27
1-28-82
24 to 21.15
I-1112

(1)

UCID-19300

MASTER

Air-Quality-Model Update

Joyce E. Penner
John J. Walton

January 15, 1982

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W 7405 Eng-48.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

UCID--19300

DE82 007145

Air Quality Model Update

Joyce E. Penner and John J. Walton

Lawrence Livermore National Laboratory, University of California
Livermore, California 94550

Abstract

The Livermore Regional Air Quality Model (LIRAQ) has been updated and improved. This report describes the changes that have been made in chemistry, species treatment, and boundary conditions. We report the results of smog chamber simulations that were used to verify the chemistry as well as simulations of the entire air quality model for two prototype days in the Bay Area. The results reported here for the prototype day simulations are preliminary due to the need for improvement in meteorology fields, but they show the dependence and sensitivity of high hour ozone to changes in selected boundary and initial conditions.

DISCLAIMER

This book 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.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1. Introduction

The Livermore Region Air Quality Models (LIRAQ-1 and LIRAQ-2) were developed in 1975 through a grant from the National Science Foundation under the Research Applied to National Needs (RANN) program. The original work was a joint effort by the University of California Lawrence Livermore National Laboratory (LLNL), the Bay Area Air Pollution Control District (BAAPCD)*, and the NASA Ames Research Center (ARC). These codes and their application to the Bay Area are described in a User's Guide (Mac Cracken, 1975), a two-volume report (MacCracken and Sauter, 1975 a,b), and two journal articles (MacCracken et al., 1978; Duewer et al., 1978).

In 1976, the codes were further modified to include sulfur chemistry. Data processors were developed so that the models could be applied to St. Louis and participate in the EPA supported Regional Air Pollution Study (RAPS). These codes were designated LIRAQ-1S and LIRAQ-2S. Their application to St. Louis is described in Duewer et al, 1980.

The work in 1976 was limited and included only minimal model development. In addition, no final emissions inventory was available for St. Louis when that work was completed, so that no verification of the model was possible. The LIRAQ-2S model was used by the Association of Bay Area Governments, the Bay Area Air Pollution Control District and the Metropolitan Transportation Commission to develop the aspects of the 1979 Bay Area Air Quality Maintenance Plan (ABAG, et al., 1979) dealing with O_3 attainment. It has also been used to simulate the future response of nitrogen dioxide concentrations in the San Francisco Bay Area to hydrocarbon and NO_x controls

*Now the Bay Area Air Quality Management District.

(De Mandel, et al., 1980). These studies provided partial verification for LIRAQ-2S.

The original verification studies for the LIRAQ-2 model (MacCracken and Sauter, 1975) and those associated with the LIRAQ-2S model (ABAG et al., 1979; DeMandel et al., 1980) used meteorology for prototype days in 1973 and 1976. The emissions inventory for model year 1975 was used in these studies. It was prepared as part of the original model development (MacCracken and Sauter, 1975) and included a total of 1096 tons/day hydrocarbon emissions and 702 tons/day NO_x (as NO_2).

Since these studies were performed, new emissions inventory preparation techniques have become available. These techniques imply that smaller anthropogenic hydrocarbon emissions were actually present than previously estimated for 1975. Thus the model verification using the earlier estimate of emissions is no longer appropriate. As part of the 1982 State Implementation Plan, a new emissions inventory using new estimation techniques was developed. In addition, preliminary prototype day meteorology appropriate for several days in 1978 and 1979, was prepared. However, attempts to verify LIRAQ-2S with the new emissions inventory were not satisfactory; the model produced too little O_3 . Application of the LIRAQ-2S model to St. Louis was also unsatisfactory. Again, too little O_3 was produced.

The chemistry used in LIRAQ-2S was current as of 1976 (Duewer et al., 1980). Since that time, several reaction rate coefficients have been re-measured or measured for the first time. In addition, a chemical mechanism for the oxidation of aromatic hydrocarbons is now available. This mechanism is quite different from mechanisms for the oxidation of alkenes, alkanes, or aldehydes as treated in LIRAQ-2S. We therefore updated the LIRAQ model to

include a fourth hydrocarbon category. At the same time the organic and inorganic rates in LIRAQ were updated to values current as of 1981. These changes are reported in Section 2 of this report.

The model chemistry in LIRAQ-1 was originally verified and tuned against smog chamber data from U.C. Riverside and EPA (MacCracken and Sauter, 1975). Smog chamber data are notorious for poorly understood effects and, therefore, no attempt at re-tuning was made after the original study, even though several inorganic rates were changed. Nevertheless, since explicit mechanisms for hydrocarbon oxidation are developed based on chamber data, lumped mechanisms, which simulate the same organic species in a simplified manner, should do reasonably well in smog chamber simulations. We therefore tested the new mechanism against a selected set of smog chamber experiments.

In Section 3 we present simulation results for a series of multi-hydrocarbon-NO_x smog chamber experiments. These experiments were chosen because they represent tests of the model on a complex mixture of hydrocarbons and therefore test our lumping procedures as well as how well the model simulates oxidation of individual species. Tests of the model chemistry on individual hydrocarbon-NO_x smog chamber experiments were also performed, but are not reported in detail. They show that the present mechanism does equally well as other lumped mechanisms in smog chamber simulations.

The new mechanism produces more O₃ than the mechanism in LIRAQ-2S. We identified the chemistry changes that are responsible for the greater reactivity of the new chemical mechanism. These results are also reported in Section 3.

While the new chemistry is significantly improved over that used in LIRAQ-2S, further improvements are still possible. The aromatic mechanism

probably produces too much O_3 , especially at high hydrocarbon to NO_x ratios. In addition, the multi-hydrocarbon- NO_x simulations show that it would be desirable to treat ethylene as a separate hydrocarbon species. When oxidation mechanisms for biogenic emissions become available, it would be appropriate to treat them separately as well. The current reaction set, however, was judged adequate for use in the Bay Area, and was coded into the LIRAQ-2 model. The new model is designated LIRAQ-4HC.

In the last section we briefly report the results of several prototype-day simulations using the new version of LIRAQ, the updated emissions inventory and preliminary meteorology for the September 29, 1978 and September 12, 1979 prototype days. Selected boundary conditions and initial conditions were varied to study the sensitivity of maximum ozone to specification of these fields. These results form an initial verification for the updated LIRAQ model and further support that the improved chemistry is adequate.

2. Chemistry and Species Treatment

The chemical reactions and rate constants used in the new version of LIRAQ, LIRAQ-4HC, are given in Table 1. The main differences between the new reaction set and that used in the old version of LIRAQ (LIRAQ-2S) are: the inorganic rates have been updated to currently accepted values, aromatics (HC3) are treated as a separate hydrocarbon class, PAN and HNO_4 are calculated explicitly, and nitric acid (HNO_3), sulfur dioxide (SO_2), and sulfate (SO_4) are no longer calculated.

