1.3 IMPROVING THE PHOTOCHEMICAL OXIDATION MECHANISM OF ISOPRENE

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Introduction

It is well known that anthropogenic and biogenic hydrocarbons play an important role in tropospheric chemistry. The photochemical oxidation of these hydrocarbons results in a number of compounds that impact local and regional air quality through aerosol formation and production of terrestrial ozone. Isoprene is one of the most abundant biogenic hydrocarbon emission with a global average production rate of ~450 Tg yr^{-1} and is sufficiently reactive to influence oxidation levels over large portions of the continental troposphere. It has been recently reported that 50-100% of ozone attributed to volatile organic compounds in some regional areas of the U.S. is due to isoprene photo-oxidation. As much as 7% of NO emitted in North American in the summer is lost as nitrates formed during isoprene degradation. In addition isoprene nitrates is believed to be responsible for about 4% of NO_x transported from North America and, therefore, have a significant impact not only on regional but global tropospheric chemistry.

The atmospheric oxidation of isoprene is initiated by reaction with OH, O_3, NO_3, or the halogen radicals. Since isoprene is emitted from vegetation only during daylight hours, the reaction with OH is the dominant tropospheric removal pathway. Field measurements indicate that isoprene is detected in considerable amounts at night. The nitrate radical, which is formed by the reaction of NO_2 and ozone, is a major nighttime oxidant. The reaction between isoprene and nitrate radicals hence contributes significantly to the nighttime degradation of isoprene. In addition, the ozonolysis of isoprene provides an important source of nighttime OH radicals on the regional scale. The bimolecular reactions of the carbonyl oxides arising from the O_3-isoprene reactions could also play a role in aerosol formation (i.e., oxidation of SO_2 by carbonyl oxides). Clearly, the atmospheric effects of isoprene oxidation are far-reaching.

In this paper, recent experimental and theoretical studies in our group on the isoprene reactions initiated by OH, NO_3, O_3, and Cl are summarized. Our latest results are incorporated into a box model to improve our understanding on isoprene chemistry and to assess the impact of isoprene oxidation on tropospheric chemistry.

OH Oxidation of Isoprene

The reaction between isoprene and OH occurs almost entirely by OH addition to the >C=C< bonds, yielding hydroxyalkyl radicals. The resulting hydroxyalkyl radicals react rapidly with oxygen molecules to form hydroperoxy radicals. The reaction of the hydroperoxy radicals with NO results in either the formation of nitrates or the formation of hydroxyalkoxy radicals along with the conversion of NO to NO_2. The subsequent reaction of hydroxyalkoxy radicals involves competition between decomposition, isomerization or reaction with O_2, leading to the formation of various oxygenated organic compounds. Figure 1 shows the first two steps in the OH-initiated oxidation of isoprene and illustrates some of its inherent complexity.

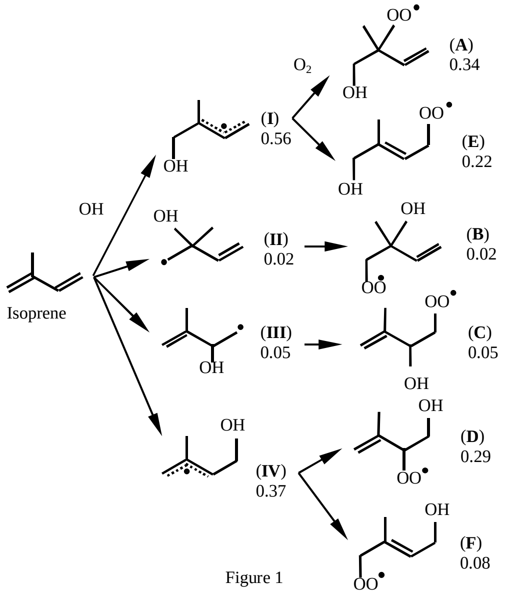

Figure 1

Figure 1 also summarizes isomeric branching ratios for the OH-initiated reactions of isoprene, based on our recently experimental and theoretical studies of the OH-isoprene reaction system (Zhang, 2001; Lei et al., 2001; Lei and Zhang, 2001). For the allylic OH-isoprene radicals addition occurs predominately at the more highly substituted sites, resulting in a preference

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for α-hydroxy peroxy radicals over β-hydroxy peroxy radicals.

Isoprene Ozonolysis

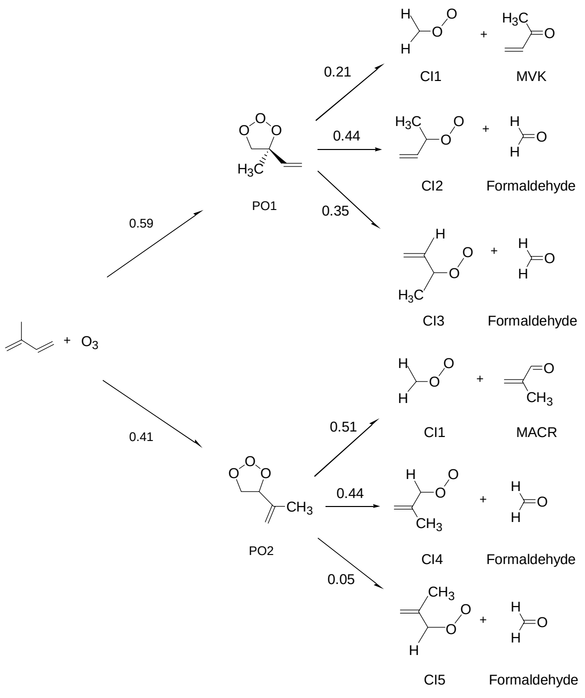

Figure 2. Reaction mechanism of isoprene ozonolysis.

