Incorporation of Chlorine Reactions into the Carbon Bond IV Mechanism: Mechanism Updates and Preliminary Performance Evaluation

Report on Contract 9880077600-18 between
The University of Texas and the Texas Natural Resource Conservation Commission

Submitted by

Paul L. Tanaka
David T. Allen

Department of Chemical Engineering and
Center for Energy and Environmental Resources
The University of Texas
Austin, Texas 78712

512-471-0049
allen@che.utexas.edu

July 9, 2001

Summary

In previous work for the Texas Natural Resource Conservation Commission (Contract 98-80076000, *Impact of Molecular Chlorine Emissions on Ozone Formation in Southeast Texas*), the University of Texas developed a simplified mechanism for incorporating chlorine reactions in photochemical modeling simulations. This report updates that mechanism, The updated mechanism is summarized; a detailed description of each reaction in the mechanism is provided; the methods that were used to evaluate the rate parameters and the differences between the modified mechanism and the original mechanism (if any) are described, and, the effect of omitting certain classes of reactions on ozone, hydrocarbon and NOx concentrations is assessed.

Background and Overview

Previous work (Tanaka, et al., 2000) has demonstrated that emissions of molecular chlorine, Cl_2, may have a significant impact on the formation of ozone in the Houston area. The reactions of molecular chlorine (Cl_2), and chlorine radical ($Cl\cdot$) are not accounted for, however, in the chemical mechanism (CB-IV) commonly used in regional photochemical modeling (for an analysis of the CB-IV mechanism, see Adelman, 1999).

In previous work for the Texas Natural Resource Conservation Commission, the University of Texas modified the CB-IV mechanism to account for the dominant features of the urban, tropospheric chemistry of molecular chlorine. This report updates that mechanism. The updated mechanism is summarized below; the summary is followed by a detailed description of each reaction in the mechanism, the methods that were used to evaluate the rate parameters, and the differences between the modified mechanism and the original mechanism (if any). Finally, the effect of omitting certain classes of reactions on ozone, hydrocarbon and NOx concentrations is assessed.

Summary of Mechanism

- The proposed mechanism is intended to be compatible with the CB-IV mechanism. It employs lumped chemical species used in the CB-IV mechanism and eleven new chemical species (two chlorinated isoprene reaction products, two chlorinated 1,3-butadiene reaction products, and one each for 1,3-butadiene, molecular chlorine, atomic chlorine, hydrochloric acid, hypochlorous acid [HOCl], formyl chloride [HCOCl], and chlorine oxide [ClO]). Also provided are suggested rate parameters reported either as ratios (rate of the reaction divided by the rate of the analogous or similar hydroxyl radical reaction employed in the CB-IV mechanism) or a temperature dependent expression. This report does not provide a tutorial on the CB-IV mechanism, although a description of all of the CB-IV mechanism terms cited in this document are given in Table 1. An analysis of the CB-IV mechanism has been performed elsewhere by Adelman (1999).

- The proposed mechanism incorporates chlorine and HOCl photolysis, subsequent reactions of atomic chlorine with major hydrocarbon classes, and two unique reaction product markers arising from the reaction of Cl with isoprene and 1,3-butadiene. Other reactions, such as the reactions of chlorine with nitrogen oxides and chlorinated radical termination reactions are not currently included in the mechanism. An assessment of the importance of these reactions is provided at the end of this report. The number of reactions used to describe the chlorine chemistry was intentionally kept small to keep computational requirements to a minimum. Despite the small number of reactions, this mechanism should capture the major features of chlorine reactions in Houston. Because concentrations of anthropogenic and biogenic hydrocarbons are high relative to ozone in Houston, the reactions of chlorine with ozone and nitrogen oxides are likely to be less important than reactions with hydrocarbons. If modeling with this simplified mechanism confirms the importance of chlorine chemistry, it may be appropriate to include additional reactions.

The proposed, 13-step mechanism consists of the following reactions:

1. Cl2 = 2Cl

2. HOCl = OH + Cl

3. Cl + PAR = HCl + 0.87*XO2 + 0.13*XO2N + 0.11*HO2 + 0.11*RCHO + 0.76*ROR – 0.11 PAR

4. Cl + OLE = FMCL + RCHO + 2 XO2 + HO2 – 1*PAR

5. Cl = HCl + XO_2 + FORM + HO_2

6. Cl + ETH = FORM + 2 XO_2 + FMCL + HO_2

7. Cl + ISOP = 0.15 HCl + XO2 + HO2 + 0.28 ICL1

8. OH + ICL1 = ICL2

9. Cl + BUTA = XO2 + HO2 + 0.70 BCL1

10. OH + BCL1 = BCL2

11. Cl + O3 = ClO + O2

12. ClO + NO = Cl + NO2

13. ClO + HO2 = HOCl + O2

A description of these reactions, suggested rate parameters, and the rationale for excluding other classes of reactions is given below.

Photolysis of Cl_2 (revised):

The rate of photolysis for Cl_2 in the modified mechanism is referenced to the rate constant for NO_2 photolysis, even though the rate of Cl_2 photolysis can be explicitly calculated. This was also done in the original mechanism to simplify execution and minimize additional calculational complexity in the modified mechanism. The rate constant for photolysis of Cl_2 can be represented as follows:

$$k_{p,Cl2} = 0.264*k_{p,NO2}$$

where $k_{p,x}$ denotes the rate constant for photolysis of species X in s^{-1}. The rate was determined by adding the absorption cross-section data provided in Appendix A to the Tropospheric Ultraviolet and Visible Model (TUV) [NCAR, 2001] to yield photolysis rates for Cl_2 and NO_2. The suggested rate expression is the average ratio of Cl_2 photolysis to NO_2 photolysis for a typical series of conditions (Yarwood, 2001):

Zenith angles: 0, 10, 20, 30, 40, 50, 60, 70, 78, 86 degrees
Elevation: 640 m above ground
Ozone column: 300 Dobson Units
UV surface albedo: 0.06
Optical depth due to haze: 0.1

The TUV model uses the following general expression to calculate the rate of photolysis of a species as follows:

$$k_{p,x}(s^{-1}) = \sum_{l=290nm}^{l_i} s(l) f(l) J(l)$$

where,

$\sigma(\lambda)$ = Absorption cross-section (cm^2)
$\phi(\lambda)$ = Quantum yield
$J(\lambda)$ = Actinic flux of photons ($cm^{-2}s^{-1}$)
λ_i = Threshold wavelength for photolysis to occur (nm)

Values of $J(\lambda)$ were calculated by the TUV model for the typical conditions above. Tabulated values of $\sigma(\lambda)$ were obtained from Atkinson (1997a). The quantum yield for Cl_2 photolysis is unity for all wavelengths of concern (Calvert, 1966). Absorption cross-sections for Cl_2 photolysis are provided in Appendix A for reference.

The ratio of the calculated rates of photolysis of Cl_2 and NO_2 suggested for use in the actinic region 0.264.

<u>Photolysis of HOCl (new):</u>

The photolysis of HOCl was not included in the original mechanism. However, it has since been suggested that volatilization of HOCl from water may be a significant source of reactive chlorine in the Houston area. Therefore, this reaction has been added to the mechanism, even though it is not yet clear whether HOCl will be evolved into the gas phase from chlorinated water. The rate of photolysis for HOCl in the modified mechanism is also referenced to the photolysis rate of a separate species already contained in the CB-IV model. The surrogate species chosen is the lumped isoprene oxidation product (ISPD) which is based on acrolein photolysis (Yarwood, 2001). This surrogate provided a more stable ratio of photolysis rate for HOCl than NO_2 over the range of zenith angles stated above.

Although the rate of HOCl photolysis can be explicitly calculated, the suggested expression is simpler to execute and will minimize additional calculational complexity in the modified mechanism. The rate constant for photolysis of HOCl can be represented as follows:

$$k_{p,HOCl} = 143 * k_{p,ISPD}$$

where $k_{p,X}$ denotes the rate constant for photolysis of species X in s^{-1}.