The inorganic rate constants are consistent with the recommendations made by the NASA Panel for Data Evaluation given in DeMore et al. (1981) except for the reactions R17 and R19 of Table 1; these reaction rates were updated to the recommendations in WMO (1981). The organic reaction paths and rates are based on the reactions of propene (HC1), n-butane (HC2), toluene (HC3), and a 50-50 molar mixture of formaldehyde and acetaldehyde (HC4). Organic species which are produced during the oxidation of these primary hydrocarbons usually have rates based on the simplest species of that general class or are estimated from the rates of analogous inorganic reactions. The following paragraphs describe the approximations used in the simplified chemical scheme for the oxidation of aromatics.

Aromatic Chemistry

Aromatic hydrocarbons make up about 10% of the total hydrocarbon emissions (by mole) in the Bay Area. Their chemistry is still speculative (Atkinson et al., 1980), but is clearly different from oxidation of alkanes,

alkenes, or aldehydes. In the past, their emissions were lumped with either the alkane or alkene emissions in LIRAQ. For the new LIRAQ reaction set we created a separate hydrocarbon species, HC3, to represent aromatics. The chemistry for HC3 is based on one of the oxidation mechanisms, mechanism "A", proposed by Atkinson et al. (1980) for toluene. According to Atkinson et al. (1980), toluene oxidation can proceed via two reaction pathways, OH abstraction and addition:

Atkinson et al., assigned rates for (1) and (2) of $1 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ and $5.4 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$, respectively. The abstraction product reacts with NO to form NO_2 and, subsequently, benzaldehyde 75% of the time.

Twenty-five percent of the time the benzyl radical reacts with NO to form benzyl nitrate, which does not react further. The subsequent reactions of benzaldehyde can lead to further conversions of NO to NO_2 and ultimately to NO_x sinks.

The addition product can react with NO_2 or with O_2 via two paths:

Atkinson et al. (1980) assign rate constants to 3), 4), and 5) equal to 1.2×10^{-15} , 3.5×10^{-15} , and 5.2×10^{-12} , respectively, for mechanism "A".

For simulation in LIRAQ, we have condensed the reactions (1) through (5) to two reactions,

They are listed in Table 1 as R34 and R35. Reaction R34 is a condensation of (2) followed by (4). BR020HHH is the oxygenated radical formed in (4). Reaction R35 lumps together the less important initial abstraction reaction of toluene with (2) followed by (3) or (5). The rate for R34 is taken as the fraction of the addition product formed in (2) that follows path (4) times the

rate for (2) or, as long as NO_2 is less than 200 ppm,

$$\frac{3.5 \times 10^{-15}}{1.2 \times 10^{-15} + 3.5 \times 10^{-15}} \times 5.4 \times 10^{-12} = 4.0 \times 10^{-12} .$$

The rate for reaction R35 lumps together all reaction pathways not explicitly followed and thus is equal to the sum of the rates for (1) and (2), less the rate for R34:

$$6.4 \times 10^{-12} - 4.0 \times 10^{-12} = 2.4 \times 10^{-12} .$$

As described in Atkinson et al. (1980), the addition product from (4) can react with NO to eventually form HO_2 , methylglyoxal and a dicarbonyl. Of these products methylglyoxal is the most reactive and may photolyze or react with HO. These reactions are represented in LIRAQ as

The reactions of the dicarbonyl are neglected in LIRAQ.

The simplified reaction mechanism for toluene oxidation only includes oxidation via the most important path. In smog chamber simulations of toluene- NO_x systems at high hydrocarbon to NO_x ratios, this simplified mechanism produces too much O_3 . The paths that were neglected tend to slow ozone formation possibly due to NO_x loss (Whitten, et al. 1980b). Since there is a discrepancy between the mechanism developed by Atkinson et al.

(1980) and that developed by Whitten et al. (1980b) regarding minor oxidation paths and the NO_x loss efficiency via these paths, we chose to leave them out at this time. Their neglect should not be too important for ozone formation at the low aromatic concentrations and low hydrocarbon to NO_x ratios expected from the emissions inventory in the Bay Area. As shown below, the LIRAQ mechanism as a whole is able to adequately simulate multi-hydrocarbon smog chamber experiments, even though these experiments have a larger fraction of aromatics than expected in the Bay Area.

3. Smog Chamber Simulations

Simulation of smog chamber experiments represents one of the only ways available to independently check the chemistry used in the model. Unfortunately, many smog chamber rates and processes are poorly characterized. For example, smog chambers have a large surface to volume ratio (compared to the atmosphere) and wall reactions (either sources or sinks) have often been invoked to improve model simulations. In addition, smog chambers cannot be used to test all features of the chemistry important to the urban atmosphere. For example, the UCR indoor smog chamber experiments have a fairly well characterized light source, but do not accurately reproduce the sun's light and diurnal variations. The level of photolysis is usually higher than that for the sun. Emissions cannot be continuously injected into a smog chamber as they are in an urban atmosphere, and initial radical formation processes are probably quite different, especially at low hydrocarbon to NO_x ratios.

In spite of these problems, smog chamber results have been used extensively to validate both explicit and lumped chemical mechanisms for hydrocarbon- NO_x systems. As a check on our general methods, we have used the mechanism of Table 1 to simulate the series of seven-hydrocarbon- NO_x smog chamber experiments reported by Pitts et al., (1979).

While the results lend confidence to our modeling procedures, it would be optimistic to conclude that photochemical smog formation is fully understood. As we point out later, the hydrocarbon to NO_x ratios used in the smog chamber experiments are large compared to those observed in the Bay Area. Unfortunately, as the hydrocarbon abundance is decreased in the experiment,

the smog chamber results begin to be dominated by wall effects. Since wall effects do not occur in the atmosphere, no testing of the mechanism at the appropriate concentration levels is possible, unless the wall effects are fully characterized. Although recent work at UCR has tried to characterize these dirty chamber effects (Carter et al., 1981), they are still poorly understood. Thus, the simulation of smog chamber experiments as a test of a chemical mechanism cannot constitute proof of the mechanism's validity in the atmosphere. Still these simulations are the only independent tests available.

Procedures

In order to calculate concentrations for comparison with smog chamber experiments, it is essential to add a dilution rate for each species and smog chamber-dependent wall reactions to the reaction set given in Table 1. The dilution (due to sampling) is different for each experiment and has been provided in the data sheets given in Pitts et al. (1979). In addition, since O_3 and H_2O_2 are thought to attach to the walls of the chamber the reactions

and

with rate constants of $2.8 \times 10^{-5} \text{ sec}^{-1}$ and $7.0 \times 10^{-5} \text{ sec}^{-1}$, respectively, are used (Carter et al. 1979). Carter et al. (1979) and Carter et al. (1981) suggest that a source of radicals from the walls is needed for simulations of the UCR smog chamber. For most of the simulations reported below, we did not include this source, but we will show examples of its effect.

Photolysis rates in a smog chamber experiment are dependent on the light source used. We have used the experimentally determined rate constant for photolysis of NO_2 for each smog chamber experiment. The other photolysis rates for the experiment were calculated by multiplying the rates in Table 1 by the ratio of the measured NO_2 photolysis rate to the NO_2 photolysis rate given in Table 1. This procedure gives rather different photolysis rates than those used by Whitten et al. (1979), Carter et al. (1979), or Atkinson et al. (1980). A comparison of the photolysis rates used in our smog chamber simulations with those reported by these authors is given in Table 2. Carter et al. (1979) and Atkinson et al (1980) determined the photolysis rate for each experiment from the measured NO_2 rate, the absorption coefficients and quantum yields of the photolyzing species, and the measured relative spectral distribution of the photolysis light source. This procedure is more appropriate to the smog experiment than our procedure.

