

To be presented at the IX International Conference on Photochemistry,  
Cambridge, England; August 7-9, 1978.

Conf-780832--1

BNL-24610

Construction of Surrogate CHEMical MEchanisms (SCHEMES)  
for Atmospheric Photochemical Systems

by

Stuart Z. Levine and Stephen E. Schwartz

Brookhaven National Laboratory  
Atmospheric Sciences Division  
Upton, New York 11973

MASTER

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This work was performed under the auspices of the United States Department of Energy under Contract No. EY-76-C-02-0016.

By acceptance of this article, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive royalty-free license in and to any copyright covering this paper.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

leg

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

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

Stuart Z. Levine and Stephen E. Schwartz

Atmospheric Sciences Division  
Brookhaven National Laboratory  
Upton, N. Y. 11973 U. S. A.

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  $\text{SO}_2$ , occur to a great extent by elementary reactions involving chain carrying free-radicals ( $\text{HO}$ ,  $\text{HO}_2$ ,  $\text{RO}$ ,  $\text{RO}_2$ ,  $\text{RCOO}_2$ ) whose concentrations are governed by the concentrations of trace molecular constituents including  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ ,  $\text{O}_3$ , and organics, as well as sunlight<sup>1-3</sup>. 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 models<sup>4-6</sup>, 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  $\text{SO}_2$ . 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-Dodge<sup>7</sup> model for  $\text{NO}_x$ -hydrocarbon mixtures; however, ATMOS incorporates revised rate constant values and additional reactions. This model test quite well against reported smog chamber data<sup>8</sup> for the  $\text{NO}_x$ -propylene system. ATMOS has been used to simulate the six-hour irradiation of a typical urban pollution mixture containing  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ , olefin, and  $\text{CO}$  at initial concentrations of 75, 25, 10, 100, and  $10^4$  ppb, respectively. For bright sun conditions ( $z = 40^\circ$ ) and an ambient  $\text{H}_2\text{O}$  concentration of  $2 \times 10^4$  ppm, the model predicts  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{O}_3$  profiles characteristic of photochemical smog as shown by the curves in Figure 2. The  $\text{SO}_2$  oxidation rate, after the first 10 minutes of irradiation, is typically 1-4%  $\text{hr}^{-1}$  and is controlled principally by reactions with  $\text{HO}$ ,  $\text{HO}_2$ , and  $\text{RO}_2$  radicals; as the reactive system

ages the relative importance of these reactions to the total oxidation rate shifts markedly from the HO reaction to those of the HO<sub>2</sub> and RO<sub>2</sub> 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, NO<sub>2</sub>, SO<sub>2</sub>, olefin), 4 intermediate species (O<sub>3</sub>, HONO, H<sub>2</sub>O<sub>2</sub>, aldehyde), and 4 free-radicals (HO, HO<sub>2</sub>, RO<sub>2</sub>, RCOO<sub>2</sub>). 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., O<sub>2</sub>) 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<sub>x</sub>, SO<sub>2</sub>, 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.

#### References

1. K.L. Demerjian, J.A. Kerr, and J.G. Calvert, *Advan. Environ. Sci. Technol.*, 4, 1 (1974).
2. J.G. Calvert, F. Su, J.W. Bottenheim, and O.P.-Strausz, "Mechanism of the Homogeneous Oxidation of Sulfur Dioxide in the Troposphere," presented at the International Symposium on Sulfur in the Atmosphere, Dubrovnik, Yugoslavia (September 1977).
3. J.G. Calvert and R.D. McQuigg, *Int. J. Chem. Kinetics, Symposium No. 1, Proceedings of the Symposium on Chemical Kinetic Data for the Upper and Lower Atmosphere*, pp. 113-154, (1975).
4. A.Q. Eschenroeder and J.R. Martinez, *Adv. Chem. Series*, No. 113, 101 (1972).
5. S.D. Reynolds, P.M. Roth, and J.H. Seinfeld, *Atmospheric Environment*, 7, 1033 (1973).
6. J.H. Seinfeld and S.D. Reynolds, *Adv. Chem. Series*, No. 113, 58 (1972).
7. T.A. Hecht, J.H. Seinfeld, and M.C. Dodge, *Environ. Sci. Technol.*, 8, 327 (1974).
8. J.N. Pitts, Jr., K.R. Darnall, A.M. Winer, and J.M. McAfee, EPA-600/3-77-014b (February 1977).

