Incorporation of Chlorine Reactions into the Carbon Bond-IV Mechanism

A supplement to the final report on Contract 98-80076000 between
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Submitted by

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Summary

The objective of Contract 98-80076000 (*Impact of Molecular Chlorine Emissions on Ozone Formation in Southeast Texas*) was to determine the effect of molecular chlorine emissions on the kinetics of ozone formation in the Houston area. The final report for the project (Oldfield and Allen, 1999) and a draft publication (Tanaka, et al., 1999) conclude that the effect of chlorine emissions on ozone formation in the Houston area may be substantial. Consequently, it may be appropriate to incorporate a simplified mechanism for chlorine reactions in photochemical modeling simulations. This supplement to the final report provides a set of chlorine reactions, compatible with the CB-IV mechanism, that could be incorporated into air quality simulations for the Houston area.
**Introduction**

Previous work (Oldfield and Allen, 1999; Tanaka, et al., 1999) 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·) 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).

This report suggests additions to the CB-IV mechanism that would account for the dominant features of the urban, tropospheric chemistry of molecular chlorine. Several points concerning the proposed mechanism are worthy of note.

- 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 six new chemical species (one each for a chlorinated isoprene reaction product, methane, molecular chlorine, atomic chlorine, hydrochloric acid, and HCOCl). Also provided are suggested rate parameters reported either as ratios (rate of the reaction involving chlorine divided by the rate of the analogous hydroxyl radical reaction employed in the CB-IV mechanism) or a temperature dependent expression (methane only – there is no methane-hydroxyl radical analog in CB-IV). 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 mechanism has been performed by Adelman (1999).

- The proposed mechanism incorporates chlorine photolysis and subsequent reactions of atomic chlorine with major hydrocarbon classes. Other reactions, such as the chlorine-ozone reaction, the reactions of chlorine with nitrogen oxides, and chlorinated radical termination reactions are not currently included in the mechanism. 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.

**Mechanism**

The proposed, 6-step mechanism consists of the following reactions:

1. Cl\(_2\) = 2Cl
2. \[ \text{Cl} + \text{PAR} = \text{HCl} + 0.87*\text{XO}_2 + 0.13*\text{XO}_2\text{N} + 0.11*\text{HO}_2 + 0.11*\text{RCHO} + 0.76*\text{ROR} - 0.11 \text{PAR} \]

3. \[ \text{Cl} + \text{OLE} = \text{HOCCl} + \text{RCHO} + 2 \text{XO}_2 + \text{HO}_2 - 1*\text{PAR} \]

4. \[ \text{Cl} + \text{METH} = \text{HCl} + \text{XO}_2 + \text{HCHO} + \text{HO}_2 \]

5. \[ \text{Cl} + \text{C:C} = \text{HCHO} + 2 \text{XO}_2 + \text{HCOCl} + \text{HO}_2 \]

6. \[ \text{Cl} + \text{ISOP} = 2 \text{XO}_2 + \text{OLE} + \text{HCHO} + \text{HO}_2 + \text{ISOP} \]

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

**Photolysis of Cl\(_2\):**

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 expression is simpler to execute and will minimize additional calculational complexity in the modified mechanism. The rate constant for photolysis of Cl\(_2\) can be represented as follows:

\[ k_{p,\text{Cl}_2} = 0.284*k_{p,\text{NO}_2} \]

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

This rate expression is based on a comparison made between the rates of photolysis of Cl\(_2\) and NO\(_2\) over the actinic region. The expression for calculating the rate of photolysis of a species is as follows:

\[ k_{p,x}(s^{-1}) = \sum_{\lambda=290nm}^{\lambda_i} \sigma(\lambda)\phi(\lambda)J(\lambda) \]

where,

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

Tabulated values of \( J(\lambda) \) (Finlayson-Pitts, 1986) were adjusted for noontime exposure on August 1 for the Houston area. Tabulated values of \( \phi(\lambda) \) for NO\(_2\) and all \( \sigma(\lambda) \) were obtained from Atkinson (1997a). The quantum yield for Cl\(_2\) photolysis is unity for all wavelengths of concern (Calvert, 1966).
The ratio of the calculated rates of photolysis of Cl₂ and NO₂ in the actinic region was 0.284.