To test the effect of variations in photolysis rates on smog simulations we used each set of photolysis coefficients given in Table 2 (after adjusting by ratio to the measured NO_2 photolysis rate) in a series of simulations of the smog chamber experiment EC231. These are shown in Figs. 1-4. As shown there, the photolysis rates assigned by Carter et al. (1979), Whitten et al. (1979), and Atkinson et al. (1980), produced somewhat less O_3 than our rates. Since the maximum O_3 produced was in all cases within 5% of that produced using our rates, we judged our procedures adequate.

Figures 5-7 show the effect of adding a chamber-dependent source of HO as suggested by Carter et al. (1979) and Carter et al. (1981), an initial concentration of HONO, as suggested by Whitten et al. (1980), and both, respectively. As shown there, adding a source of radicals can speed up O_3 formation in the chamber but the peak O_3 formed is not significantly changed. Since our mechanism and lumping procedures appear to be adequately fast in these simulations, we did not include these sources in the following.

Seven-hydrocarbon- NO_x simulations

Pitts et al. (1979) provide data for eleven seven-hydrocarbon- NO_x smog chamber experiments. In the following we have simulated only the first nine of these, because EC246 is quite similar to EC232 and because the data for O_3 was missing in our copy of Pitts et al. (1979) for experiment EC247. The initial concentrations specified by Pitts et al. are given in Table 3. Reactivity-weighted concentrations for use with the mechanism of Table 1 are given in Table 4. The simulations are shown in Figs. 8-16.

Initial concentrations for NO_x in these experiments ranged from 0.1 ppm to 1.0 ppm. Initial hydrocarbons (ppmC) as specified by Pitts et al. (1979) ranged from 4.97 ppmC to 13.19 ppmC (see Table 3). The hydrocarbon to NO_x ratios (ppmC/ppm) range from 10.1 to 26.9. The hydrocarbon to NO_x ratio for averaged data from 6-9 a.m. in San Francisco on September 29, 1978 is 5.7 (ppmC/ppm). Total non-methane hydrocarbon was 1.80 ppmC and NO_x ($NO+NO_2$) was 0.3 ppm. Thus, none of the smog experiments can be considered typical of a morning parcel of air in San Francisco. Similar remarks apply to data from

San Jose, San Rafael, and Livermore. In addition, none of the reactivity-weighted initial concentrations of hydrocarbons for these experiments are equal to the reactivity-weighted emissions used in LIRAQ (see Table 4). Nevertheless, simulations of these experiments provide a reasonable test for the chemical mechanism shown in Table 1. As discussed before, at the low hydrocarbon to NO_x ratios typical in the Bay Area, smog chamber results are dominated by poorly understood chamber effects. Thus the tests provided here are the best available for testing chemistry appropriate to the atmosphere.

In all simulations, the mechanism used here appears to overestimate O_3 , although the error between the simulated and observed peak O_3 is similar to simulation errors reported in Falls and Seinfeld (1978) and Whitten et al. (1980a). The calculated NO to NO_2 conversion rate and subsequent O_3 development are reasonably close to the observed rates, even though no radical chamber source has been used (Carter et al. 1979, 1981). A significant problem is the over-prediction of PAN. We believe the over-prediction of PAN and O_3 could be eliminated by treating ethylene (whose oxidation produces very little PAN) as a separate species. In addition, the chemistry could be slowed and O_3 decreased by adding NO_x sinks to the aromatic mechanism. Limitations of time have prevented exploring these possibilities. However, since ethylene and aromatics are both over-represented in these smog chamber experiments compared to their representation in the San Francisco Bay Area (see Table 4), we expect the application of the mechanism in Table 1 to the San Francisco Bay Area should be more accurate than its application to these experiments.

As described previously, the chemical mechanism used in LIRAQ-2S and

described in Duewer et al. (1980), is significantly less reactive than the mechanism in Table 1. This is shown in Fig. 17, where the LIRAQ-2S mechanism has been used to simulate EC245 (compare Fig. 16). Part of the difference between the results in Fig. 16 and those in Fig. 17 is due to the treatment of aromatics. Figure 18 shows a simulation of EC245 using the mechanism of Table 1 but treating aromatics as they are treated in LIRAQ-2S. Maximum O_3 is lowered, but not as much as in the LIRAQ-2S mechanism. The remaining differences may be explained by the updated rate constants and products for the reactions listed in Table 5. The new values have been based on new rate constant measurements that have become available since LIRAQ was developed. To show which new rate constants are responsible for the largest changes, we sequentially changed the LIRAQ-2S mechanism to the new values and simulated EC11 (a propylene- NO_x experiment) with each new change. The results for maximum O_3 are reported in Table 5. Each change in that table includes all of the changes made up to that point with one additional chemistry change. As shown there, the major changes are due to changes in the rate for $HO_2 + NO$ (R14), addition of the chemistry of HO_2NO_2 (R20 and R21), changes in N_2O_5 chemistry (R7 and R8), changes in the products of $HCl + O_3$ (R25 and R26), and changes in the chemistry of HC4 (R31, R32, J10, and J11). All of these changes are in accord with what is currently understood for these chemical systems.

4. Application of LIRAQ to the Bay Area

We have tested the new chemical mechanism in simulations for two prototype days in the Bay Area. Although the results are preliminary because they use preliminary meteorology, they are presented here in order to show the sensitivity of LIRAQ to selected changes in initial conditions and boundary conditions. A more detailed report describing these tests will be prepared later. The boundary conditions normally used in LIRAQ-4HC are given in Table 6.

The tests made for the September 29, 1978 simulations are described in Table 7a. Tests made for the September 12, 1979 simulations are described in Table 7b.

Statistics associated with these simulations are given in Tables 8a and 8b, respectively. RUN 081481 appears to adequately simulate O_3 and the other pollutants for September 29, 1978, at least in comparison with previous LIRAQ simulations (see MacCracken and Sauter, 1975). None of the simulations for September 12, 1979, however, were judged adequate (too little O_3 was formed). Changes in meteorology can have significant impact on the ozone simulation (compare RUN 092681 with RUN 081481 for September 29, 1978). Thus, we expect that improvements in the meteorology for September 12, 1979 will alleviate the problem of O_3 underprediction. As the tests and statistics of Tables 8a and 8b show, the maximum predicted ozone appears to be sensitive to a variety of different factors that are poorly known in the Bay Area. In the future, we expect to analyze these results and others in order to improve our ability to realistically model air quality in the Bay Area.

Acknowledgment

We wish to thank the Bay Area Air Quality Management District and the California Air Resources Board for their financial support of this work under the Work for Others Agreement between the Department of Energy and the Bay Air Quality Management District. Support was also provided by the Biomedical and Environmental Research Program of the Department of Energy for eventual use of this model in an assessment of air quality impacts of diesel powered light duty vehicles.

