Advances in ENVIRONMENTAL SCIENCE AND TECHNOLOGY

Volume 4

Advances in
ENVIRONMENTAL SCIENCE AND TECHNOLOGY

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INTRODUCTION TO THE SERIES

Advances in Environmental Science and Technology is a series of multiauthored books devoted to the study of the quality of the environment and to the technology of its conservation. Environmental sciences relate, therefore, to the chemical, physical, and biological changes in the environment through contamination or modification; to the physical nature and biological behavior of air, water, soil, food, and waste as they are affected by man's agricultural, industrial and social activities and, in turn, as they affect the health and welfare of man; and to the application of science and technology to the control and improvement of environmental quality.

The deterioration of environmental quality, which began when man first assembled into villages and utilized fire, has existed as a serious problem since the industrial revolution. In the second half of the twentieth century, under the ever-increasing impacts of exponentially growing population and of industrializing society, environmental contamination of air, water, soil, and food has become a threat to the continued existence of many plant and animal communities of the ecosystem and may ultimately threaten the very survival of the human race.

It seems clear that if we are to preserve for future generations some semblance of the existing biological order and if we hope to improve on the deteriorating standards of urban public health, environmental sciences and technology

must quickly come to play a dominant role in designing our social and industrial structure for tomorrow. Scientifically rigorous criteria of environmental quality must be developed and, based in part on these, realistic standards must be established, so that our technological progress can be tailored to meet such standards. Civilization will continue to require increasing amounts of fuels, transportation, industrial chemicals, fertilizers, pesticides, and countless other products, as well as to produce waste products of all descriptions. What is urgently needed is a total systems approach to modern civilization through which the pooled talents of scientists and engineers, in cooperation with social scientists and the medical profession, can be focused on the development of order and equilibrium among the presently disparate segments of the human environment.

It is our belief that solutions will come about only through the establishment of a sound scientific, technical and medical data base generated by researchers in the several segments in our society, including government agencies, industry, universities and research institutes. To be truly effective, such a data base must also be deemed reliable by these diverse groups. To this end, the editors have solicited contributions from experts having a wide variety of professional backgrounds, expertise and affiliations, not only in the United States but on a world-wide basis since "pollution knows no boundaries."

Most of the skills and tools that are needed already exist. Surely a technology that has created manifold environmental problems is also capable of solving them.

It is our hope that the series in Environmental Science and Technology will not only serve to make this challenge more explicit to the established professional but will also help to stimulate the student toward the career opportunities in this vital area.

The chapters in this series of Advances are written by experts in their respective disciplines, who also are involved with the broad scope of environmental science. As editors, we asked the authors to give their "points of view" on key questions; we were not concerned simply with literature surveys. They have responded in a gratifying manner with thoughtful and challenging statements on critical environmental problems.

Volume IV of the Series is an example of the flexibility of the approach of the publishers, editors and authors. Thus, it consists of only two chapters, yet the chapters are of sufficient importance, depth and relevance to the problems of pollution in the upper and lower atmospheres that they constitute the entire volume.

We are pleased that Dr. Alan C. Lloyd, Assistant Director of the University of California Statewide Air Pollution Research Center, continues as Associate Editor to the Series.

To facilitate communications with our contributors and readers, we are including below our addresses and telephone numbers.

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Contents

The Mechanism of Photochemical Smog Formation

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I. INTRODUCTION

In the early 1950's an interesting yet perplexing new phenomenon was observed by many residents in the Los Angeles area: On certain bright sunny days, when the automobile traffic level was high and the ventilation of pollutants was restricted by atmospheric conditions, eye irritation was a common complaint of the citizen. Analyses of the atmosphere showed that high levels of oxidant, largely ozone, formed during the day. The diurnal variation of the concentration of ozone and the oxides of nitrogen can be seen from the data of Figure 1 obtained on a typical smoggy day in Los Angeles, July 19, 1965 (1). Note that the level of the nitrogen oxides rises as the peak traffic hours arrive. It can be seen also that the nitric oxide concentration begins to decline as that for nitrogen dioxide is still rising to its maximum, suggesting a conversion of NO to NO_2. After most of the nitric oxide has disappeared, the ozone concentration rises to a maximum near the middle of the day and

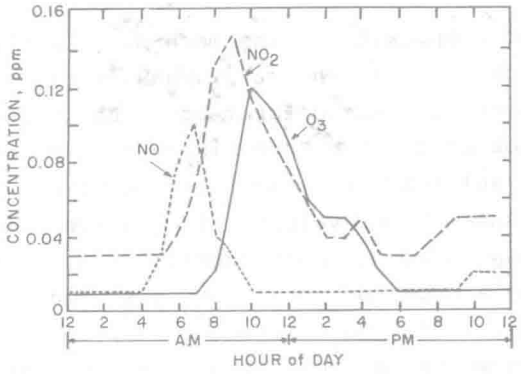

FIGURE 1. Example of photochemical smog buildup in Los Angeles, California; the diurnal variation of NO, NO_2, and O_3 concentrations on July 10, 1965 (1).

then falls off again toward the afternoon. The dependence of the phenomenon on the intensity of the solar radiation and the extent and the nature of the contamination present, suggested to the early investigators that the effect resulted in large part from the action of sunlight on the auto-exhaust-polluted atmospheres. Thus the unpleasant character of these atmospheres was designated as "photochemical smog."