This rate expression was derived in a manner similar to that used for deriving the rate of photolysis of Cl_2. Tabulated values of $\sigma(\lambda)$ for HOCl were obtained from DeMore (1997) and are provided in Appendix A. All other tabulated data were obtained from the same sources as cited for the photolysis of Cl_2.

Paraffins (no modifications):

As suggested from results of initial environmental chamber experiments (Oldfield and Allen, 1999; Tanaka, et al., 1999), alkanes are expected to contribute most significantly to additional ozone formation when the reactions of chlorine are included. High molecular weight (C_{6+}) alkanes have been shown to contribute very little, or even negatively to ozone formation (Carter, 1995) in the absence of chlorine.

We have observed in environmental chamber experiments that the addition of chlorine into an air mass with high concentrations of alkanes promotes the formation of ozone. This effect is particularly pronounced when the ratio of volatile organic compounds (VOCs) to nitrogen oxides (NO_x) is between 5 and 10 (parts per billion carbon per part per billion volume (ppb_c/ppb_v)).

The CB-IV mechanism currently accounts for alkane oxidation through hydrogen abstraction by hydroxyl radical. In the presence of sufficient NO_x, the resulting alkyl radical will continue to react to convert nitrogen oxide (NO) to NO_2 and produce peroxyl radicals (HO_2) and aldehydes.

According to known reaction mechanisms (Atkinson, 1997b), chlorine radicals initiate oxidation of alkanes by abstraction of hydrogen, in a pathway similar to the reactions of hydroxyl radicals. To incorporate chlorine-alkane chemistry, the abstraction of hydrogen from alkanes by chlorine radicals will be included. Only one additional reaction is needed to incorporate chlorine-alkane chemistry because the alkyl radical formed is the same regardless of whether it is formed through reaction of the alkane with hydroxyl or chlorine radical and because the $Cl\cdot$ is consumed to form stable HCl during this abstraction.

Because the reaction pathway is the same for alkyl radicals initially formed by either $OH\cdot$ or $Cl\cdot$, the overall product stoichiometry would also be expected to be the same for both the hydroxyl and chlorine radical initiated oxidation of alkanes. The product stoichiometries are as follows:

OH + PAR = 0.87*XO2 + 0.13*XO2N + 0.11*HO2 + 0.11*RCHO + 0.76*ROR – 0.11*PAR
Cl + PAR = HCl + 0.87*XO2 + 0.13*XO2N + 0.11*HO2 + 0.11*RCHO + 0.76*ROR – 0.11 PAR

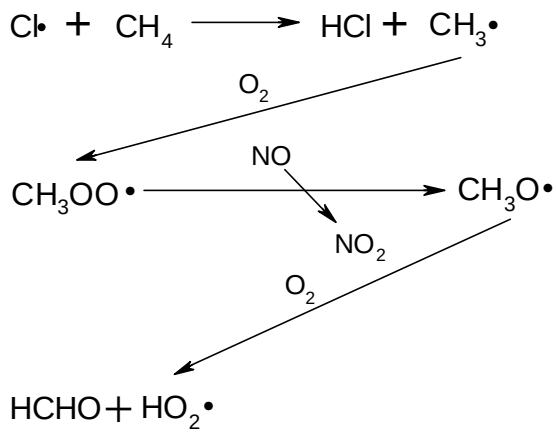
Based on the ratio of average of reaction rate constants (Atkinson, 1997b) for $Cl\cdot$ to $OH\cdot$ with 20 alkanes (Table 2) a reaction rate constant for Cl + PAR of $78*k_{OH+PAR}$ is proposed. Thus, the rate constant for reaction of $Cl\cdot$ with a paraffinic carbon can be represented as follows:

$k_{Cl,PAR} = 78*k_{OH,PAR}$

Methane (revised):

The reaction rate constant for the chlorine-methane reaction is almost two orders of magnitude greater than that of the hydroxyl radical-methane reaction. Because of this significantly higher

reactivity, we have included the methane-chlorine reaction in the proposed mechanism. The reaction kinetics are well known and the reaction mechanism proceeds as follows:



Methane is represented implicitly within the CB-IV mechanism. A global average 1.85 ppm methane is assumed and used to provide a "unimolecular" rate expression for OH. The reaction stoichiometry proposed here for chlorine radials is based on the representation of the OH-methane reaction in the current CB-IV mechanism:

$Cl = HCl + XO_2 + FORM + HO_2$

The rate constant for the reaction of chlorine radicals with methane is (Atkinson, 1999):

6.6×10^{-12} [exp(-1240/T)] cm^3 $molecule^{-1}$ s^{-1}, for $200K \leq T \leq 300K$.

Assuming the ideal gas law and a constant mixing ratio of 1.85 ppm methane, the proposed rate expression for the mechanism provided above is:

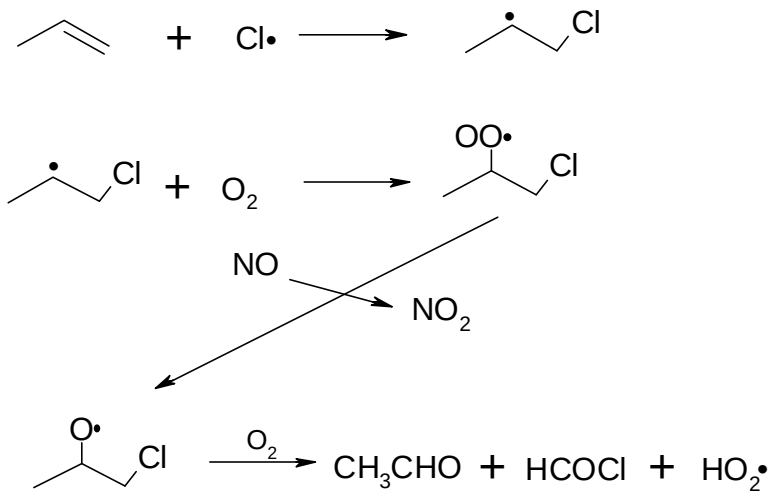
$k_{Cl,METH} = 8.95 \times 10^4/T$ [exp(-1240/T)] s^{-1}, for $200K \leq T \leq 300K$.

<u>Olefins (revised):</u>

The products of the hydroxyl radical oxidation reaction with alkenes in the CB-IV mechanism are formaldehyde, aldehydes, and HO_2 in addition to the conversion of NO to NO_2. The stoichiometry given in the CB-IV mechanism is:

$OH + OLE = FORM + RCHO + XO_2 + HO_2 - 1*PAR$

However, with the addition of chlorine, we expect a reaction path that gives the following products: HCOCl (FMCL), aldehydes, and $HO_2\cdot$ resulting from the following, generalized mechanism:



This pathway yields the following model stoichiometry:

Cl + OLE = FMCL + RCHO + 2 XO2 + HO2 – 1*PAR

Note that although formyl chloride is photolyzable in the troposphere, the lifetime of this species is more than one month against photolysis.

Based on the ratio of average reaction rates (Atkinson, 1997b) (per double bond) for Cl· to OH with 4 alkenes (Table 3), a reaction rate constant for Cl + OLE of $20*k_{OH+OLE}$ is proposed. This rate constant is slightly different than the rate constant in the original mechanism, because the original and updated mechanisms consider the rates of different olefin species. In addition to propene and 1,2-propadiene considered in the original mechanism, the update incorporates data that has since been published for 1-butene and 1-pentene. Since 1,3-butadiene, isoprene, and ethene (see below) are treated as separate species in this mechanism, the proposed rate constant omits these species in the calculation of average olefin reactivity. The revised rate constant for reaction between Cl· and an olefin bond is represented as follows:

$k_{Cl,OLE} = 20*k_{OH,OLE}$

<u>Ethene (no modifications):</u>

The reaction mechanism of the chlorine-ethene reaction is similar to the chlorine-olefin reaction above. The pathway yields the following model stoichiometry:

Cl + ETH = FORM + 2 XO_2 + FMCL + HO_2

As noted in the olefins section, although FMCL is photolyzable in the troposphere, the lifetime of this species is more than 1 month against photolysis.

