{A_2\left[1 - \exp\left(-\frac{\sqrt{A^2+4\sigma}}{\bar{\varepsilon}}\right)\right]}{\frac{A_2}{A_1} + \exp\left(-\frac{\sqrt{A^2+4\sigma}}{\bar{\varepsilon}}\right)} + \frac{\sqrt{F^2(\sigma)+4} - F(\sigma)}{2} - A_1 \tag{30}$$

valid for all σ. The concentration of ozone in physical units is then given by $C_{O_3}(t) = k_1\sqrt{K_2}Z_0(\sigma = \varepsilon k_1 t)/k_2$. Equation (30) shows clearly the full parametric dependence of the main parameters involved. Figure 2 shows the reaction rates of the elementary reactions as a function of time for $\alpha = 0.1$, $\beta = 1$ obtained from the numerical calculation. The three first reactions involved in the photolysis of NO_2, are the fastest reactions (two orders in magnitude) in comparison to the other fuel decomposition reactions. Here it can be shown that in a couple of minutes, the global reaction *I* reaches partial equilibrium. The fuel decomposition reactions are characterized by times scales of order of hours. Finally in Fig. 3 we show a comparison of the numerical results with the theoretical model obtained with the leading order, for the temporal evolution of the main species. We can see in this figure that the concordance is excellent at short times, indicating a slight divergence at longer times, which can be corrected including the first order correction.

The transient analysis leading to the ozone production in the lower atmosphere is studied in this paper using both numerical analysis based in computational singular perturbation (CSP) and asymptotic analytical methods. The reduced kinetic mechanism is obtained after solving the evolution equations and evaluating the CSP data. We obtain a closed form solution of the temporal evolution of the concentration of ozone showing the full parametric dependence. We must emphasize that this first step to derive analytical solutions, can be improved by employing a more complex set of the kinetic mechanism.

Acknowledgments

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