The mechanism of formation of photochemical smog has been the subject of extensive research efforts in the years since it was first noted. Haagen-Smit and his colleagues then observed that oxidant, including ozone, is produced when low concentrations of nitrogen dioxide and certain organic compounds mixed in air are irradiated (2,3). In the subsequent experimentation of several research groups, it was shown that irradiated dilute mixtures of auto exhaust in air can lead to the usual manifestations related to photochemical smog: ozone formation [Haagen-Smit and Fox (4)], eye irritation [Schuck and coworkers (5,6,7)]; Morriss and Bolze (8)], plant damage [Middleton and Haagen-Smit (9); Middleton (10)], and aerosol formation [Doyle and Renzetti (11)] with its associated light scatter and haze.

The great complexity of the mechanism of the chemical reactions which occur in the auto-exhaust-polluted atmospheres has been recognized for years. Leighton, in his monumental book on the "Photochemistry of Air Pollution" published in 1961 (12), was the first to make a significant quantitative attempt to evaluate alternative reaction paths which may be operative in photochemical smog. In the years since Leighton's book appeared there has been a significant increase in the knowledge related to many of the potential reaction modes which he considered. Some new alternatives have appeared, although the number of really new ideas related to photochemical smog mechanisms which have surfaced since the publication of Leighton's book is surprisingly small.

The authors have prepared this review and evaluation of the mechanism of photochemical smog with several objectives in mind. Our primary objective was to evaluate the various alternative mechanisms and reaction rate constants proposed for the homogeneous reactions in smog in view of the best kinetic data in hand today. In the process we wanted to quantify our own thinking and, hopefully, that of our colleagues in the area. It was obvious to us, and as it will be evident to the readers of this review, that there is a need for a great deal more fundamental scientific research before the full predictive potential of the computer simulation of the chemistry of the urban atmosphere and truly scientific air pollution control measures and methods can be realized. Therefore our second objective of this review was to attempt to identify some of those potentially important reactions in the mechanism of photochemical smog formation for which there was insufficient basic kinetic data to allow for a realistic judgment of their importance. In this regard we hope that this review and evaluation might

serve to stimulate the research activity related to this most important and interesting area of chemistry.

There is a large number of potentially important reactions involved in the kinetic analysis of even the simplest possible analogues to the auto-exhaust-polluted atmosphere. For example, Westberg and Cohen (13) postulated the involvement of 71 different chemical reactions to describe the chemistry of the simulated smog chamber reaction of the simple starting mixture of propylene, nitrogen dioxide, and nitric oxide in air. Obviously any attempt to make a realistic fit of the rate data involving the many hundreds of reactive components present in the real auto-exhaust-polluted atmosphere must result in the participation of literally thousands of different chemical reactions. Although many of these reactions involve structurally related compounds for which some of the reactions will have near equal rate constants, the fact remains that the development of a complete reaction scheme for the real atmosphere is a problem of enormous complexity. We feel that the only real hope of defining the reactions which are important in the real atmospheres lies in the elucidation of the simpler smog chamber experiments. Even the quantitative fit of relatively simple smog chamber data requires the judicious use of computer techniques to allow the simultaneous solution of the enormous number of interrelated rate functions.

The use of the digital computer to solve the complex rate equations is relatively simple in principle. We attempt to explain the product formation and reactant disappearance of a particular smog chamber study with respect to a rational series of elementary chemical reactions. Then the kinetic mechanism can be expressed in terms of a set of first-order differential equations, where the change in concentration of reacting components, intermediates, and products is expressed with respect to a change in time. Given the

initial conditions and the rate constants for the elementary reactions involved, the computer will generate by a numerical solution the reactant and product concentration versus time curves for the kinetic mechanism proposed.*

There have been several recent efforts in the computer modeling of photochemical smog in addition to our own (14-17); Westberg and Cohen of the Aerospace Corporation (13); Eschenroeder and Martinez at General Research Corporation (18); Friedlander and Seinfeld (19); Hecht and Seinfeld (20) at the California Institute of Technology; Wayne and Ernest at the University of Southern California (21); and Niki, Daby, and Weinstock of the Ford Motor Company (22). In addition there are probably many unpublished efforts of industrial, research institutional, and governmental laboratories concerned with the quantitative evaluation of photochemical smog mechanisms. The chemical sophistication of the published efforts extend from the relatively simple generalized reaction mechanism of Friedlander and Seinfeld to the much more detailed mechanistic considerations of Niki, Daby, and Weinstock. The general features of the rates of oxidant formation, nitric oxide removal, nitrogen dioxide formation, and hydrocarbon loss can be rationalized at least qualitatively using even the chemically simplistic approach of Friedlander and Seinfeld. They employed only the following seven generalized reaction steps to describe the time dependence of the concentrations of NO, NO_2, hydrocarbon (RH), and O_3 in irradiated auto exhaust:

$$NO_2 + \underline{h}\nu \rightarrow NO + O$$

*In this work we have used the IBM System/370, scientific subroutine package, 360A-CM-03X, version III. This numerical method for solving differential equations is based on Hamming's modified predictor-corrector method.