We acknowledge the advice, support, and critical remarks of members of the Bay Area Air Quality Modeling committee, especially Gary Kendall, Rob DeMandel, Tom Perardi, Lew Robinson, and Ron Wada. We thank Dick Duker, who provided the meteorology for the new prototype days, and Tom Umeda for stimulating comments and interaction and invaluable assistance in the continuing efforts to verify and evaluate model performance on the new prototype days. Finally we thank Mike MacCracken for his continued interest in this work and in particular for his editorial remarks on this manuscript.

Work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

References

1. Atkinson, R., W. P. Carter, K. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., "A Smog Chamber and Modeling Study of the Gas-Phase NO_x -Air Photooxidation of Toluene and the Cresols," Int. J. Chem. Kin. 12, 779-836, 1980.
2. Carter, W.P.L., A. C. Lloyd, J. L. Sprung, J. N. Pitts, Jr., "Computer Modeling of Smog Chamber Data: Progress in Validation of a Detailed Mechanism in the Photooxidation of Propene and n-Butane in Photochemical Smog," Int. J. Chem. Kin. 11, 45, 1979.
3. Carter, W.P.L., R. Atkinson, A. M. Winer, J. N. Pitts, Jr., "Evidence for Chamber-dependent Radical Sources: Impact on Kinetic Computer Models for Air Pollution," preprint 1981.
4. Darnall, K. R., R. Atkinson, and J. N. Pitts, Jr., "Observation of Biacetyl from the Reaction of OH Radicals with o-Xylene: Evidence for Ring Cleavage," J. Phys. Chem. 83, 1943-1946, 1979.
5. DeMore, W. B., L. J. Stief, F. Kaufman, D. M. Golden, R. F. Hampson, M. J. Kurylo, J. J. Margitan, M. J. Molina, R. T. Watson, "Chemical Kinetic and Photochemical Data for use in Stratospheric Modeling," JPL Publication 81-3, 1981.
6. Duewer, W. H., J. J. Walton, K. E. Grant, H. Walker, "Livermore Regional Air Quality Model (LIRAQ) Transfer to EPA," Lawrence Livermore National Laboratory report UCRL-52846, March 1980.
7. Falls, A. H. and J. H. Seinfeld, "Continued Development of a Kinetic Mechanism for Photochemical Smog," Env. Sci. and Tech. 12, 1398-1406, 1978.

8. Koppe, R. K., "Ambient Hydrocarbon Concentration Field Sampling and Analysis Program," Final Report to the Bay Area Air Quality Management District Preliminary Draft, March 1981.
9. Morris, E. D., Jr. and H. Niki, "Reaction of Dinitrogen Pentoxide with Water," J. Phys. Chem. 77, 1929, 1973.
10. Pitts, J. N., Jr., K. Darnall, W.P.L. Carter, A. M. Winer, and R. Atkinson, "Mechanism of Photochemical Reactions in Air," Final Report EPA-600/3-79-110, 1979.
11. Platt, U., D. Perner, A. M. Winer, G. W. Harris, and J. N. Pitts, Jr., "Detection of NO_3 in the Polluted Troposphere by Differential Optical Absorption," Geoph. Res. Lett. 7, 89-92, 1980.
12. Whitten, G. Z., H. Hogo, and J. P. Killus, "The Carbon-bond Mechanism: A Condensed Kinetic Mechanism for Photochemical Smog," Env. Sci. and Tech. 14, 690-700, 1980a.
13. Whitten, G. Z., J. P. Killus, and H. Hogo, "Modeling of Simulated Photochemical Smog with Kinetic Mechanisms," Vol. 1 Final Report, EPA-600/3-80-028A, February 1980b.
14. World Meteorological Organization (WMO) Global Ozone Research and Monitoring Project Report, "The Stratosphere 1981: Theory and Measurements," Working Draft, edited by R. D. Hudson, E. I. Reed, and R. D. Bojkov, 1981.

Table 1: Chemistry

		Reaction Rate Coefficients*			
No.	Reaction	A	B	C	Notes
<u>Inorganic Reactions:</u>					
R1	$O+O_2+M \rightarrow O_3+M$	5.58-29 ⁺	-2.0	0	1
R2	$O_3+NO \rightarrow NO_2+O_2$	2.30-12	0.0	1450	1
R3	$O+NO \rightarrow NO_2$	1.08-8	-1.5	0	1
R4	$O+NO_2 \rightarrow NO+O_2$	9.30-12	0.0	0	1
R5	$O+NO_2 \rightarrow NO_3$	1.39-7	-2.00	0	1
R6	$O_3+NO_2 \rightarrow NO_3+O_2$	1.20-13	0.0	2450	1
R7	$NO_3+NO_2 \rightarrow N_2O_5$	4.10-11	-0.7	0	1
R8	$N_2O_5 \rightarrow NO_2+NO_3$	3.60+16	-0.7	11180	1
R9	$NO_3+NO \rightarrow NO_2+NO_2$	2.00-11	0.0	0	1
R10	$N_2O_5+H_2O \rightarrow 2HNO_3$	3.00-21	0.0	0	2
R11	$HO+NO_2 \rightarrow HNO_3$	5.87-8	-1.5	0	1
R12	$HO+NO \rightarrow HNO_2$	3.38-8	-1.5	0	1
R13	$HO+CO \rightarrow HO_2+CO_2$	2.7-13	0.0	0	1
R14	$HO_2+NO \rightarrow HO+NO_2$	3.5-12	0.0	-250	1
R15	$HNO_2+HO \rightarrow H_2O+NO_2$	6.6-12	0.0	0	1
R16	$HO_2+HO_2 \rightarrow H_2O_2+O_2$	8.4-14	0.0	-1250	1
R17	$HO+HO_2 \rightarrow H_2O + O_2$	8.0-11	0.0	0	3
R18	$HO+H_2O_2 \rightarrow HO_2+H_2O$	1.6-12	0.0	0	1
R19	$HO+HNO_4 \rightarrow H_2O+NO_2+O_2$	4.0-12	0.0	0	3
R20	$HNO_4 \rightarrow HO_2+NO_2$	5.0+14	0.0	10720	1

Table 1: Chemistry (continued)

		Reaction Rate Coefficients*			
No.	Reaction	A	B	C	Notes
<u>Inorganic Reactions:</u>					
R21	HO ₂ +NO ₂ → HNO ₄	4.22	-5.0	0	1
R22	HO+O ₃ → HO ₂ +O ₂	1.6-12	0.0	940	1
R23	HO ₂ +O ₃ → HO+O ₂ +O ₂	1.1-14	0.0	580	1
<u>Reactions of HCl:</u>					
R24	HCl+HO → RO ₂ +HC4	4.0-11	0.0	120	
R25	HCl+O ₃ → HO ₂ +HC4	3.5-15	0.0	1900	
R26	HCl+O ₃ → HC4	3.5-15	0.0	1900	
R27	HCl+O → RO ₂ +RCO ₃	1.0-11	0.0	360	
R28	HCl+NO ₃ → RO ₂ +products	1.0-12	0.0	1400	
<u>Reactions of HC2:</u>					
R29	HC2+HO → RO ₂ +H ₂ O	5.0-11	0.0	900	
R30	HC2+O → RO ₂ +HO	1.6-11	0.0	2000	
<u>Reactions of HC4:</u>					
R31	HC4+HO → RCO ₃ +H ₂ O	8.0-12	0.0	0	
R32	HC4+HO → CO+HO ₂ +H ₂ O	7.79-12	0.0	150	
R33	HC4+NO ₃ → RCO ₃ +HNO ₃	3.0-15	0.0	200	
<u>Reactions of HC3:</u>					
R34	HC3+HO → BRO2OHMH	4.0-12	0.0	0	4
R35	HC3+HO → HO ₂ +products	2.4-12	0.0	0	4