Based on the ratio of reaction rate constants at 298 K for the chlorine-ethene and hydroxyl radical-ethene reactions, the proposed rate constant for the Cl + ETH reaction is 12.6 * $k_{OH.ETH}$. Therefore, the rate constant for the reaction between Cl· and ethene can be represented as follows:

$k_{Cl,ETH} = 12.6*k_{OH,ETH}$

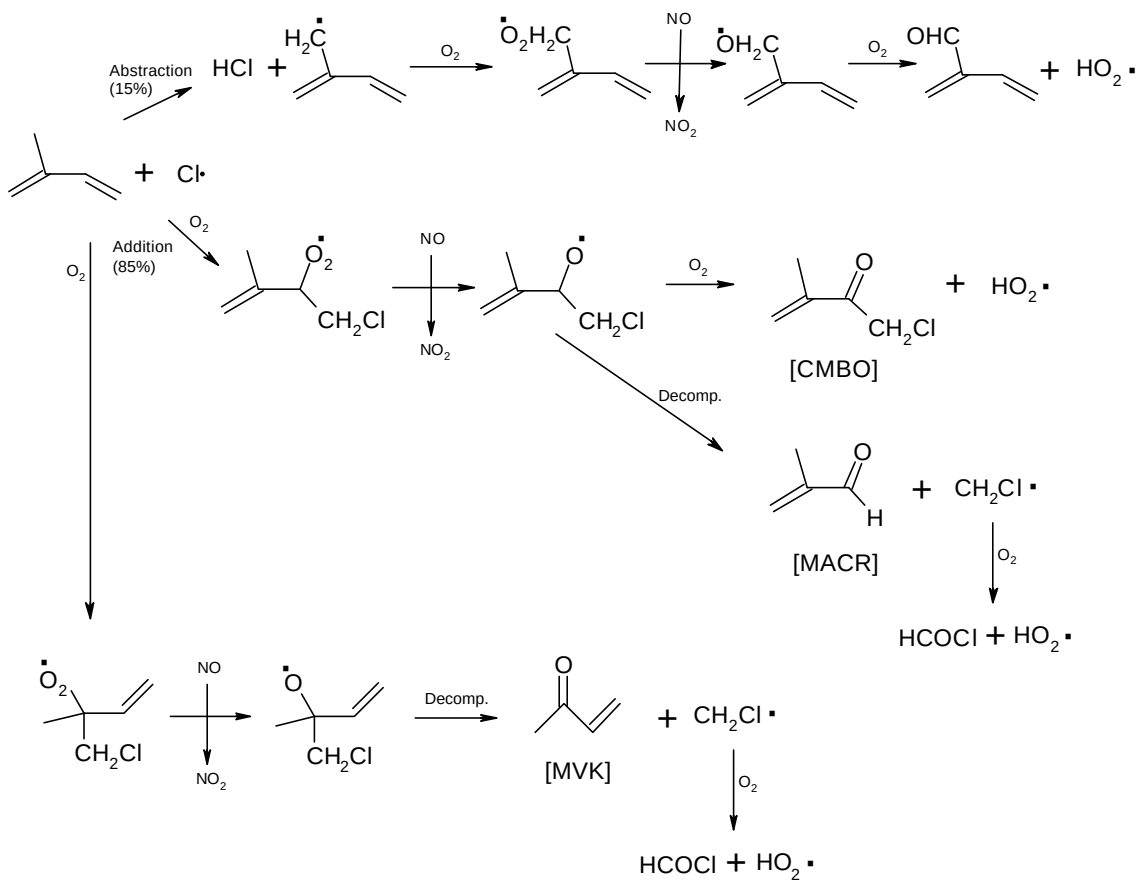
Isoprene (revised):

The primary purpose for including the isoprene-chlorine radical reaction is to track the unique marker species (1-chloro-3-methyl-3-butene-2-one [CMBO]) for this reaction. The reaction mechanism of the chlorine-isoprene reaction is very complex and is not explicitly understood in the presence of NO_x. Because CMBO (ICL1) can react with OH, the corresponding reaction has been added to account for consumption of CMBO after being produced by the Cl + ISOP reaction.

The following simplifying assumptions were made to provide a stoichiometry for the Cl + ISOP reaction. These assumptions are as follows:

- Organic nitrate formation from isoprene is ignored and
- Measurements of the rate of reaction of CMBO with OH are not available. The stated rate constant is estimated from contributions from OH addition to the olefinic bond and abstraction of the methyl and chloromethyl hydrogens. Rationale provided in Appendix B describes how this rate constant was estimated.

The reaction mechanism for Cl + ISOP is based on the work of Ragains et al. (1997) and Nordmeyer (1997) and is provided below:



This reaction pathway will lead to the following stoichiometry;

Cl + ISOP = 0.15 HCl + XO2 + HO2 + 0.28 ICL1.

Because OH can react with CMBO (ICL1), the following reaction should be added to account for consumption of ICL1 after it is produced:

OH + ICL1 = ICL2

Where ICL1 = CMBO = 1-chloro-3-methyl-3-butene-2-one and ICL2 = the reaction products of the OH+ICL1 reaction. None of the other organic products are tracked, since ambient measurements are only available for CMBO.

Based on the ratio of reaction rate constants for the chlorine-isoprene and OH + ICL1 versus hydroxyl radical-isoprene reactions, the proposed rate constants for the Cl + ISOP and OH + ICL1 reactions are 4.5 * $k_{OH,ISOP}$ and 0.19 * $k_{OH,ICL1}$, respectively. Therefore, the rate constants for the reactions for $Cl\cdot$ + isoprene and OH + CMBO (ICL1) can be represented as follows:

$k_{Cl,ISOP} = 4.5*k_{OH,ISOP}$

$k_{OH,ICL1}=0.19*k_{OH,ISOP}$

As stated above, Appendix B includes the rationale for estimating the specified rate constants.