**Paraffins:**

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 (C₆+) alkanes have been shown to contribute very little, or even negatively to ozone formation (Carter, 1995) in the absence of chlorine. We have observed, however, that the addition of chlorine into an air mass with high concentrations of alkanes, promotes the formation of ozone, particularly when the ratio of volatile organic compounds (VOCs) to nitrogen oxides (NOₓ) is between 5 and 10 (parts per billion carbon per part per billion volume (ppb_c/ppbᵥ)).

The CB-IV mechanism currently accounts for alkane (non-methane) oxidation through hydrogen abstraction by hydroxyl radical. In the presence of sufficient NOₓ, the resulting alkyl radical will continue to react to convert nitrogen oxide (NO) to NO₂ and produce peroxy radicals (HO₂⁻) 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. 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⁻ is consumed to form stable HCl during this abstraction, only one additional reaction is needed to incorporate chlorine-alkane chemistry.

Because the reaction pathway is the same for alkyl radicals initially formed by either OH⁻ or Cl⁻, 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:

\[
\text{OH + PAR} = 0.87\times\text{XO}_2 + 0.13\times\text{XO}_2\text{N} + 0.11\times\text{HO}_2 + 0.11\times\text{RCHO} + 0.76\times\text{ROR} - 0.11\times\text{PAR}
\]

\[
\text{Cl + PAR} = \text{HCl} + 0.87\times\text{XO}_2 + 0.13\times\text{XO}_2\text{N} + 0.11\times\text{HO}_2 + 0.11\times\text{RCHO} + 0.76\times\text{ROR} - 0.11\times\text{PAR}
\]

Based on the ratio of average of reaction rate constants (Atkinson, 1997b) for Cl⁻ to OH⁻ 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⁻ with a paraffinic carbon can be represented as follows:

\[k_{\text{Cl,PAR}} = 78\times k_{\text{OH,PAR}}\]
Methane:

The CB-IV mechanism does not currently account for methane oxidation because the oxidation of methane by hydroxyl radicals is relatively slow. The reaction rate constant for the chlorine-methane reaction, however, 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:

\[
\begin{align*}
\text{Cl} & \rightarrow \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \cdot \\
\text{CH}_3 \text{OO} \cdot & \rightarrow \text{O}_2 \rightarrow \text{CH}_3 \text{O} \cdot \\
\text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 \cdot 
\end{align*}
\]

The reaction stoichiometry is provided as follows:

\[
\text{Cl} + \text{METH} = \text{HCl} + \text{XO}_2 + \text{HCHO} + \text{HO}_2
\]

Because there is no methane-OH reaction currently in the CB-IV mechanism, the actual rate constant at 298 K and a temperature-dependent rate expression are provided as follows (Atkinson, 1999):

\[
\begin{align*}
\text{k}_{\text{Cl,METH}} &= 1.01 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{K and 760 Torr in air} \\
&= 6.6 \times 10^{-12} [\exp(-1240/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ for } 200 \text{K} \leq T \leq 300 \text{K}.
\end{align*}
\]

Olefins:

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:

\[
\text{OH} + \text{OLE} = \text{HCHO} + \text{RCHO} + \text{XO}_2 + \text{HO}_2 - 1\text{PAR}
\]
However, with the addition of chlorine, we expect a reaction path that gives the following products: HCOCl, aldehydes, and HO$_2$. resulting from the following, generalized mechanism:

\[
\text{CH}_2=\text{CH}_2 + \text{Cl} \cdot \rightarrow \text{CH}_2\text{CHCl} \\
\text{CH}_2\text{CHCl} + \text{O}_2 \rightarrow \text{CH}_2\text{CHO} + \text{HO}_2 \cdot \\
\text{CH}_2\text{CHO} + \text{Cl} \cdot \rightarrow \text{CH}_3\text{CHO} + \text{HCOCl} + \text{HO}_2 \cdot
\]

This pathway yields the following model stoichiometry:

\[
\text{Cl} + \text{OLE} = \text{HCOCl} + \text{RCHO} + 2\text{XO}_2 + \text{HO}_2 - 1*\text{PAR}
\]

Note that although the species HCOCl is photolyzable in the troposphere, the lifetime of this species is more than 1 month against photolysis.