Table 1: Chemistry (continued)

		Reaction Rate Coefficients*			
No.	Reaction	A	B	C	Notes
<u>Reaction of HC3:</u>					
R36	BR020HHH+NO → M-GLY+HO ₂ +NO ₂	2.0-10	0.0	0	4
R37	M-GLY+HO → RCO ₃ +H ₂ O+CO	1.60-11	0.0	0	4
<u>Reactions of organic radicals:</u>					
R38	RCO ₃ +HO ₂ → peroxide	6.0-12	0.0	0	
R39	RCO ₃ +NO → RO ₂ +NO ₂	2.57-12	0.0	0	
R40	RCO ₃ +NO ₂ → PAN	1.36-12	0.0	0	
R41	PAN → RCO ₃ +NO ₂	7.9+14	0.0	12516	
R42	RO ₂ +NO → RO+NO ₂	7.0-12	0.0	0	
R43	RO ₂ +HO ₂ → peroxide+O ₂	2.7-12	0.0	0	
R44	RO ₂ +RO ₂ → RO+RO+O ₂	4.0-13	0.0	0	
R45	RO ₂ +O ₃ → RO+O ₂	1.1-14	0.0	580	
R46	RO+O ₂ → HO ₂ +HC1	5.0-13	0.0	2000	
R47	RO+NO ₂ → nitrate	1.0-11	0.0	0	
<u>Photolysis reactions:</u>					
J1	NO ₂ → NO+O	9.44-3			5
J2	O ₃ → O+O ₂	5.18-4			5
J3	O ₃ → O ₂ +2HO	2.69-6			5,6
J4	HNO ₂ → HO+NO	2.12-3			5
J5	H ₂ O ₂ → HO+HO	1.18-5			5

Table 1: Chemistry (continued)

No.	Reaction	Reaction Rate Coefficients*			Notes
		A	B	C	
<u>Photolysis Reactions:</u>					
J6	NO ₃ → NO ₂ +O	1.80-1			5
J7	NO ₃ → NO+O ₂	2.20-2			5
J8	N ₂ O ₅ → NO ₂ +NO ₂ +O	3.88-8			5
J9	HC4 → CO+H ₂	1.48-5			5,7
J10	HC4 → CO+HO ₂ +HO ₂	1.21-5			5,7
J11	HC4 → CO+RO ₂ +HO ₂	1.21-5			5,7
J12	M-GLY → HO ₂ +RCO ₃ +CO	4.77-4			5.8

*Rate = $A \times T^B \times e^{-C/T}$ in $\text{cm}^3 \text{sec}^{-1}$ for 2-body reactions or $\text{cm}^6 \text{sec}^{-1}$ for 3-body reactions. Thermal decomposition rates and photolysis rates are in sec^{-1} .

*Notation: $5.58-29 = 5.58 \times 10^{-29}$.

Notes:

1. Based on recommendations in DeMore et al. (1981).
2. This reaction proceeds both heterogeneously and homogeneously. Morris and Niki (1973) established an upper limit for this reaction of $1.0 \times 10^{-20} \text{ cm}^3 \text{sec}^{-1}$. The choice used here is consistent with the interpretation of NO_3 removal seen in the atmosphere by Platt et al. (1980).
3. Based on recommendations in WMO (1981).
4. Based on reaction mechanism "A" of Atkinson et al. (1980). See text.
5. Photolysis rate constants were calculated using the absorption cross sections recommended in Hudson and Reed (1979) and assumed an overhead abundance of O_3 of $8.202 \times 10^{18} / \text{cm}^2$. The values reported here are appropriate for noon at the latitude of San Francisco (37.75°N) on September 29. In LIRAQ all photolysis rates may be further reduced by a "cloud factor" that simulates absorption due to clouds and aerosols.

6. This value assumes an H_2O concentration of $2.94 \times 10^{17} \text{ cm}^{-3}$.
7. The photolysis rates J9 and J10 for HC4 are equal to one-half the values calculated for HCHO. The rate of photolysis of CH_3CHO was assumed to equal the rate calculated for $\text{HCHO} \rightarrow \text{HCO} + \text{H}$, and then halved for implementation in LIRAQ as J11.
8. Taken as 4.5% of the NO_2 photolysis rate, as suggested by the study of Darnall et al. (1979). We had originally used 15% of the NO_2 rate constant for this reaction, in accord with the choice of Atkinson et al. (1980). Changing this rate in LIRAQ for the September 29, 1978 simulation, had little effect on results. The effects are larger in smog chamber simulations.

Table 2. Photolysis rate constants used in smog chamber simulations.

Photolysis Reactions:

(1) $\text{NO}_2 + \text{h}\nu \rightarrow \text{NO} + \text{O}$	(7) $\text{H}_2\text{O}_2 + \text{h}\nu \rightarrow \text{HO} + \text{HO}$
(2) $\text{O}_3 + \text{h}\nu \rightarrow \text{O}({}^1\text{D}) + \text{O}_2$	(8) $\text{HONO} + \text{h}\nu \rightarrow \text{HO} + \text{NO}$
(3) $\text{O}_3 + \text{h}\nu \rightarrow \text{O}({}^3\text{P}) + \text{O}_2$	(9) $\text{CH}_3\text{COCHO} + \text{h}\nu \rightarrow \text{CH}_3\text{CO} + \text{HCO}$
(4) $\text{HCHO} + \text{h}\nu \rightarrow \text{HCO} + \text{H}$	(10) $\text{NO}_3 + \text{h}\nu \rightarrow \text{NO} + \text{O}_2$
(5) $\text{HCHO} + \text{h}\nu \rightarrow \text{H}_2 + \text{CO}$	(11) $\text{NO}_3 + \text{h}\nu \rightarrow \text{NO}_2 + \text{O}$
(6) $\text{CH}_3\text{CHO} + \text{h}\nu \rightarrow \text{CH}_3 + \text{CHO}$	

Author	Photolysis rate constant (sec^{-1})										
	1	2	3	4 ²	5 ²	6 ²	7	8	9	10	11
This work	5.0-3 ¹	1.6-5	2.7-4	1.3-5	1.6-5	1.3-5	6.2-6	1.1-3	2.3-4	1.2-2	9.5-2
Carter et al.(1979)	5.0-3	4.7-5	1.0-4	7.5-6	not given	4.2-6	1.4-5	1.5-3	6.5-4	1.3-2	3.5-2
Whitten et al.(1980) ³	5.0-3	1.2-5	1.5-4	1.7-5	1.7-5	2.5-6	6.0-6	1.4-3	1.8-4	4.0-2	9.9-2
Atkinson et al.(1980)	6.6-3	9.8-6	2.4-4	1.5-5	4.1-5	not given	4.7-6	1.1-3	1.0-3	2.8-2	7.4-2
Atkinson, scaled ⁴	5.0-3	7.4-6	1.8-4	1.1-5	3.1-5		3.6-6	8.3-4	7.6-4	2.1-2	5.6-2