The ozonolysis of isoprene proceeds through a complex series of reactions and intermediates. The initial product of the O_3-isoprene reaction is a primary ozonide, a five-membered ring formed from addition of O_3 to either of the isoprene's double bonds. Because ozone addition to isoprene is expected to be strongly exothermic, the available reaction enthalpy will be retained as the internal energy of the product, resulting in formation of the vibrationally excited ozonide (PO),

$O_3 + C_5H_8 \rightarrow PO^*$ (R1)

where asterisk denotes the chemically activated form. The excited ozonide further reacts via unimolecular reaction or is collisionally stabilized by the bath gas; decomposition of the primary ozonide yields a chemically activated carbonyl oxide (the Criegee intermediate, CI) and an aldehyde/ketone,

$PO^* + M \rightarrow PO + M$

or $PO^* \rightarrow CI^* + RCOR'$ (R2)

where M is an inert partner for the collisional stabilization and RCOR' represents the aldehyde/ketone. The RCOR' includes formaldehyde, methyl vinyl ketone (MVK), or methacrolein (MACR) and is unlikely to possess sufficient energy for further degradation. A large fraction of the carbonyl oxide will have ample internal energy, also rendering them susceptible to unimolecular reactions or stabilization. There are two primary reaction pathways for the carbonyl oxide, ring closure to form dioxirane or H-migration to form a hydroperoxide intermediate,

$CI^* + M \rightarrow CI + M$

CI^* (or CI) → dioxirane or hydroperoxide (R3)

Dissociation of the hydroperoxide subsequently forms OH and RCO radicals. Alternatively, thermally stabilized carbonyl oxides may engage in bimolecular reactions. Figure 2 illustrates the likely unimolecular reaction pathways of the primary ozonide and carbonyl oxide, respectively. The isomeric branching ratios for each reaction pathway are also labeled.

Box Model Simulations

We have employed a box model to evaluate the isoprene chemistry. The box model is based on a NCAR master mechanism MM2.1 discussed previously by Madronich and Calvert (1989). We have updated the photochemical oxidation mechanisms of isoprene initiated by OH (Zhang, 2001; Lei et al., 2001; Lei and Zhang, 2001), O_3 (Zhang et al., 2002; Zhang and Zhang, 2002), and NO_3 (Suh et al., 2001).

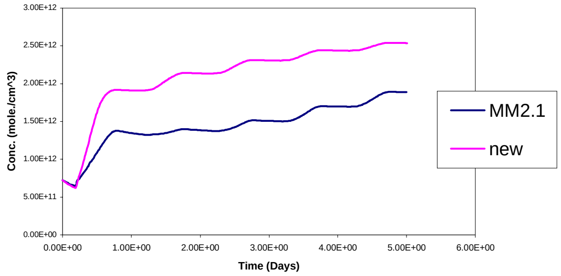

Figure 3. Modeled ozone concentrations.

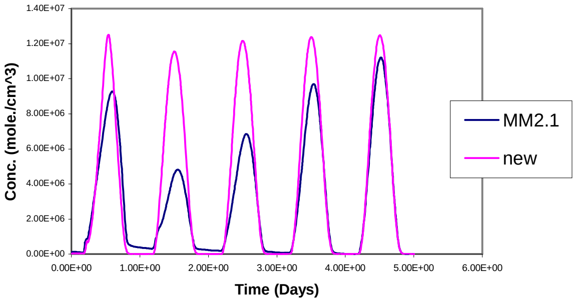

Figure 4. Modeled OH concentrations.

Figure 3 shows a comparison of modeled O_3 concentrations between the MM2.1 and our updated mechanism. The model simulations were performed assuming ambient concentrations of 20 ppb for NO_2 and 10 ppb for isoprene, respective. The mixing ratio of H_2O was assumed to be constant in the calculations. At reaction times longer than one day, the ozone concentrations predicted by using the updated mechanism are about 50% higher than those predicted by using the MM2.1 mechanism.

Figure 4 shows a comparison of modeled OH concentrations. The initial concentrations of NO_2 and isoprene are similar to those in Figure 3. The modeled OH concentrations are also significantly higher than those predicted using the MM2.1 mechanism.

Conclusions

Results form recent experimental and theoretical studies of atmospheric photochemical oxidation of isoprene are employed to improve the isoprene mechanism currently represented in atmospheric chemistry models. Simulations using a box model indicate that the modeled OH and O_3 concentrations are strongly affected by the isoprene chemical mechanisms used.

References

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