$$O + O_2 + \underline{M} \rightarrow O_3 + \underline{M}$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$O + RH \rightarrow R\cdot + \text{Products}$$

$$RH + O_3 \rightarrow \text{Products (including } R\cdot)$$

$$NO + R\cdot \rightarrow NO_2 + R'\cdot$$

$$NO_2 + R\cdot \rightarrow \text{Products (including PAN)}$$

Friedlander and Seinfeld chose empirically rate parameters for the seven reactions which allowed a reasonable match of typical photochemical smog product rate data. The intent of these workers was not to explain the detailed chemistry involved in photochemical smog formation, but to allow the development of an empirical relation which provided for the incorporation of chemical change into the atmospheric diffusion models of polluted atmospheres.

The first attempts to describe the individual chemical steps important for the irradiation of mixtures containing propylene (RH), NO, and NO_2 in air were reported by Westberg and Cohen (13) and Wayne and Ernest (21). The simplified 7 reactions of Friedlander and Seinfeld mushroomed into 40 and 71 elementary reactions, respectively, in the work of Wayne and Ernest and Westberg and Cohen.

In the highly abbreviated reaction sequences such as that outlined above, many of the proposed steps are not elementary reactions, and they have little or no physical meaning. Thus the reaction of O atoms with RH above consists of five elementary reactions in the mechanism of Westberg and Cohen. However some of the "elementary" reactions employed in all of the first attempts at a more complete reaction mechanism involved such extreme structural rearrangement or unfavorable energy requirements for reactants to form products, that they cannot be important in real systems, or they were so generalized as to provide no clue as to the real

intermediates or transient species involved. Actually such mechanistic unreality does not hamper a good computer fit of the experimental data when rate constants for a great number of reactions are available to manipulate as independent variables. If the rate constant for each reaction, established or imagined, is adjusted independently to provide the best computer fit of the product rate data, obviously a better fit is obtained for a greater number of variable parameters. It is evident that a good computer match of smog chamber rate data obtained using arbitrarily chosen rate data for the extremely complex systems involved in photochemical smog is no evidence of the uniqueness or the correctness of the chosen mechanism. In fact, conclusions and predictions based on the extrapolation of such a mechanism to conditions not employed experimentally can be completely misleading, since the actual intermediates involved and their competitive reaction steps may not be included.

In recent simulations of the irradiated propylene-NO-NO_2-air mixtures of Hecht and Seinfeld (20) and Niki, Daby, and Weinstock (22), much more complete and seemingly accurate reaction schemes have been employed. However, as with all such complicated systems for which accurate reaction rate data are not available for many of the reactions, a reasonably large degree of chemical intuition has been employed in the choice of rate constants. In reality many of the chemical reactions which are believed to be involved in photochemical smog have been studied experimentally, and their rate constants have been determined. In these cases the experimental rate constants must be employed in kinetic matching attempts; they should not be considered as variables which can be adjusted outside of the experimental error limits in the attempted fit by

computer.* On the other hand there are many reactions of potential importance in these systems for which no experimental data or very limited information exist. In these cases it is necessary to estimate the rate constants "theoretically," avoiding any completely arbitrary choice of values. Such estimates must be consistent with the present knowledge of chemical kinetics and thermodynamics. For example, the procedures outlined by Benson (23) allow reasonable guidance in making many necessary "theoretical" rate constant estimates. We have used this approach in this work and have attempted to develop as precise a chemical mechanism as possible for several simple simulated atmospheres and different photochemical smog chamber systems involving several different olefins and paraffin hydrocarbons and aldehydes.

In attempting a quantitative treatment of the existing chamber data one must recognize that there is often relatively poor reproducibility between chamber product rate studies run by different laboratories, and the results of one individual study may be rather inaccurate and misleading. We have attempted to overcome this problem and to develop a consistent set of chemical reactions related to photochemical smog systems through the treatment of several very different systems studied by a variety of investigators. We have chosen as model systems only those published chamber rate studies based on rather complete and apparently unambiguous product analyses.

*For example the choice of Hecht and Seinfeld (20) for the rate constant for the reaction, $2HO_2 \rightarrow H_2O_2 + O_2$, $k = 7.0 \times 10^{-1}$ ppm^{-1} min^{-1}, seems unjustified in view of the reasonably good experimental estimates of this constant: $k = 5.3 \times 10^3$, 4.4×10^3, 1.4×10^4 ppm^{-1} min^{-1}; see the Appendix. Computer fits of experimental data based on such inaccurate choices of kinetic data obviously provide no validation of the mechanism choice, but represent a sophisticated exercise in curve fitting.