Notes:

1. Notation: 5.0-3 = 5.0×10^{-3}
2. This table lists the rates for these reactions as if HCHO and CH₃CHO are treated separately. When they are lumped together as HC4, these rates are divided by 2.
3. Whitten et al. (1980) used different photolysis rate coefficients for different experiments. The ones shown here are those given for EC-257 (a propene/NO_x experiment), and are generally consistent with rates used for other experiments. The glyoxal rate coefficient (reaction (9)) was set to 0.036 times the rate for NO₂ photolysis as suggested for use in their carbon-bond mechanism. The photolysis rates for NO₃ were taken from Table 1 (page 21). This rate seems to have been used for all experiment simulations in that work regardless of changes in the NO₂ photolysis rate.
4. Since Atkinson et al. (1980) only give rates consistent with $J_{\text{NO}_2} = 6.6 \times 10^{-3} \text{ sec}^{-1}$, we scaled these by $5.0 \times 10^{-3} / 6.6 \times 10^{-3}$ to obtain rates consistent with the NO₂ photolysis rates for the seven-hydrocarbon/NO_x experiments.

Table 3. Initial conditions for the seven-hydrocarbon/NO_x experiments as given in Pitts et al. (1979)

Experiment No.	Initial Concentration (ppm)											
	NO	NO ₂	Ethene	Propene	t-2- Butene	n- Butane	2,3- DMB	Toluene	m- Xylene	HCHO	CH ₃ CHO	Total HC (ppmC)
EC-231	0.440	0.052	1.051	0.108	0.055	1.130	0.715	0.121	0.108	0.020	0.000	13.19
EC-232	0.469	0.024	0.258	0.051	0.026	1.102	0.612	0.032	0.029	0.009	0.002	9.32
EC-233	0.096	0.007	0.260	0.051	0.025	1.085	0.648	0.034	0.033	0.004	0.001	9.51
EC-237	0.377	0.106	0.875	0.100	0.005	1.025	0.463	0.086	0.091	0.000	0.001	10.28
EC-238	0.718	0.234	0.982	0.093	0.047	0.966	0.420	0.083	0.084	0.026	0.001	10.10
EC-241	0.379	0.110	0.484	0.045	0.024	0.464	0.211	0.040	0.044	0.018	0.001	4.97
EC-242	0.377	0.125	2.014	0.109	0.108	0.558	0.203	0.306	0.306	0.028	0.002	12.86
EC-243	0.366	0.115	1.939	0.109	0.110	0.568	0.084	0.155	0.154	0.000	0.001	9.74
EC-245	0.743	0.259	2.055	0.104	0.102	0.534	0.185	0.321	0.317	0.016	0.000	12.88
Measured**	0.19	0.12										1.80

*2,3-DMB = 2,3-Dimethylbutane

**Average concentration measured between 6:00 a.m. and 9:00 a.m. on September 29, 1978 in San Francisco

Table 4: Reactivity weighted initial conditions used for simulation of the seven-hydrocarbon/NO_x smog chamber experiments.

	NMHC/NO _x	Total NMHC	Initial concentration* (percent of total HC)			
	(ppm/ppm)	(ppm)	HC1	HC2	HC3	HC4
EC-231	7.09	3.489	20.8	59.8	19.0	0.5
EC-232	4.76	2.346	10.2	81.8	7.5	0.4
EC-233	22.98	2.367	9.5	82.3	8.0	0.2
EC-237	5.82	2.810	22.3	58.4	19.3	0.0
EC-238	2.84	2.707	24.2	56.3	18.6	0.9
EC-241	2.75	1.346	24.1	55.3	19.3	1.3
EC-242	7.96	3.995	32.6	20.8	46.0	0.7
EC-243	5.99	2.879	44.2	23.6	32.2	0.0
EC-245	3.99	3.994	32.4	19.5	47.7	0.4
measured**	1.43	0.45	29.4 ⁺	57.2 ⁺	10.9 ⁺	2.4 ⁺

*HC1 = alkenes; HC2 = alkanes; HC3 = aromatics; HC4 = aldehydes and ketones

**Average concentration measured between 6:00 a.m. and 9:00 a.m. on September 29, 1978 in San Francisco. The conversion from ppmC to ppm assumed a mean carbon chain length of 4.

⁺The percentages given here refer to the reactivity weighted emissions for the entire region modeled by LIRAQ. The reactivity weighted proportions of alkenes, alkanes, and aromatics determined for 6:00 a.m.-9:00 a.m. in San Francisco on October 8, 1980 were 10%, 53%, and 37%, respectively. Total non-methane hydrocarbons as measured by Koppe (1981) were only 0.135 ppm on that day.

Table 5: Effects of chemistry changes in simulations of EC-11.

Change:	maximum O ₃ (ppm)
LIRAQ-2S chemistry	.26
1. Increase rate for HO ₂ +NO from 3.09x10 ⁻¹² to 8.10x10 ⁻¹²	.34
2. Increase rate for RCO ₃ +NO ₂ from 2.7x10 ⁻¹³ to 1.30x10 ⁻¹²	.33
3. Increase rate for HO ₂ +NO ₂ from 2x10 ⁻¹⁴ to 2x10 ⁻¹² and include thermal decomposition of HNO ₄	.37
4. Decrease thermal decomposition rate for N ₂ O ₅ from .203 to .034	.32
5. Increase rate for NO ₃ +NO from 8.7x10 ⁻¹² to 2.0x10 ⁻¹¹	.325
6. Increase rate for HO+CO from 1.4x10 ⁻¹³ to 2.7x10 ⁻¹³	.345
7. Change products of HCl+O ₃ from HO ₂ +HC ₄ +RO to HC ₄ +0.5HO ₂	.27
8. Increase rate of HC ₄ +HO → RCO ₃ +H ₂ O from 4.72x10 ⁻¹² to 8.0x10 ⁻¹²	.24
9. Increase rate of RO ₂ +NO from 1.48x10 ⁻¹² to 7.0x10 ⁻¹²	.26
10. Increase rate of RO+NO ₂ from 2.0x10 ⁻¹² to 1.0x10 ⁻¹¹	.27
11. Increase rate of HO ₂ +HO ₂ from 3.26x10 ⁻¹² to 5.22x10 ⁻¹²	.265
12. Increase rate of HO ₂ +RO ₂ from 2.7x10 ⁻¹² to 8.0x10 ⁻¹²	.255
13. Include photolysis of RO ₂ H	.255
14. Increase RO ₂ +RO ₂ from 2.7x10 ⁻¹³ to 1.0x10 ⁻¹²	.255
15. Set rates for HO ₂ +HC ₄ and RO ₂ +HC ₄ to zero	.255
16. Decrease rate for HC ₄ +O from 1.64x10 ⁻¹³ to 1.91x10 ⁻¹⁴	.255
17. Increase rate for HC ₄ +NO ₃ from 1.5x10 ⁻¹⁶ to 1.5x10 ⁻¹⁵	.255
18. Increase rate for HO+HO ₂ from 2.0x10 ⁻¹¹ to 1.0x10 ⁻¹⁰	.255
19. Decrease rate for HO+HC ₄ → HO ₂ +CO+H ₂ O from 9.4x10 ⁻¹² to 4.7x10 ⁻¹²	.245

Table 5: Effects of chemistry changes in simulations of EC-11 (continued).