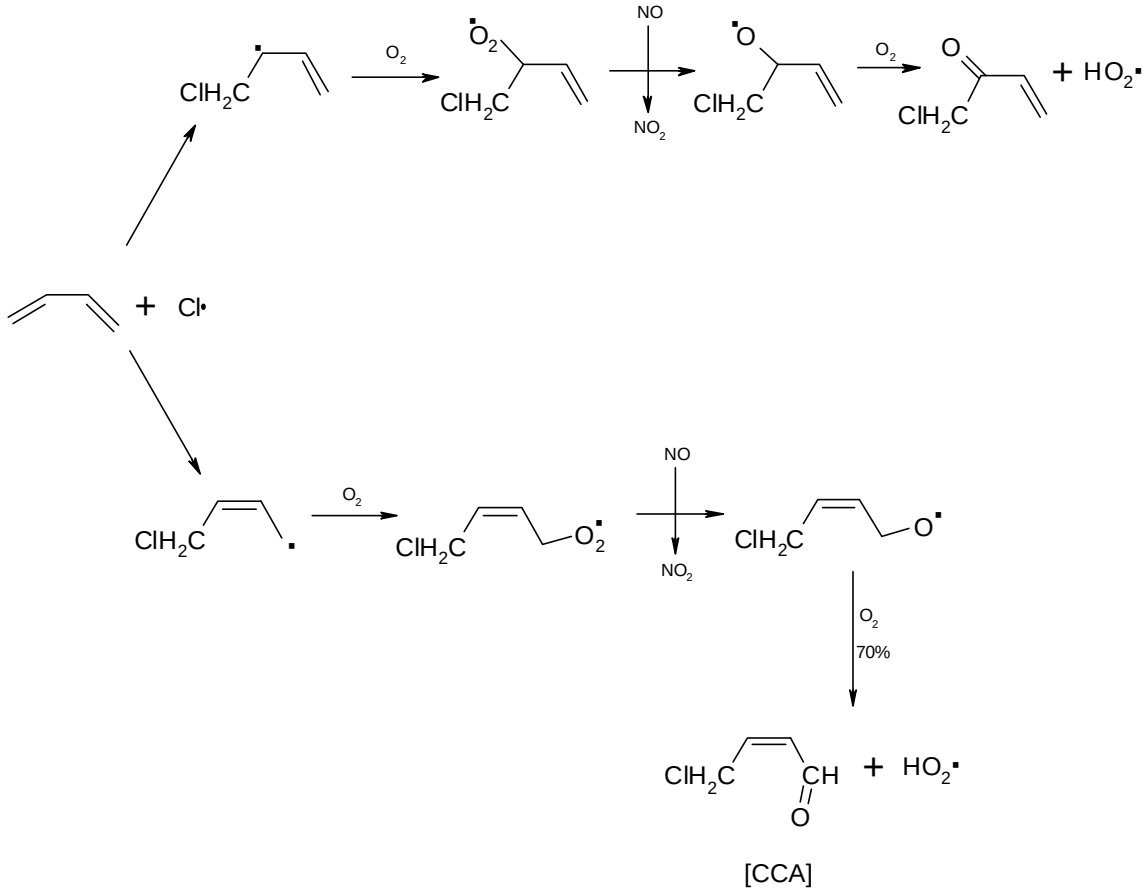
<u>1,3-Butadiene (new):</u>

The purpose for explicitly including the reaction of 1,3-Butadiene (BUTA) in this revision is because reaction with Cl yields a unique product, 4-chlorocrotonaldehyde (CCA) identified by Wang and Finlayson-Pitts (2000). In the presence of NO_x, the yield of CCA is approximately 70%. As with the isoprene+Cl marker species, CCA (BCL1) is the only organic reaction product that is retained. Because this species can react with OH, a second reaction (OH + BCL1) is added.

The following simplifying assumptions have been made:

- Organic nitrate formation from 1,3-Butadiene is ignored; and
- Measurements of the rate of reaction of 4-Chlorocrotonaldehyde with OH are not available. However, it is expected that the rate of reaction is similar to that of crotonaldehyde with OH. Therefore, the reaction rate for CCA + OH is stated as the same as that for crotonaldehyde + OH. For simplicity, the rates are presented as ratios of the OH + isoprene reaction rate at 298K.

The reaction mechanism for Cl + BUTA is based on the work of Wang and Finlayson-Pitts (2000) and is provided below:



This reaction mechanism will lead to the following stoichiometry:

Cl + BUTA = XO2 + HO2 + 0.70 BCL1

Because OH can react with CCA (BCL1), the following reaction should be added to account for consumption of BCL1 after it is produced:

OH + BCL1 = BCL2

Where BCL1 = CCA = 4-Chlorocrotonaldehyde and BCL2 = the reaction products of the OH + BCL1 reaction. As noted above, none of the other organic products are tracked for this reaction.

Based on the ratio of reaction rate constants for the chlorine-1,3-butadiene (BUTA) and OH + BCL1 versus OH + isoprene reactions, the proposed rate constants for the Cl + BUTA and OH + BCL1 reactions can be represented as follows:

$k_{Cl,BUTA}=4.2*k_{OH,ISOP}$

$k_{OH,BCL1}=0.36*k_{OH,ISOP}$

Aromatics (no modifications):

The reaction between Cl· and the aromatic ring ($k_{Cl,benzene}$=9x10^{-15} cm^{3}molecule^{-1}s^{-1}, Ariya, 1996) is slower than that of the OH· with aromatic ring ($k_{OH,benzene}$=1.1x10^{-12} cm^{3}molecule^{-1}s^{-1}, Atkinson, 1994). We suggest not including any Cl· + Aromatic reaction in the modified mechanism because the rate of chlorine atom addition to the aromatic ring proceeds at such a slow rate.

Ozone (revised):

Although the Cl· + ozone reaction is an important reaction in the chlorine-catalyzed destruction of stratospheric ozone, this chemistry is not believed to result in significant ozone destruction in the troposphere. In the urban troposphere, the reaction rate constant for ozone with Cl· is more than an order of magnitude slower than the rate constants of Cl· with hydrocarbon species (Atkinson, 1997a). According to Oum (1998), when considering the reaction of Cl· with ozone (40 ppb) versus the reaction of Cl· with background methane and 10 ppb of organics other than methane, approximately 70 percent of Cl atoms would react with the methane and organics. In the Houston atmosphere, where hydrocarbon concentrations are high (~1000 ppb_c) relative to ozone concentrations (150 ppb_v), it is anticipated that a very small fraction of chlorine atoms would react with ozone. However, the reaction of Cl· + ozone and subsequent reaction of the corresponding reaction product (ClO) are included for completeness.

The reactions suggested for incorporation are:

A) Cl + O3 = ClO + O2;

B) ClO + NO = Cl + NO2; and

C) ClO + HO2 = HOCl + O2

The rate constants associated with these reactions are as follows (Atkinson, 2000):

A) $k_{Cl,O3}(298)$=1.2x10^{-11} cm^{3}molecule^{-1}s^{-1}, or as a function of temperature (in K),
$k_{Cl,O3}(T)$=2.9x10^{-11}exp(-260/T) cm^{3}molecule^{-1}s^{-1}

B) $k_{ClO,NO}(298)$=1.7x10^{-11} cm^{3}molecule^{-1}s^{-1}, or as a function of temperature (in K),
$k_{Cl,NO}(T)$=6.2x10^{-12}exp(295/T) cm^{3}molecule^{-1}s^{-1}

C) $k_{ClO,HO2}(298)$=5.0x10^{-12} cm^{3}molecule^{-1}s^{-1}, or as a function of temperature (in K),
$k_{ClO,HO2}(T)$=4.6x10^{-13}exp(710/T) cm^{3}molecule^{-1}s^{-1}

Assessing the Impact of Omitted Reactions:

As in previous versions of this proposed modification to the Carbon Bond IV mechanism, chlorine radical reactions with other non-organic species are not included for incorporation. Justification for this omission is provided below.

A sensitivity analysis was performed on a version of the SAPRC-99 model (Carter, 2000) that was modified to include chlorine radical chemistry. The purpose of this analysis was to justify the omission of certain chlorine reactions from the proposed modification to the Carbon Bond-IV mechanism. The results of the sensitivity runs indicate that the importance of the omitted reactions is not significant to the production of ozone.

The chlorine mechanism incorporated into the SAPRC-99 model chemistry is based, in part, on the chlorine reactions included by Carter et al. (1997) for use in an earlier version of the SAPRC model. The chemistry incorporated into SAPRC-99 includes the reactions of chlorine radicals with NO, NO_2, ozone, nitrate radicals, hydroperoxy radicals, and various organic species.

Experimental data from an environmental chamber run with a pentane-NO_x-air mixture was used as input to the model for the sensitivity analysis. The initial mixing ratios (in ppb) of ozone, pentane, NO, and NO_2 were 0.27, 68.9, 46, and 6, respectively. The inherent wall reactivity of the environmental chambers was kept constant for all model runs during the analysis.

As each chlorine reaction was omitted from consideration, the output from the run was compared to the run with all chlorine reactions active (referred to here as the 'base case'). All of these sensitivity runs resulted in no significant difference in model response. As shown in Figures 1 through 4, the elimination of all chlorine radical reactions with non-organic species does not result in noticeable difference in the ozone, pentane, NO, or NO_2 mixing ratios within the chamber. However, if all chlorine radical reactions are retained except for the pentane-chlorine reaction, the response in ozone and pentane mixing ratios is clear.

