



Project Summary

Evaluation of Chemical Reaction Mechanisms for Photochemical Smog: Part 1. Mechanism Descriptions and Documentation

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Over the past ten years or so a great deal of effort has been devoted to developing chemical reaction mechanisms for photochemical air pollution. Because the actual number of atmospheric organic species is too large for the detailed chemistry of each to be included in a mechanism, it has been necessary to reduce the number of organic species to a manageable set by a process referred to as lumping. The manner in which this lumping has been carried out constitutes one of the major differences among existing mechanisms. It has recently been demonstrated that different chemical mechanisms predict different degrees of hydrocarbon and NO_x control to achieve the same level of ozone reduction under identical conditions. Because of the necessity of using reaction mechanisms for photochemical smog in determining air pollution control strategies, these results point to a serious need to analyze the fundamental behavior of such mechanisms and to understand the key elements of their behavior. Such an analysis is the subject of this two part report. The current volume, Part I, contains a detailed description of six mechanisms that have been developed to describe photochemical smog chemistry, including analyses of the treatments of the basic chemistry, of photolysis reactions and organic lumping in initial conditions and rate constants. It is found that the mechanisms differ in virtually all aspects. Part II is devoted to a detailed analysis of the behavior of each of the mechanisms.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Over the past ten years or so, a great deal of effort has been devoted to developing chemical reaction mechanisms for photochemical air pollution, and, as a result, several mechanisms exist at the present time. Since the atmosphere contains literally scores of hydrocarbon species, it is virtually impossible to write a reaction mechanism that includes the detailed chemistry of each hydrocarbon species present. Although each mechanism is based, more or less, on the same body of experimental kinetic data, the manner of treatment of the hydrocarbon chemistry varies among them. Because the actual number of hydrocarbon species is, as we have noted, too large for the detailed chemistry of each to be included in a mechanism, it has been necessary to reduce the number of hydrocarbon species to a manageable set by a process referred to as lumping. The manner in which this lumping has been carried out constitutes one of the major differences among existing mechanisms.

The differences among the several existing reaction mechanisms would not be of concern if their predictions were in essential agreement over the range of conditions of interest for atmospheric

predictions. It has recently been demonstrated, however, that different mechanisms predict rather different degrees of hydrocarbon and NO_x control to achieve the same level of ozone reduction under identical conditions. Because of the necessity of using reaction mechanisms for photochemical smog in determining air pollution control strategies, these results point to a serious need to analyze the fundamental nature of such mechanisms and to understand the key elements of their behavior. Such an analysis is the subject of this work.

Lumped Photochemical Mechanisms

Figure 1 depicts the ways in which hydrocarbon lumping has been approached in photochemical smog mechanisms. In the surrogate species approach, typified by the mechanism of Dodge (1977), the entire atmospheric mixture is represented by a small number of surrogate hydrocarbon species. In the mechanism of Dodge (1977), propene and n-butane, together with small quantities of formaldehyde and acetaldehyde, represent the entire atmospheric mix.

The other lumping approaches are indicated in Figure 1. Lumped molecule approaches refer to those in which the atmospheric hydrocarbons are lumped into identifiable molecular species. For example, in the surrogate species lumped molecule approach, certain hydrocarbons serve as surrogate species for an entire group of actual species. For example, n-butane can be used to represent all atmospheric alkanes, and the alkane portion of the full mechanism then consists of the detailed explicit chemistry of n-butane. Thus, a mixture of many alkanes is represented by a comparable concentration of n-butane. A mechanism based on this approach is that of Atkinson et al. (1982). We should point out that the mechanism of Dodge (1977), referred to above, is, in essence, also a surrogate species mechanism. However, the n-butane and propene are not necessarily identified with alkane and alkene species, respectively. Rather, propene and n-butane represent the entire atmospheric mix, where only the total concentration of non-methane hydrocarbons in parts per million by carbon is matched to the initial concentrations of propene and n-butane.

The other type of lumped molecule approach is that of generalized species lumping, in which an entire group of compounds is represented by a generalized species, the chemistry of which reflects the common features of that of the whole

