

CONSTRUCTION OF SURROGATE CHEMICAL MECHANISMS (SCHEMES) FOR ATMOSPHERIC
PHOTOCHEMICAL SYSTEMS

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During the past several years it has become apparent that homogeneous gas-phase reactions of pollutants in the troposphere, i.e., the formation of photochemical smog and the oxidation of SO_2 , occur to a great extent by elementary reactions involving chain carrying free-radicals (HO , HO_2 , RO , RO_2 , RCOO_2) whose concentrations are governed by the concentrations of trace molecular constituents including NO , NO_2 , CO , O_3 , and organics, as well as sunlight¹⁻³. Some of the important reaction paths and products of these chemical transformations are shown pictorially in Figure 1. The reaction kinetics of such a multi-species, multi-reaction system is commonly modeled by a set of coupled ordinary nonlinear differential equations in the concentrations of the species, and such treatment has been rather successful in modeling these concentrations as measured in "smog chamber" experiments. However, for the purpose of modeling chemical transformations in the ambient atmosphere, which requires incorporating a reaction mechanism within an atmospheric transport model, it is necessary to develop a mechanism that includes a minimum number of chemical species, since the computational time and cost involved in solving the set of partial differential equations describing the diffusion-advection-reaction problem increases dramatically with the number of species modeled. Although photochemical mechanisms employing fewer than 15 species have been developed previously for use within urban airshed models⁴⁻⁶, those reduced, or surrogate, mechanisms do not include sulfur chemistry and do not appear applicable to the more widely varying conditions possible as gases become chemically depleted while being transported away from emission sources. Therefore, in order to meet the time and cost constraints of an atmospheric transport model, we have constructed a 12-species Surrogate CHEMical MEchanism (SCHEME) incorporating reactions for the homogeneous gas-phase oxidation of SO_2 . A preliminary but much more detailed and comprehensive Atmospheric Model for Sulfur (ATMOS) has been used to generate SCHEME and test its applicability to a broad range of chemical conditions.

ATMOS is a 30-constituent reaction mechanism including generalized hydrocarbon chemistry based largely upon the Hecht-Seinfeld-Dodge⁷ model for NO_x -hydrocarbon mixtures; however, ATMOS incorporates revised rate constant values and additional reactions. This model test quite well against reported smog chamber data⁸ for the NO_x -propylene system. ATMOS has been used to simulate the six-hour irradiation of a typical urban pollution mixture containing NO , NO_2 , SO_2 , olefin, and CO at initial concentrations of 75, 25, 10, 100, and 10^4 ppb, respectively. For bright sun conditions ($z = 40^\circ$) and an ambient H_2O concentration of 2×10^4 ppm, the model predicts NO , NO_2 , and O_3 profiles characteristic of photochemical smog as shown by the curves in Figure 2. The SO_2 oxidation rate, after the first 10 minutes of irradiation, is typically $1-4\% \text{ hr}^{-1}$ and is controlled principally by reactions with HO , HO_2 , and RO_2 radicals; as the reactive system