The results of this analysis suggest that chlorine radical chemistry is adequately described by the reactions of chlorine radicals with organic species only.

REFERENCES:

Adelman, Z.E., "A Reevaluation of the Carbon Bond-IV Photochemical Mechanism", M.S. Thesis, University of North Carolina at Chapel Hill, 1999.

Ariya, P., Studies of tropospheric halogen chemistry: Laboratory and field measurements, Ph.D. thesis, York Univ., North York, Ontario, Canada, May 1996.

Atkinson, R., Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds, *J. Phys. Chem. Ref. Data Monogr.*, **1**, 1 (1989).

Atkinson, R., Gas phase tropospheric chemistry of organic compounds, *J. Phys. Chem. Ref. Data Monogr.*, **2**, 1 (1994).

Atkinson, R., et al. "Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V," *J. Phys. Chem. Ref. Data*, **26**, 521 (1997a).

Atkinson, R., "Gas-Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes," *J. Phys. Chem. Ref. Data*, **26**, 215 (1997b).

Atkinson, R. et al., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Organic Species: Supplement VII," *J. Phys. Chem. Ref. Data*, **28**, 191 (1999).

Calvert, J.G. and Pitts, J.N. Jr. Photochemistry, pp. 899 (John Wiley, New York, 1966).

Carter, W.P.L., Pierce, J.A., and Malkina, I.L., "Environmental Chamber Study of Maximum Incremental Reactivities of Volatile Organic Compounds," *Atm. Env.*, **29**, 2499 (1995).

Carter, W.P.L., D. Luo, and I. Malkina, "Investigation of the Atmospheric Ozone Formation Potential of Trichloroethylene," Draft Report to the Halogenated Solvents Industry Alliance, University of California Riverside, August 29, 1997.

Carter, W.P.L., "SAPRC-99 Mechanism Files and Associated Programs and Examples," http://pah.cert.ucr.edu/~carter/SAPRC99.htm, June 10, 2000.

Coquet, S. and P. Ariya, "Kinetics of the Gas-Phase Reactions of Cl Atom with Selected C_2-C_5 Unsaturated Hydrocarbons at 283<T<323K," *Int. J. Chem. Kin.*, **32**, 478 (2000).

DeMore, W.B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling* (Rep. 97-4), Jet Propulsion Laboratory, Pasadena, CA (1997).

Finlayson-Pitts, B.J. and Pitts, J.N. Jr. Atmospheric Chemistry: Fundamentals and Experimental Techniques, pp.1098 (John Wiley, New York, 1986).

Finlayson-Pitts, B.J. and Pitts, J.N. Jr. Chemistry of the Upper and Lower Atmosphere, pp. 969 (Academic Press, New York, 2000).

Hov, O., "The Effect of Chlorine on the Formation of Photochemical Oxidants in Southern Telemark, Norway," *Atmos. Env.*, **19**, 471 (1985).

National Center for Atmospheric Research (NCAR), Tropospheric Ultraviolet and Visible Radiation Model (TUV), http://acd.ucar.edu/models/UV/TUV/index.html. *(Accessed June, 2001)*.

Nordmeyer, T. et al, "Unique products of the reaction of isoprene with atomic chlorine: Potential markers of chlorine atom chemistry," *Geophys. Res. Letters*, **24**, 1615 (1997).

Oldfield, S. and Allen, D.T., "The Impact of Molecular Chlorine Emissions on Ozone Formation in Southeast Texas", Final report to the Texas Natural Resource Conservation Commission on Contract 98-80076000, 1999.

Oum, K.W., et al., "Formation of Molecular Chlorine from the Photolysis of Ozone and Aqueous Sea-Salt Particles," *Science*, **279**, 74 (1998).

Ragains, M.L. and Finlayson-Pitts, B.J., "Kinetics and Mechanism of the Reaction of Cl Atoms with 2-Methyl-1,3-butadiene (Isoprene) at 298K," *J. Phys. Chem. A*, **101**, 1509 (1997).

Tanaka, P.L., et al. "Anthropogenic Sources of Chlorine and Ozone Formation in Urban Atmospheres," *Env. Sci. Tech.*, **34**, 4470 (2000).

Wang, W. and Finlayson-Pitts, B.J. “4-Chlorocrotonaldehyde as a Unique Chlorine-Containing Compound from the Reaction of Atomic Chlorine with 1,3-Butadiene in Air at Room Temperature,” *Geophys. Res. Letters*, **27**, 947 (2000).

Yarwood, Greg. Memorandum. “Treatment of Chlorine Photolysis Reactions in CAMx Modeling,” Environ, June 13, 2001.

TABLES

TABLE 1

KEY TO CB-IV ABBREVIATIONS IN THIS REPORT

Name	Description
BUTA	1,3 Butadiene
BCL1	4-Chlorocrotonaldehyde (CCA)
BCL2	CCA + OH reaction products
ETH	Ethene
Cl	Chlorine atom
Cl2	Molecular chlorine
ClO	Chlorine Oxide
CO	Carbon monoxide
FORM	Formaldehyde
FMCL	Formyl chloride
HCl	Hydrochloric acid
HOCl	Hypochlorous acid
HO2	Hydroperoxy radical
ISOP	Isoprene
ICL1	1-Chloro-3-methyl-3-butene-2-one (CMBO)
ICL2	CMBO + OH reaction products
OH	Hydroxyl radical
OLE	Olefinic bond (Carbon double bond)
PAR	Paraffinic carbon
RCHO	Higher aldehyde
ROR	Organic nitrate forming peroxy radical
XO2	Universal peroxy radical operator
XO2N	Nitrate forming peroxy radical operator

Example: Propene would be represented as 1 PAR + 1 OLE.

TABLE 2

REACTION RATE CONSTANTS OF OH AND Cl WITH 20 SELECTED ALKANES

Compound	$10^{11}xk_{298,Cl}$* ($cm^3molecule^{-1}s^{-1}$)	Number of Carbons	$10^{11}xk_{298,Cl,C}$ ($cm^3carbons^{-1}s^{-1}$)	$10^{11}xk_{298,OH}$* ($cm^3molecule^{-1}s^{-1}$)	Number of Carbons	$10^{11}xk_{298,OH,C}$ ($cm^3carbons^{-1}s^{-1}$)	$k_{298,Cl,C}/k_{298,OH,C}$
Ethane	5.9	2	3.0	0.0254	2	0.0127	232
Propane	13.7	3	4.57	0.112	3	0.0373	122
n -Butane	21.8	4	5.45	0.244	4	0.061	89
2-Methylpropane	14.3	4	3.58	0.219	4	0.0548	65
n -Pentane	28	5	5.6	0.4	5	0.08	70
2-Methylbutane	22	5	4.4	0.37	5	0.074	59
2,2-Dimethylpropane	11.1	5	2.22	0.0848	5	0.0170	131
n -Hexane	34	6	5.7	0.545	6	0.0908	62
2-Methylpentane	29	6	4.8	0.53	6	0.088	55
3-Methylpentane	28	6	4.7	0.54	6	0.09	52
2,3-Dimethylbutane	23	6	3.8	0.578	6	0.0963	40
n -Heptane	39	7	5.6	0.702	7	0.100	56
2,4-Dimethylpentane	29	7	4.1	0.5	7	0.07	58
2,2,3-Trimethylbutane	20	7	2.9	0.424	7	0.061	47
n -Octane	46	8	5.8	0.871	8	0.109	53
2,2,4-Trimethylpentane	26	8	3.3	0.357	8	0.0446	73
2,2,3,3-Tetramethylbutane	17.5	8	2.19	0.105	8	0.0131	167
n -Nonane	48	9	5.3	1	9	0.11	48
n -Decane	55	10	5.5	1.12	10	0.112	49
cis -Bicyclo[4,4,0]decane	48	20	2.4	1.9	20	0.095	25
						AVERAGE:	78