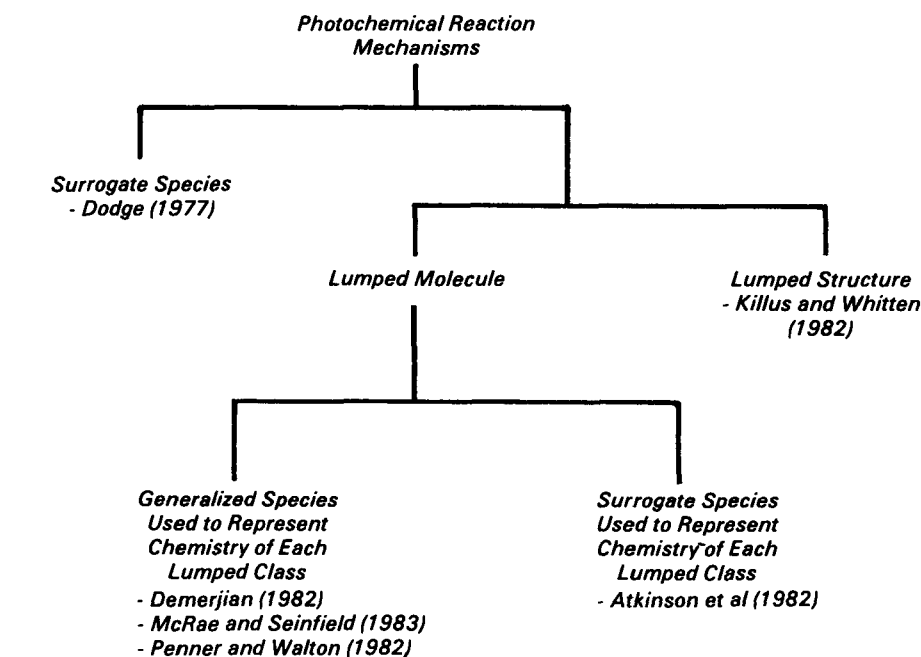


Figure 1. Classification of photochemical reaction mechanisms used in evaluation.

group. For example, alkanes could be represented by a species called ALKANE, whose rate constants and reaction mechanisms are, in some manner, an average of those of all alkanes. Mechanisms in this class include those of McRae and Seinfeld (1983), Demerjian (1982), and Penner and Walton (1982).

Finally in the lumped structure approach, lumped species represent various classes of structural units, such as, single-bonded carbon atoms, double-bonded carbon atoms, and carbonyl carbon atoms. An initial mixture of organics is therefore apportioned by bond type rather than by molecule type to obtain the lumped species. The one mechanism of this type is that of Killus and Whitten (1982). The Killus and Whitten mechanism, referred to as the Carbon Bond mechanism, treats the reactions of six different types of carbon atoms: 1-alkene carbon atoms except ethene, ethene, single bonded carbon atoms, reactive aromatic rings, carbonyl carbon atoms including carbon atoms from internal olefins, and α -dicarbonyls.

It is important to point out that any reaction mechanism for the atmospheric chemistry of photochemical smog must involve some aspect of hydrocarbon lumping. It is sometime mistakenly assumed that lumping is not involved in a surrogate mechanism, since a surrogate mechanism consists of the explicit chemistry of the surrogate species. Although the mechanism itself contains

only explicit chemical steps, not involving any generalized species, the representation of an atmospheric mixture requires that many species not explicitly included in the mechanism be apportioned to the surrogate species. It is, in fact, the way in which species are apportioned that really constitutes the differences among mechanisms, although mechanisms do differ in the values of rate constants used and in the importance of mechanistic steps where the available experimental information is open to interpretation.

Procedure

The particular mechanisms chosen for initial testing in this study are shown in Figure 1 and Table 1. Several different criteria were used to select representative mechanisms including: the availability of supporting documentation and the degree of testing against smog chamber experiments. One additional requirement was that each mechanism had to have been implemented in an air quality model and used in emissions control calculations. With this background the following material was requested from each investigator responsible for the development of the reaction mechanism: (1) All the available open and report literature references that describe the scientific basis and testing of the reaction mechanism; (2) A computer listing of the reactions, species names and a duplication of a test case. This latter information was requested to ensure that the mechanism has been

Table 1. Photochemical Reaction Mechanisms Considered for Evaluation — Their Characteristics and Their Validation Base

Reaction Mechanism	Type ^a	Number of Reactions/ Species	Number of Organic Classes ^b	Experiment Numbers ^c	Validation Basis	Type of Experiment
Atkinson et al. (1982) ^c	LM	81/52	14	EC-178 EC-143 EC-146 EC-216 EC-340 EC-344 EC-161 EC-237,EC-242,EC-246 AGC-119,AGC-133,AGC-134, AGC-135,AGC-138,AGC-150, AGC-156 AP-28,AP-30,AP-35,AP-37	n-butane/NO _x ethene/NO _x tr-2-butene/NO _x propene/NO _x toluene/NO _x m-xylene/NO _x 4 alkenes/NO _x 7 hydrocarbons/NO _x surrogate (multi- hydrocarbon)/NO _x hydrocarbon/NO _x /SO ₂	
Demerjian (1982)	LM	45/30	4			40 Bureau of Mines smog chamber experiments with dilute auto exhaust and added NO _x . Several UCR aromatic hydrocarbon/NO _x experiments
Dodge (1977)	S	76/39	4			17 Bureau of Mines smog chamber experiments with dilute auto exhaust and added NO _x
Killus and Whitten (1982)	LS	79/41	5	EC-231,EC-232,EC-233, EC-237,EC-238,EC-242, EC-243,EC-245,EC-246, EC-247 ---		7 hydrocarbons/NO _x experiments at SAPRC 2 day urban hydrocarbon mix at UNC
McRae and Seinfeld (1983)	LM	52/32	6	EC-237 SUR-119J,SUR-121J, SUR-126J,SUR-132J, SUR-133J,SUR-134J		7 hydrocarbons/NO _x surrogate atmospheric mix
Penner and Walton (1982)	LM	59/22	4	--- EC-231,EC-232,EC-233, EC-237,EC-238,EC-241, EC-242,EC-243,EC-245		several individual hydrocarbon/NO _x experiments 7 hydrocarbons/NO _x

^aThe mechanism type refers to: LM - Lumped molecule, S - Surrogate and LS - Lumped structure.