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

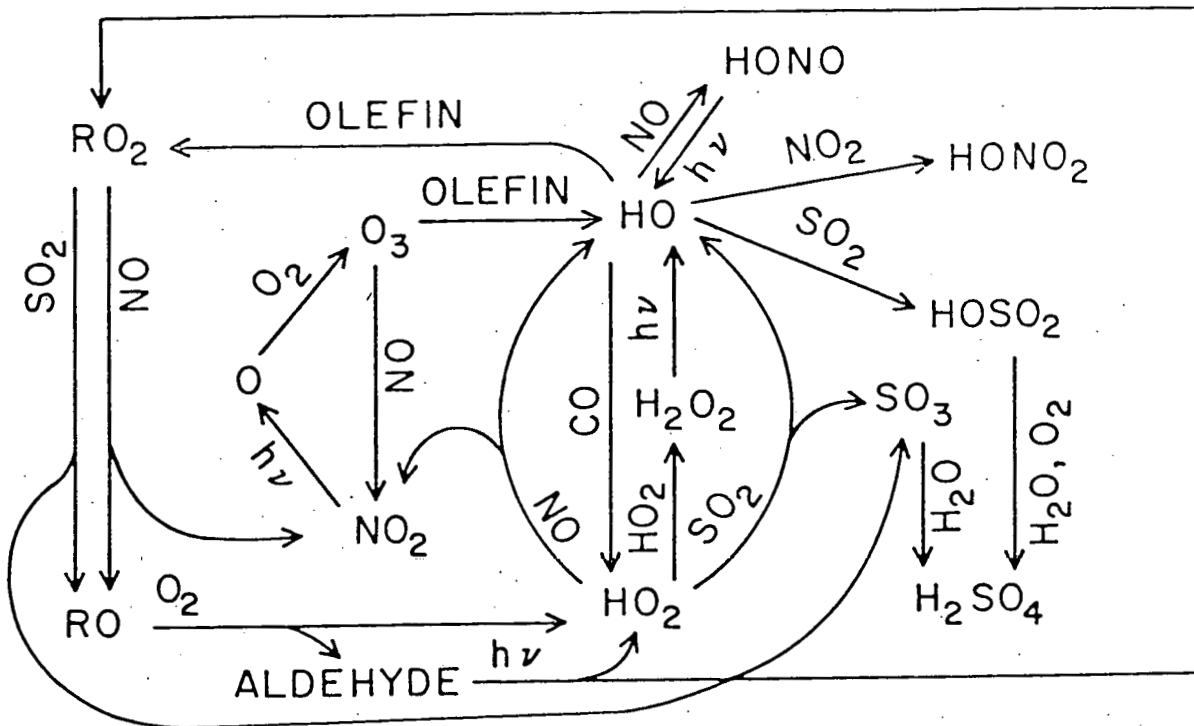


Figure 1. Reactions represented by the present models.

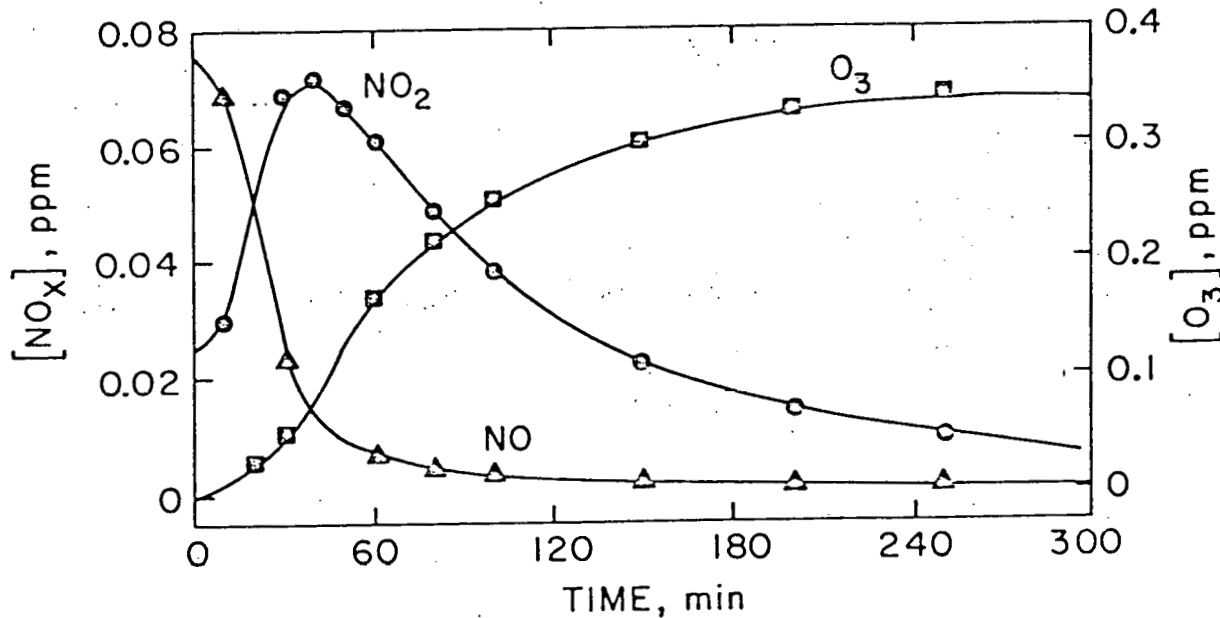


Figure 2. Comparison of simulation results obtained with ATMOS (curves) and SCHEME (points).