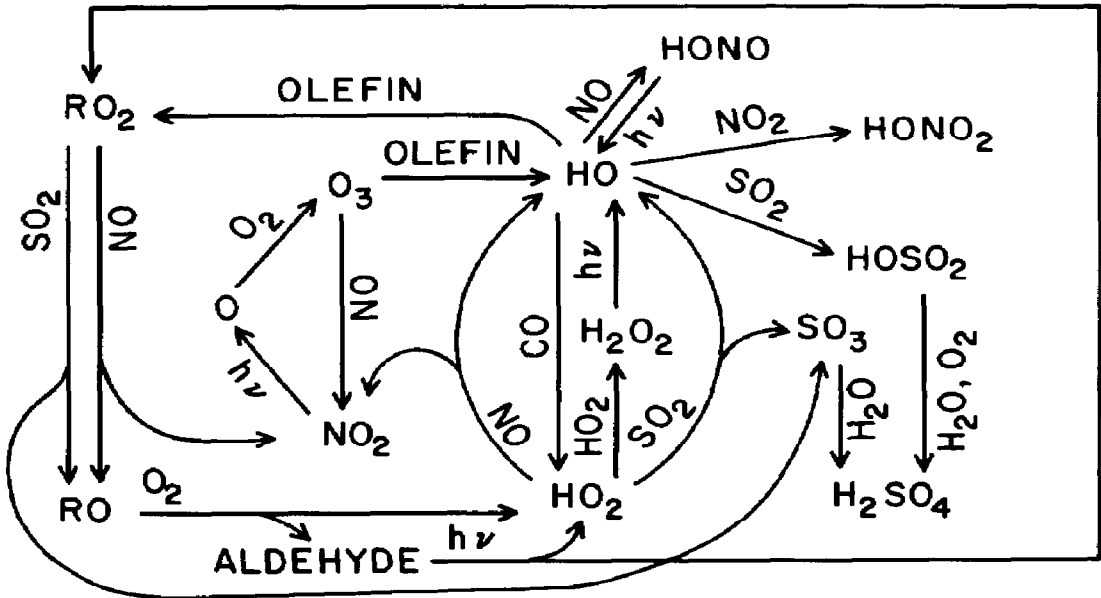


Figure 1. Reactions represented by the present models.

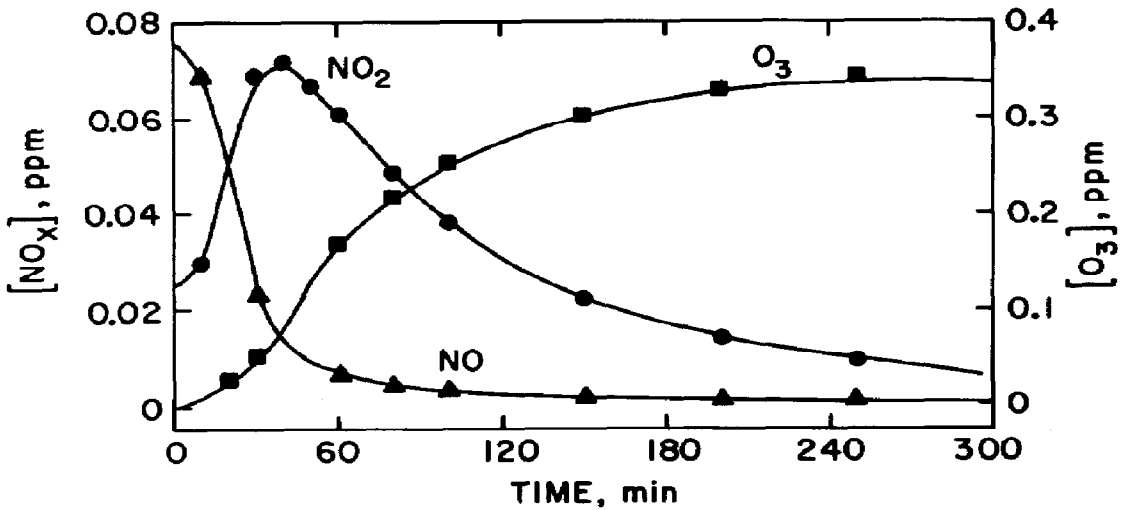


Figure 2. Comparison of simulation results obtained with ATMOs (curves) and SCHEME (points).

ages the relative importance of these reactions to the total oxidation rate shifts markedly from the HO reaction to those of the HO₂ and RO₂ radicals.

Using the simulation results of ATMOS, we have analyzed the time dependence of species concentrations and reaction rates to develop the 12-species surrogate mechanism SCHEME which models the concentration profiles of 4 initial reactant species (NO, NO₂, SO₂, olefin), 4 intermediate species (O₃, HONO, H₂O₂, aldehyde), and 4 free-radicals (HO, HO₂, RO₂, RCOO₂). The reduction in the number of modeled species has been accomplished without loss in the chemical integrity of the system by: 1) removing from the mechanism those reactions and species which do not appreciably influence the chemistry of the remaining species, 2) incorporating the essentially constant concentrations of stable species (e.g., O₂) into the appropriate rate constants, and 3) using rate limiting reaction steps and steady-state relationships to formulate surrogate reactions and rate constants. SCHEME accurately reproduces the results of ATMOS, as indicated by the comparisons in Figure 2, and does so with a 5-fold decrease in execution time. For all 12 species modeled by SCHEME, the close agreement with the concentration profiles predicted by ATMOS continues even when the initial concentrations of NO_x, SO₂, or olefin are changed by an order of magnitude. Additionally, the kinetic relationships used in the construction of SCHEME may be used at little additional computational cost to algebraically determine concentration profiles for many of the deleted species. Specific methods utilized in the construction of SCHEME will be presented.

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This work was performed under the auspices of the U.S. Department of Energy under contract No. EY-76-C-02-0016.