^bNumber of reactive organic groupings for which either emissions or initial conditions must be specified in practical applications.

^cThe mechanism presented here corresponds to that in the most recent reference cited.

^dThis mechanism was developed by Falls and Seinfeld (1978), with updated rate constants presented by McRae and Seinfeld (1983).

^eThe experiment numbers refer to the following laboratories:

EC,SUR Statewide Air Pollution Research Center (SAPRC) of
 the University of California, Riverside
UNC University of North Carolina

implemented in the manner intended by the developer. A summary of the mechanism characteristics, documentation sources and bases for validation is shown in Table 1. The validation bases of the Atkinson et

al. (1982), Killus and Whitten (1982) and Penner and Walton (1982) mechanisms are experiments conducted at the University of California, Riverside, whereas the Demerjian (1982) and Dodge (1977)

mechanisms were evaluated on Bureau of Mines smog chamber data. The Killus and Whitten (1982) mechanism has also been tested against outdoor smog chamber data from the University of North Carolina.

Chapter 2 contains summaries of the mechanisms.

Results

We discuss the basis of the lumping approaches of the five lumped mechanisms: Atkinson et al. (1982), Demerjian (1982), Killus and Whitten (1982), McRae and Seinfeld (1983), and Penner and Walton (1982). Our discussion of the chemistry of photochemical smog is based almost exclusively on the extensive review of Atkinson and Lloyd (1983). We then examine the specification of photolysis rates and initial conditions in each of the mechanisms.

Conclusions

This report has presented a detailed description of six lumped reaction mechanisms for photochemical smog:

Atkinson et al. (1982)
Demerjian (1982)
Dodge (1977)
Killus and Whitten (1982)
McRae and Seinfeld (1983)
Penner and Walton (1982)

The description includes a discussion of the basic assumptions in each mechanism's treatment of the fundamental chemistry, photolysis reactions, and organic lumping via initial conditions and organic rate constants. In general, it is found that the mechanisms differ in virtually all aspects, and, without detailed, quantitative, numerical comparisons, it is difficult to predict simply from inspection how each mechanism will perform in a particular application. Nevertheless, if one removes those mechanism aspects included only to account for smog chamber-dependent radical sources, such as a wall source of OH radicals or initial HONO, it is possible to rank the mechanisms according to overall "reactivity." We find on the basis of our analysis that such a ranking is:

Killus and Whitten (1982)
Demerjian (1982)
McRae and Seinfeld (1983)

} most
reactive

Atkinson et al. (1982)
Penner and Walton (1982)

} less
reactive

The Dodge (1977) mechanism cannot be ranked in this scale because the split between propene and n-butane is fixed.

Our object is to be able to tell specifically what aspects of each mechanism are key to its performance, as measured by its "reactivity." To do so requires the detailed, quantitative, numerical comparisons referred to above. Such comparisons are the subject of Part II.

References

- Atkinson, R. and Lloyd, A.C. (1983), "Evaluation of Kinetic and Mechanistic Data for Modeling of Photochemical Smog," *J. Phys. Chem. Ref. Data* (in press).
- Atkinson, R., Lloyd, A.C. and Wines, L. (1982), "An Updated Chemical Mechanism for Hydrocarbons/NO_x/SO₂ Photooxidations Suitable for Inclusion in Atmospheric Simulation Models," *Atmospheric Environment*, 16, 1341-1355.
- Demerjian, K.L. (1982), "Personal Communication."
- Dodge, M.C. (1977), "Combined Use of Modeling Techniques and Smog Chamber Data to Derive Ozone — Precursor Relationships," U.S. Environmental Protection Agency Report, EPA-600/3-77-001a, 881-889.
- Falls, A.H. and Seinfeld, J.H. (1978), "Continued Development of a Kinetic Mechanism for Photochemical Smog," *Environmental Science and Technology*, 12, 1398-1406.
- Killus, J.P. and Whitten, G.Z. (1982), *A New Carbon-Bond Mechanism for Air Quality Modeling*, U.S. Environmental Protection Agency Report No. EPA-600/3-82-041.
- McRae, G.J. and Seinfeld, J.H. (1983), "Development of a Second-Generation Mathematical Model for Urban Pollution II: Model Performance Evaluation," *Atmospheric Environment*, 17, 501-523.
- Penner, J.E. and Walton, J.J. (1982) *Air Quality Model Update*, Lawrence Livermore Laboratory Report UCID - 19300, Lawrence Livermore National Laboratory, University of California, Livermore, California, 55 pp.

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The complete report, entitled "Evaluation of Chemical Reaction Mechanisms for Photochemical Smog: Part I. Mechanism Descriptions and Documentation," (Order No. PB 83-263 251; Cost: \$16.00, subject to change) will be available only from:

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