Change:	maximum O ₃ (ppm)
20. Change products of $\text{HCl} + \text{NO}_3$ from $\text{NO}_2 + \text{HC}_2$ to RO_2 ; change rate from 4.9×10^{-15} to 9.8×10^{-15}	.25
21. Set rate for $\text{HCl} + \text{HO} \rightarrow \text{RO}_2 + \text{H}_2$ to zero	.225
22. Set rate for $\text{RO} + \text{NO}$ to zero	.225
23. Change products of $\text{HC}_4 + \text{hv} \rightarrow \text{RCO}_3 + \text{HO}_2$ to $0.5(\text{RO}_2 + \text{HO}_2 + \text{CO}) + 0.5(\text{HO}_2 + \text{HO}_2 + \text{CO})$	.275
24. Add photolysis of RNO_2 , NO_3 , and N_2O_5	.275
25. Add thermal decomposition of PAN	.29
26. Add reactions for $\text{HO} + \text{H}_2\text{O}_2$, $\text{HO} + \text{HNO}_2$, and $\text{RCO}_3 + \text{HO}_2$	.29
27. Add reaction for $\text{RO}_2 + \text{O}_3$	.29
28. Decrease rate for $\text{NO}_3 + \text{NO}_2$ from 3.8×10^{-12} to 7.5×10^{-13} and decrease rate for $\text{O} + \text{NO}_2 \rightarrow \text{NO}_3$ from 9.4×10^{-12} to 1.5×10^{-12}	.32
29. Decrease rate for $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ from 5.5×10^{-21} to 3.0×10^{-21}	.32
30. Increase rate for $\text{HO}_2 + \text{RO}_2$ from 2.7×10^{-12} to 8.0×10^{-12} and set rate for $\text{HC}_4 + \text{O}$ to zero	.33
31. Increase rate for $\text{HO} + \text{O}_3$ from 5.88×10^{-14} to 7.14×10^{-14}	.33
32. Increase rate for $\text{HO}_2 + \text{O}_3$ from 1.07×10^{-15} to 1.65×10^{-15}	.325

Table 6: Boundary conditions used in the simulations for September 29, 1978 and September 12, 1979.

Specie	C ₀ (ppm)					ρ		Notes
	West	East	South	North	Top	horizontal	vertical	
HC1	3.0-3 ¹	1.0-2	1.0-2	1.0-2	1.0-2	0.3	0.1	
HC2	5.0-2	5.0-2	5.0-2	5.0-2	5.0-2	0.3	0.1	
HC3	1.0-2	1.0-2	1.0-2	1.0-2	1.0-2	0.3	0.1	
HC4	1.0-3	1.0-3	1.0-3	1.0-3	1.0-3	0.3	0.1	
HONO	4.0-8	4.0-8	4.0-8	4.0-8	4.0-8	0.3	0.1	
PAN	1.0-4	1.0-4	1.0-4	1.0-4	1.0-4	0.3	0.1	
H ₂ O ₂	4.0-8	4.0-8	4.0-8	4.0-8	4.0-8	0.3	0.1	
NO	8.0-5	4.0-3	4.0-3	4.0-3	8.0-5	0.3	0.1	2
NO ₂	8.0-5	4.0-3	4.0-3	4.0-3	8.0-5	0.3	0.1	
O ₃	1.0-2	1.0-2	1.0-2	1.0-2	1.0-1	0.3	0.85	3
CO	1.0	1.0	1.0	1.0	1.0	0.3	0.1	
M-GLY	4.0-8	4.0-8	4.0-8	4.0-8	4.0-8	0.3	0.1	
HO ₂ NO ₂	4.0-6	4.0-6	4.0-6	4.0-6	4.0-6	0.3	0.1	4
RO ₂	4.0-7	4.0-7	4.0-7	4.0-7	4.0-7	0.3	0.1	4
BRO ₂ OH ₂	4.0-8	4.0-8	4.0-8	4.0-8	4.0-8	0.3	0.1	5
NO ₃	4.0-8	4.0-8	4.0-8	4.0-8	4.0-8	0.3	0.1	5
N ₂ O ₅	4.0-8	4.0-8	4.0-8	4.0-8	4.0-8	0.3	0.1	5
RCO ₃	4.0-8	4.0-8	4.0-8	4.0-8	4.0-8	0.3	0.1	4
HO ₂	4.0-7	4.0-7	4.0-7	4.0-7	4.0-7	0.3	0.1	5

Table 6: Boundary conditions used in the simulations for
September 29, 1978 and September 12, 1979. (continued)

Notes:

1. Notation: $3.0-3 = 3.0 \times 10^{-3}$.
2. The boundary conditions used at night were 1/10 times those listed here.
3. The boundary conditions used at night were 1/10 times those listed here except for the top boundary condition which was 0.025 ppm at night.
4. The boundary conditions used at night were 10^{-2} times those listed here.
5. The boundary conditions used at night were 10^{-3} times those listed here.

Table 7a. Tests made for September 29, 1978

RUN 081481:	Boundary conditions as in Table 6. Initial conditions as interpolated by LIRAQ from measurements given on QICON file. NO ₂ on QICON file was 0.5 times value actually measured. QTRAN 81.1 was used.
RUN 092681:	Like RUN 081481 except QTRAN81.10 was used.
RUN 092081:	Like RUN 081481 except QTRAN81.12 was used.
RUN 091981:	Like RUN 081481 except QTRAN81.12 was used and initial NO field was restricted by adding small values at added UTM sites on QICON file.
RUN 091781:	Like RUN 081481 except QTRAN81.12 was used, the initial NO field was restricted as in RUN 091981 and C ₀ for O ₃ at the top was set to 0.05 ppm.
RUN 100981:	Like RUN 081481 except the emissions files did not include biogenic emissions.
RUN 101081:	Like RUN 081481 except initial NO ₂ concentrations on QICON were multiplied by 2 to be consistent with the actual measured values.
RUN 102381:	Like RUN 101081 except initial NO field was restricted as in RUN 091981.
RUN 102381:	Like RUN 101081 except the deposition velocity for O ₃ was set to 0.5 cm sec ⁻¹ . (Normally it is set to 0.66 cm sec ⁻¹ .)

Table 7b. Test made for September 12, 1979

RUN 092581:	Like RUN 081481 except QTRAN81.9 was used.
RUN 100981:	Like RUN 092581 except QTRAN81.13 was used.
RUN 100481:	Like RUN 092581 except western boundary conditions were increased as follows:
HCl:	1.0×10^{-2} ppm day; 1.0×10^{-2} ppm night
NO:	4.0×10^{-3} ppm day; 4.0×10^{-4} ppm night
NO ₂ :	1.0×10^{-2} ppm day; 4.0×10^{-3} ppm night
O ₃ :	5.0×10^{-2} ppm day
CO:	2.0 ppm day; 2.0 ppm night

Table 8a. Statistics for the tests described in Table 7a.