* Source: Atkinson, 1997b

TABLE 3

REACTION RATE CONSTANTS OF OH AND CL WITH 4 SELECTED ALKENES

Compound	$10^{11} x k_{298,Cl}$ ($cm^3 molecule^{-1} s^{-1}$)	Number of Double Bonds	$10^{11} x k_{298,Cl,DB}$ ($cm^3 double\ bond^{-1} s^{-1}$)	$10^{11} x k_{298,OH}$ [1] ($cm^3 molecule^{-1} s^{-1}$)	Number of Double Bonds	$10^{11} x k_{298,OH,DB}$ ($cm^3 double\ bond^{-1} s^{-1}$)
Propene[1]	28	1	28	2.63	1	2.63
1,2-Propadiene[1]	42	2	21	0.982	2	0.491
1-Butene[2]	35.2	1	35.2	3.14	1	3.14
1-Pentene[2]	49.3	1	49.3	3.14	1	3.14
						AVERAGE:
Ethene[1]	10.7	1	10.7	0.852	1	0.852
2-Methyl-1,3-butadiene (Isoprene)[1]	48	2	24	10.1	2	5.05
1,3-Butadiene[1]	49	2	24.5	6.66	2	3.33

Sources: [1] Atkinson, 1997b; [2] Coquet, 2000

FIGURES

Figure 1
Ozone Sensitivity Comparison

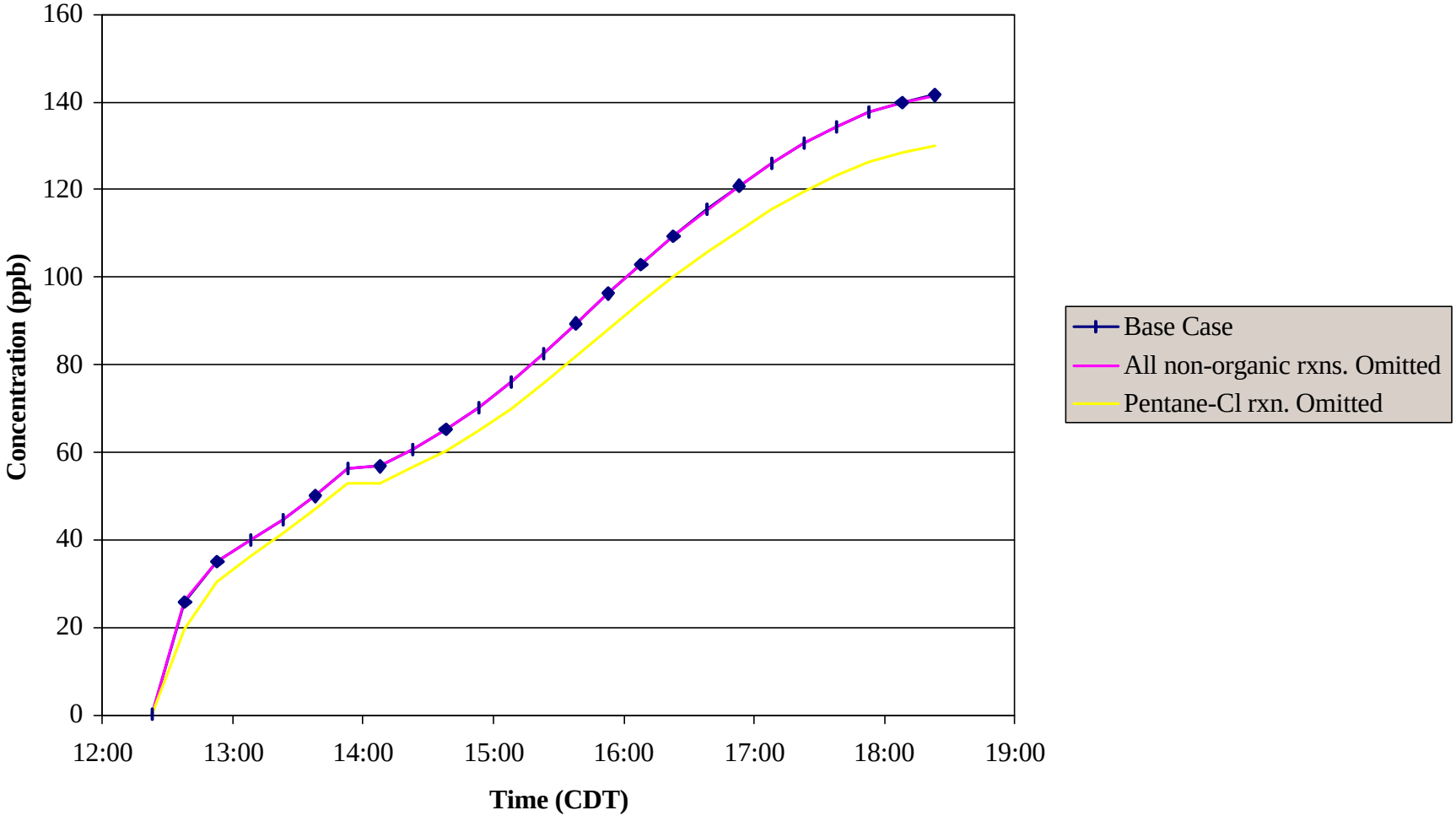


Figure 2
Pentane Sensitivity Comparison

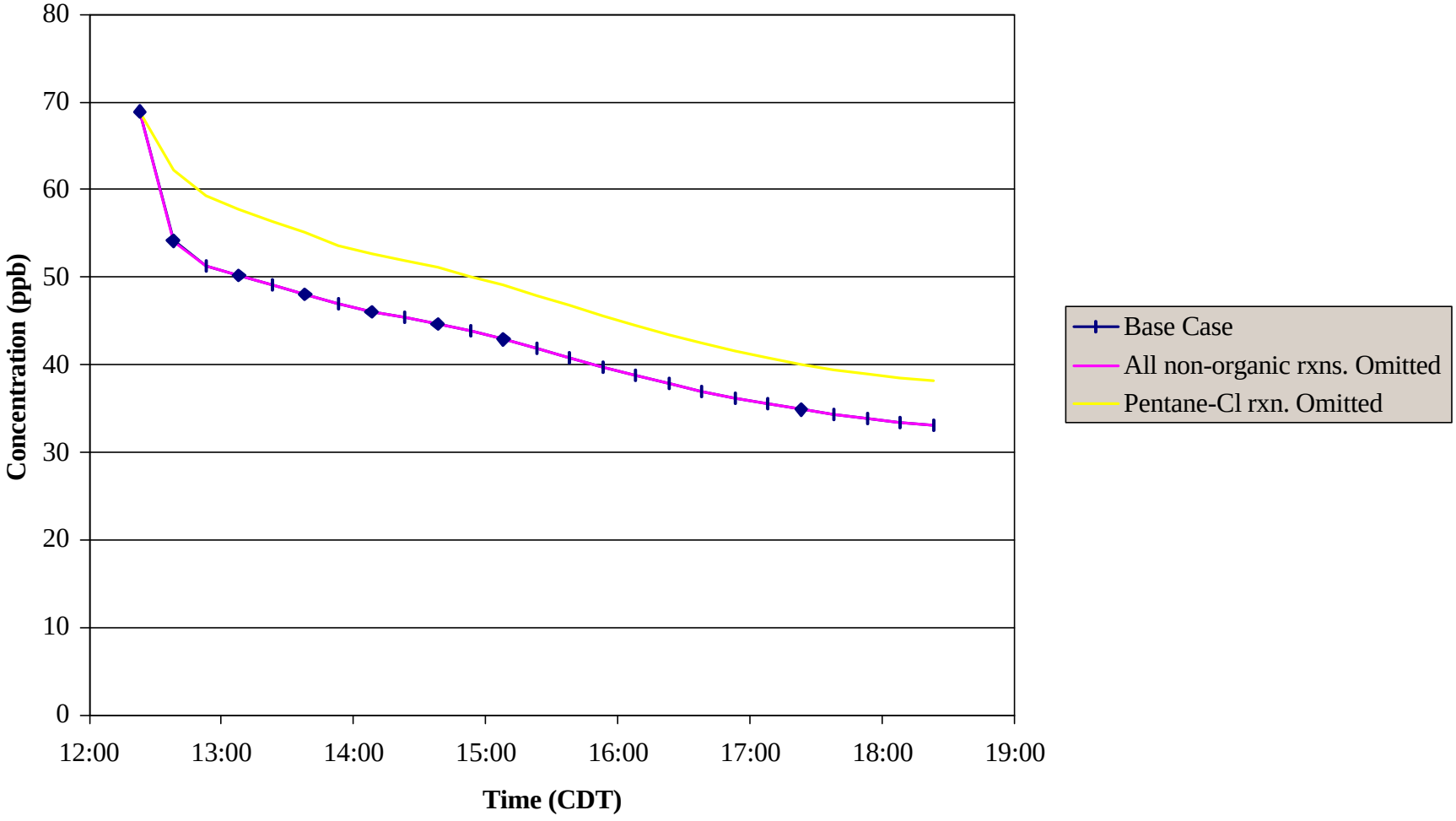


Figure 3
NO Sensitivity Comparison

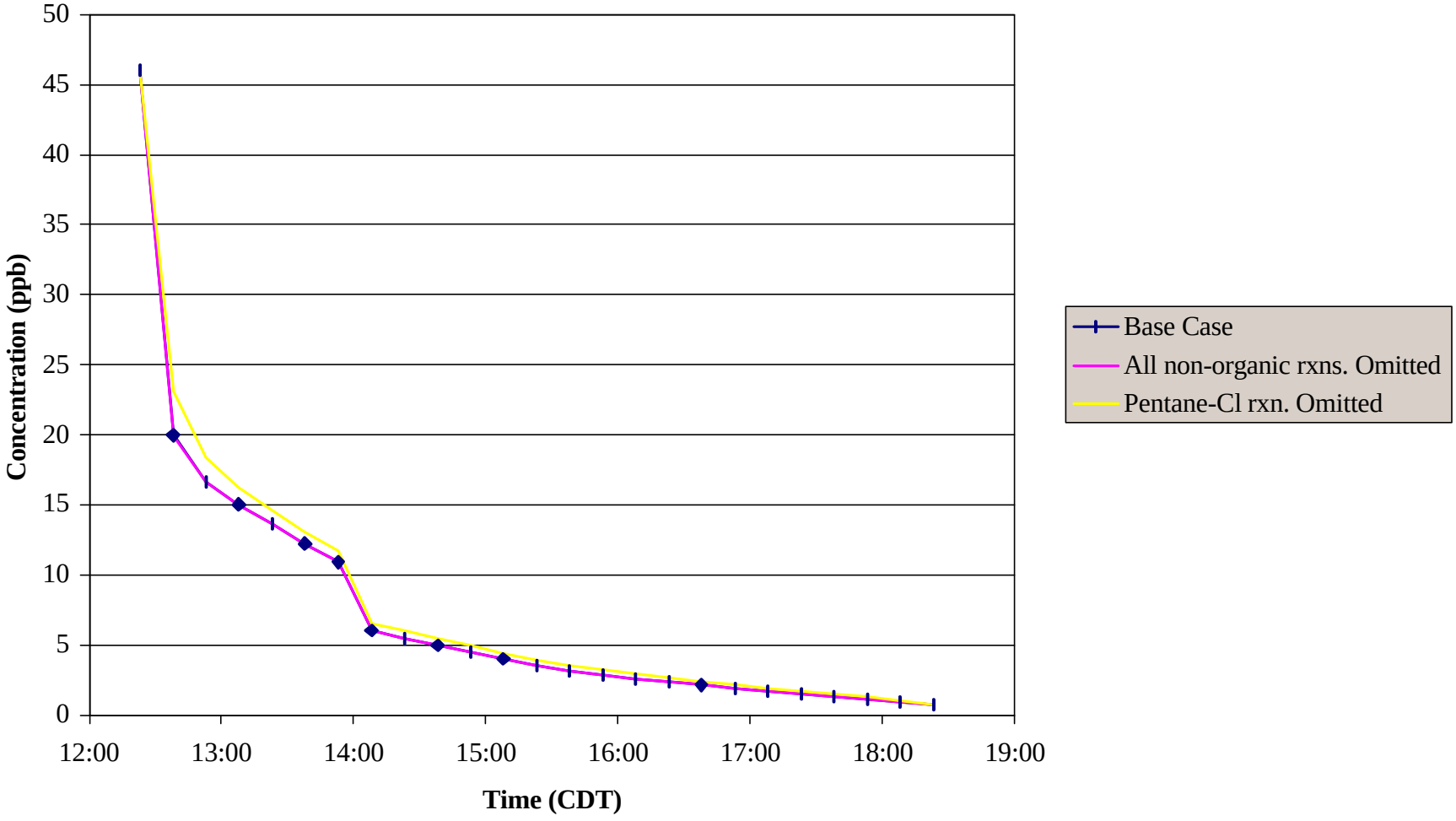
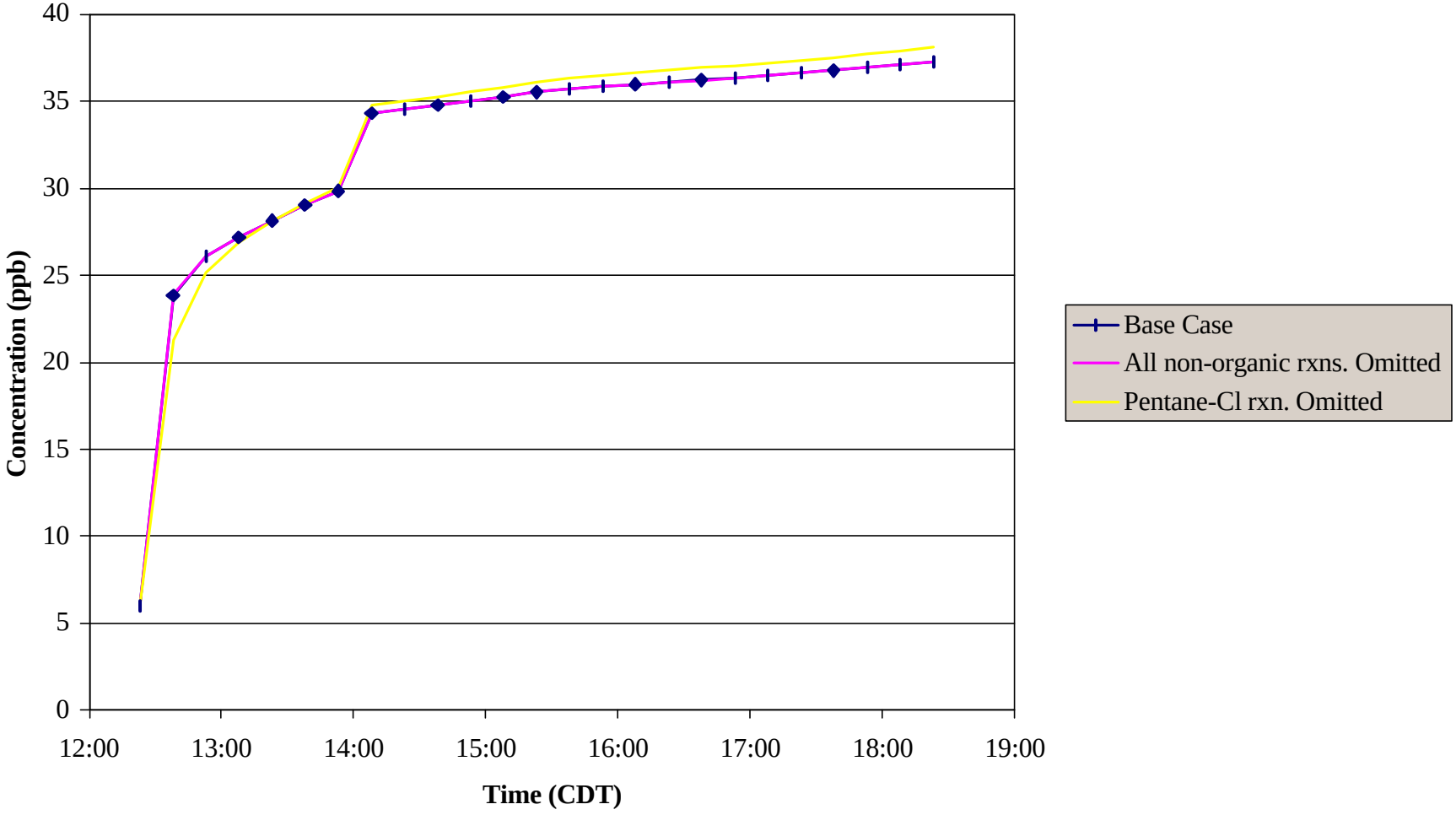