Based on the ratio of average rates of reaction (Atkinson, 1997b) (per double bond) for Cl· to OH· with 3 alkenes (Table 3), a reaction rate constant for Cl + OLE of 20*k$_{\text{OH+OLE}}$ is proposed. Thus, the rate constant for reaction between Cl· and an olefin bond can be represented as follows:

\[
k_{\text{Cl,OLE}} = 20*k_{\text{OH,OLE}}
\]

**Ethene:**

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

\[
\text{Cl} + \text{C:C} = \text{HCHO} + 2\text{XO}_2 + \text{HCOCl} + \text{HO}_2
\]

As noted in the olefins section, although HCOCl 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 for the chlorine-ethene and hydroxyl radical-ethene reactions, the proposed rate constant for the Cl + C:C reaction is 12.6 * k$_{\text{OH:C:C}}$. 
Therefore, the rate constant for the reaction between Cl· and ethene can be represented as follows:

\[ k_{\text{Cl,C:C}} = 12.6*k_{\text{OH,C:C}} \]

**Isoprene:**

The reaction mechanism of the chlorine-isoprene reaction is very complex and although attempts have been made to describe mechanistic details (Ragains, 1997), many details have yet to be adequately described. Several simplifying assumptions were made to provide a stoichiometry for the Cl + ISOP reaction. These assumptions are as follows:

- Chlorine atoms react with isoprene by adding to the C1 double bond in the isoprene molecule. Chlorine is assumed not to take part in any subsequent reaction steps;
- The chloroalkyl radical formed upon addition of Cl· to isoprene is assumed to preferentially react with oxygen at the tertiary site (C2 position). The tertiary site is expected to be the most stable radical site; and
- Because specific reaction products have not yet been identified, the actual contribution of each possible reaction pathway to the overall decomposition of isoprene with chlorine in air cannot be determined. The following reaction scheme represents the basis for the stoichiometry suggested for the Cl + ISOP reaction:
This reaction pathway will lead to the following stoichiometry:

\[ \text{Cl} + \text{ISOP} = 2 \text{XO}_2 + \text{OLE} + \text{HCHO} + \text{HO}_2 + \text{ISOP1} \]

The chlorinated keto-group in the above mechanism is represented as a new lumped species for the proposed revision to the CB-IV mechanism. The terminal double bond is represented as an OLE species, while the methyl radical continues to react to form formaldehyde, HO\(_2\), and contribute to another NO-to-NO\(_2\) conversion (XO\(_2\)).

Based on the ratio of reaction rate constants for the chlorine-isoprene and hydroxyl radical-isoprene reactions, the proposed rate constant for the Cl + ISOP reaction is 4.75 * \(k_{\text{OH-ISOP}}\). Therefore, the rate constant for the reaction between Cl\(\cdot\) and isoprene can be represented as follows:

\[ k_{\text{Cl-ISOP}} = 4.75*k_{\text{OH-ISOP}} \]

**Aromatics:**

The reaction between Cl\(\cdot\) and the aromatic ring \((k_{\text{Cl,benzene}}=9\times10^{-15} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}, \text{Ariya, 1996})\) is slower than that of the OH\(\cdot\) with aromatic ring \((k_{\text{OH,benzene}}=1.1\times10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}, \text{Atkinson, 1994})\). We suggest not including any Cl\(\cdot\) + Aromatic reaction in the modified mechanism because the rate of chlorine atom addition to the aromatic ring proceeds at such a slow rate.

**Ozone:**

Although Cl\(\cdot\) + ozone is an important reaction in the chlorine-catalyzed destruction of stratospheric ozone, this chemistry is not suggested for incorporation in the modified mechanism. In the urban troposphere, reaction rate constant for ozone with Cl\(\cdot\) is more than an order of magnitude slower than the rate constants of Cl\(\cdot\) with hydrocarbon species (Atkinson, 1997a). According to Oum (1998), when considering the reaction of Cl\(\cdot\) with background methane (10 ppb) versus ozone (40 ppb) in the troposphere, approximately 70 percent of Cl atoms would react with methane rather than ozone. In the atmosphere of Houston, 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.

**REFERENCES:**