Specie	Statistic	Run 081481	Run 092681	Run 092081	Run 091981	Run 091781	Run 100981	Run 101081	Run 102381	Run 102481
HC2	$\langle m \rangle / \langle D \rangle^1$	1.55	1.60	1.55	1.55	1.55	1.55	1.55	1.55	1.55
	$\langle \text{RMS} \rangle^2 (\text{ppm})$	0.20	0.21	0.21	0.21	0.21	0.20	0.20	0.20	0.20
	R^3	0.62	0.55	0.57	0.57	0.57	0.62	0.62	0.62	0.62
NO ₂	$\langle m \rangle / \langle D \rangle$	0.80	0.76	0.75	0.74	0.71	0.79	0.89	0.91	0.91
	$\langle \text{RMS} \rangle (\text{pphm})$	3.7	3.1	3.0	2.9	2.7	3.6	4.3	3.5	3.5
	R	0.72	0.69	0.66	0.67	0.68	0.71	0.68	0.71	0.71
NO	$\langle m \rangle / \langle D \rangle$	1.28	1.41	1.37	1.21	1.27	1.33	1.33	1.16	1.16
	$\langle \text{RMS} \rangle (\text{pphm})$	10.0	9.8	9.7	9.5	9.5	10.0	10.0	9.7	9.7
	R	0.56	0.57	0.58	0.52	0.53	0.54	0.55	0.52	0.52
O ₃	$\langle m \rangle / \langle D \rangle$	0.93	0.73	0.73	0.80	0.73	0.80	0.85	0.95	1.05
	$\langle \text{RMS} \rangle (\text{pphm})$	2.4	2.5	2.5	2.5	2.5	2.5	2.4	2.5	2.6
	R	0.82	0.84	0.84	0.83	0.84	0.81	0.82	0.81	0.81
	maximum surface concentration (pphm)	17.4	14.0	14.0	15.6	15.1	15.3	15.7	18.6	20.2
CO	$\langle m \rangle / \langle D \rangle$	0.89	0.89	0.88	0.88	0.89	0.89	0.89	0.89	0.89
	$\langle \text{RMS} \rangle (\text{ppm})$	1.90	1.90	1.90	2.00	2.00	1.90	1.90	1.90	1.90
	R	0.65	0.64	0.65	0.64	0.64	0.65	0.65	0.65	0.65

Notes:

1. " $\langle m \rangle / \langle D \rangle$ " is the calculated mean concentration divided by the observed mean concentration using only grid squares at which observations exist.
2. " $\langle \text{RMS} \rangle$ " is the root mean square deviation between model and observed station records.
3. "R" is the correlation coefficient between model and observation based on all of the hourly observations.

- Fig. 1 Simulation of smog chamber experiment EC231 using the measured NO_2 photolysis rate. The other photolysis rates were determined by ratio from values calculated for local noon conditions in San Francisco on September 29 (see Table 2).
- Fig. 2 Simulation of smog chamber experiment EC231 using the photolysis rates assigned by Carter et al. (1980) (see Table 2).
- Fig. 3 Simulation of smog chamber experiment EC231 using the photolysis rates assigned by Whitten et al. (1980) (see Table 2).
- Fig. 4 Simulation of smog chamber experiment EC231 using the photolysis rates assigned by Aktinson et al. (1980), after scaling by ratio to the measured NO_2 photolysis rate (see Table 2).
- Fig. 5 Simulation of smog chamber experiment EC231 using the mechanism of Table 1 with photolysis rates as specified in Table 2 and with a source of radicals (HO) from the chamber walls equal to 0.4 ppb-min^{-1} .
- Fig. 6 Simulation of smog chamber experiment EC231 using the mechanism of Table 1 with photolysis rates as specified in Table 2 and with an initial concentration of HNO_2 equal to $2.21 \times 10^{11} \text{ cm}^{-3}$.
- Fig. 7 Simulation of smog chamber experiment EC231 using the mechanism of Table 1 with photolysis rates as specified in Table 2. A radical source from the chamber walls of 0.4 ppb min^{-1} is assumed and the initial concentration of HNO_2 was set equal to $2.21 \times 10^{11} \text{ cm}^{-3}$.
- Fig. 8 Simulation of smog chamber experiment EC231 using the mechanism of Table 1 and photolysis rates from Table 2. (Same as Figure 1.)
- Fig. 9 Simulation of smog chamber experiment EC232 using the mechanism of Table 1 and photolysis rates from Table 2.

- Fig. 10 Simulation of smog chamber experiment EC233 using the mechanism of Table 1 and photolysis rates from Table 2.
- Fig. 11 Simulation of smog chamber experiment EC237 using the mechanism of Table 1 and photolysis rates from Table 2.
- Fig. 12 Simulation of smog chamber experiment EC238 using the mechanism of Table 1 and photolysis rates from Table 2.
- Fig. 13 Simulation of smog chamber experiment EC241 using the mechanism of Table 1 and photolysis rates from Table 2.
- Fig. 14 Simulation of smog chamber experiment EC242 using the mechanism of Table 1 and photolysis rates from Table 2.
- Fig. 15 Simulation of smog chamber experiment EC243 using the mechanism of Table 1 and photolysis rates from Table 2.
- Fig. 16 Simulation of smog chamber experiment EC245 using the mechanism of Table 1 and photolysis rates from Table 2.
- Fig. 17 Simulation of smog chamber experiment EC245 using the mechanism described in Duewer et al. (1980). Toluene and m-xylene have been apportioned as 65% HC2 and 35% HCl with reactivity weightings of 0.2 and 1.0 relative to propene, respectively. The measured NO₂ photolysis rate was used. The other photolysis rates were determined by ratio from values calculated for local noon conditions in San Francisco on September 29, as computed in LIRAQ-2S.
- Fig. 18 Simulation of smog chamber experiment EC245 using the mechanism of Table 1, but treating toluene and m-xylene as 65% HC2 and 35% HCl with reactivity weightings of 0.2 and 1.0 relative to propene, respectively.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Fig. 15

Fig. 16

Fig. 17

Fig. 18

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California 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 products, 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 the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government thereof, and shall not be used for advertising or product endorsement purposes.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$: Microfiche \$3.50

Page Range	Domestic Price	Page Range	Domestic Price
001-025	\$ 5.00	326-350	\$ 18.00
026-050	6.00	351-375	19.00
051-075	7.00	376-400	20.00
076-100	8.00	401-425	21.00
101-125	9.00	426-450	22.00
126-150	10.00	451-475	23.00
151-175	11.00	476-500	24.00
176-200	12.00	501-525	25.00
201-225	13.00	526-550	26.00
226-250	14.00	551-525	27.00
251-275	15.00	526-550	28.00
276-300	16.00	601-up ¹	
301-325	17.00		

¹ Add 2.00 for each additional 25 page increment from 601 pages up.

Technical Information Department • Lawrence Livermore Laboratory
University of California • Livermore, California 94550