Figure 4
NO_2 Sensitivity Comparison



APPENDICES

APPENDIX A

ABSORPTION CROSS-SECTIONS

FOR Cl_2 AND HOCl

Table A-1 Absorption Cross Sections of Cl_2 at Room Temperature

Wavelength (nm)	$10^{20}\sigma$ ($cm^2 molecule^{-1}$)	Wavelength (nm)	$10^{20}\sigma$ ($cm^2 molecule^{-1}$)
260	0.20	370	8.4
270	0.82	380	5.0
280	2.6	390	2.9
290	6.2	400	1.8
300	11.9	410	1.3
310	18.5	420	0.96
320	23.7	430	0.73
330	25.5	440	0.54
340	23.5	450	0.38
350	18.8	460	0.26
360	13.2	470	0.16

From Atkinson (1997a).

Table A-2 Absorption Cross Sections of HOCl at Room Temperature

Wavelength (nm)	$10^{20}\sigma$ ($cm^2 molecule^{-1}$)	Wavelength (nm)	$10^{20}\sigma$ ($cm^2 molecule^{-1}$)	Wavelength (nm)	$10^{20}\sigma$ ($cm^2 molecule^{-1}$)
200	7.1	262	9.3	322	4.6
202	6.1	264	8.3	324	4.3
204	5.6	266	7.4	326	4.2
206	5.4	268	6.6	328	3.8
208	5.5	270	6.0	330	3.5
210	5.7	272	5.5	332	3.3
212	6.1	274	5.2	334	3.1
214	6.6	276	4.9	336	2.7
216	7.5	278	4.8	338	2.5
218	8.4	280	4.7	340	2.4
220	9.7	282	4.8	342	2.1
222	10.9	284	4.8	344	1.8
224	12.2	286	4.9	346	1.8
226	13.5	288	5.1	348	1.7
228	15.0	290	5.3	350	1.5
230	16.4	292	5.4	352	1.3
232	17.7	294	5.6	354	1.3
234	18.7	296	5.8	356	1.2
236	19.7	298	5.9	358	1.0
238	20.3	300	6.0	360	0.8
240	20.7	302	6.0	362	1.0
242	21.0	304	6.1	364	1.0
244	20.5	306	6.0	366	0.9
246	19.6	308	6.0	368	0.8
248	18.6	310	5.9	370	0.8
250	17.3	312	5.7	372	1.0
252	15.9	314	5.6	374	0.8
254	14.6	316	5.4	376	0.8
256	13.2	318	5.1	378	0.6
258	11.8	320	4.9	380	0.8
260	10.5				

From DeMore *et al.* (1997)

APPENDIX B

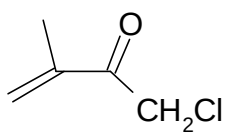
RATIONALE FOR ESTIMATING REACTION RATES

FOR OH + CMBO

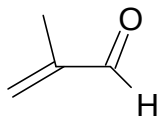
As of this revision, there is no published rate constant data for the reaction of hydroxyl radical (OH) with 1-chloro-3-methyl-3-buten-2-one (CMBO). Because this species is a unique marker for the reaction of chlorine radicals with isoprene, it is important to follow the consumption of CMBO in order to accurately predict its concentration.

This appendix includes the process used to estimate the rate constant of OH with CMBO.

Since CMBO is structurally similar to methacrolein (MACR), an estimate was made of the rate constant for CMBO + OH by examining the reaction of OH with MACR. For clarity, the structures are provided below:



[CMBO]



[MACR]

According to Orlando, et al. (Geophys. Res. Lett. 26 (1999) 14), OH attack on MACR proceeds 55% by addition to the double bond and 45% via abstraction of the aldehydic hydrogen.

Atkinson (1989) suggests that OH attacks aldehydes by H atom abstraction. Because H atom abstraction from a chloroalkane is much slower than that of an aldehyde, it would be expected that the rate of rxn. for OH + CMBO is slower than MACR + OH. For reference, the reaction rate constants for the reaction of OH with chloroethane and acetaldehyde (Atkinson, 1999) are 4.11×10^{-13} and 1.6×10^{-11} $cm^3 molecule^{-1} s^{-1}$ at 298K, repectively.

To estimate the reaction rate constant for OH + CMBO:

1) Assume that the rate of OH attack by addition to the double bond can be estimated to be 55% of the MACR + OH reaction rate. This assumes that the rate of addition to the double bond is unaffected by the substitution of the aldehydic hydrogen on MACR. This gives a contribution of $0.55 * 3.35 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$, or **$1.84 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$**.

2) CMBO also has 5 hydrogens available for abstraction: 3 alkyl hydrogens of the 3-methyl group and 2 terminal chloromethyl (CH_2Cl) hydrogens. Estimate the rate of hydrogen abstraction by OH by summing the contribution from the two types of hydrogens separately.

   a. For methyl hydrogens, consider ethane. $k_{OH,ethane} = 2.5 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$ at 298K (Atkinson, 1999). This gives a contribution of 4.17×10^{-14} $cm^3 molecule^{-1} s^{-1}$ per hydrogen. Thus, the 3 methyl hydrogens on CMBO are estimated to contribute **1.25×10^{-13} $cm^3 molecule^{-1} s^{-1}$** to the overall rate of OH + CMBO.

b. For CH_2Cl hydrogens, consider chloroethane. $k_{OH,CH3CH2Cl}$ = $4.11x10^{-13}$ $cm^3molecule^{-1}s^{-1}$ at 298K (Atkinson, 1999). This gives a contribution per CH_2Cl hydrogen of $8.22x10^{-14}$ $cm^3molecule^{-1}s^{-1}$. Thus, the 2 CH_2Cl hydrogens on CMBO are estimated to contribute **$1.64x10^{-13}$ $cm^3molecule^{-1}s^{-1}$** to the overall rate of OH + CMBO.

The reaction rate estimated for the reaction OH + CMBO is the sum of the three components: 1) addition to the double bond, 2) abstraction of alkyl hydrogens on the 3-methyl group, and 3) abstraction of hydrogens from the terminal CH_2Cl group.

The estimated rate at 298K is: $k_{OH,CMBO}$=$1.87x10^{-11}$ cm^3 $molecule^{-1}s^{-1}$. This compares to the rate of reaction of OH with isoprene at 298K: $k_{OH,ISOP}$= $9.7x10^{-11}$ cm^3 $molecule^{-1}s^{-1}$. Expressed in terms of the rate of reaction of OH with isoprene, the rate of reaction of OH with CMBO is $k_{OH,CMBO}$=0.193*$k_{OH\ ISOP}$.