Isoprene, methyl vinyl ketone and methacrolein from TROICA-12 measurements and WRF-CHEM and GEOS-CHEM simulations in the Far East region

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Supplementary Materials

S1. Basic chemical reactions of isoprene oxidation

Isoprene reactions included in the WRF-CHEM model are known to be changed with the stages of the chemical scheme development. These stages were Regional Acid Deposition Model 2nd generation (RADM2); Regional Atmospheric Chemistry Mechanism (RACM), (Stockwell et al. 1990); RACM with Mainz Isoprene Mechanism (RACM-MIM), (Pöschl et al. 2000) and Model of Ozone and Related Chemical Tracers (MOZART), (Emmons et al. 2010). Recently the isoprene mechanism has been amended with the addition of glyoxal MOZART-SOA scheme, see details in (Knote et al. 2014). The smallest dicarbonyl molecules are secondary aerosols, but on the basic isoprene gas-phase chemical reactions these changes are not significant.

As sample of the basic reactions involved in isoprene oxidation, according to MOZART gas-phase mechanism, is shown below:

\[ ISO + OH \rightarrow ISOPO2 \]  \hspace{1cm} (S1)
\[ ISO + O_3 \rightarrow 0.4MACR + 0.2MVK + \text{products} \] \hspace{1cm} (S2)
\[ ISO + NO_3 \rightarrow ISOPNO3 \] \hspace{1cm} (S3)

where

ISO – isoprene
MVK – methyl vinyl ketone
MAC – methacrolein
ISOPO2 – \( HOCH_2C(OO)CH_2CHCH_2 \) peroxy radical
ISOPNO3 – \( CH_2CHCCH_3OOCCH_2ONO_2 \) peroxy radical

S2. Secondary oxidation products of biogenic components

The chemical reactions of the isoprene secondary oxidation products also can be divided into the light and night reactions. The initial carbonyl species, which produced by isoprene oxidation, such as formaldehyde, methacrolein (below MAC), and methyl vinyl ketone (below MVK) have relatively short lifetimes in the atmosphere due to reactions with OH, O₃ and sunlight. The MVK and MACR lifetimes at the daytime are 6.09 and 4.03 h, respectively (STable 2).

The main chemical MVK and MACR reactions are the following:

\[ MVK + OH \rightarrow \text{products} \] \hspace{1cm} (S4)
\[ MACR + OH \rightarrow \text{products} \]
\[ MVK + O_3 \rightarrow \text{products} \]
\[ MACR + O_3 \rightarrow \text{products} \]  \hspace{1cm} (S5)
\[ MACR + hv \rightarrow \text{products} \]
\[ MVK + hv \rightarrow \text{products} \]  \hspace{1cm} (S6)

In addition, a secondary oxidation product ISOPO2 in the reaction between isoprene and OH (see Equation (S1)), can react with NO and NO_3, with formaldehyde, MVK and MACR being formed:
\[ \text{ISOPO2} + NO \rightarrow 0.23 \text{MACR} + 0.32 \text{MVK} + \text{products} \]
\[ \text{ISOPO2} + NO_3 \rightarrow 0.25 \text{MACR} + 0.35 \text{MVK} + \text{products} \]
\[ \text{ISOPO2} + CH_3O_2 \rightarrow 0.19 \text{MACR} + 0.26 \text{MVK} + \text{products} \]  \hspace{1cm} (S7)
\[ \text{ISOPO2} + CH_3CO_3 \rightarrow 0.25 \text{MACR} + 0.35 \text{MVK} + \text{products} \]

However, in (Rivera-Rios et al. 2014) and (Liu et al. 2013) it was written about the possibility of ISOPOOH (isoprene hydroxy hydroperoxides) decomposition on the walls of a metal chamber. Note that ISOPOOH is the second product of the daytime reaction of isoprene with OH and HO_2, see reaction below. Therefore, the subsequent reaction ISOPO2 + HO_2 mentioned above in the remark has no relation to the considered problem of anomalous high ratio (MM/ISOP) values at night and twilight. The next reactions were discussed in (Rivera-Rios et al. 2014), (Liu et al. 2013):
\[ \text{ISOPO} + \text{OH} \rightarrow \text{ISOPO2} \]
\[ \text{ISOPO2} + \text{HO}_2 \rightarrow \text{ISOPOOH} \]  \hspace{1cm} (S8)
\[ \text{ISOPOOH} + M \rightarrow \text{MVK} + \text{MACR} \]

But we do not find in (Rivera-Rios et al. 2014), (Liu et al. 2013) the answer to these questions about the decomposition of ISOPOOH on the surface of vegetation. In these studies only the decomposition on the chamber metallic walls was discussed.

Our PTR-MS does not have a cold trap; we used Teflon tubes to connect the air intake system to PTR-MS. The high speed of pumping through the tubes and the continuous shake-up railroad-carriage during moving does not allow a gas to be stagnant. Note that the characteristic time of ISOPOOH deposition on the wall chambers was \sim 15 \text{ min} \ (Bernhammer et al. 2017). Our PTR-MS is working with a 10 sec interval. Inner time of measurements in the PTR-MS is very short and equals to 0.2 ms. Thus, the probability of ISOPOOH decomposition on the walls inside the PTR-MS is negligible.

In the RACM-MIM scheme (Pöschl et al. 2000) the ISOPO2 + HO_2 reactions will look as follows:
\[ \text{ISOPO} + \text{OH} \rightarrow \text{ISOPO2} \]
\[ \text{ISOPO2} + \text{HO}_2 \rightarrow 2.0 \text{MACR}/\text{MVK} + \text{HO}_2 + \text{CH}_2O \]
\[ \text{ISOPO2} + \text{HO}_2 \rightarrow \text{ISOPOOH} \] \hspace{1cm} (S9)
\[ \text{ISOPOOH} + \text{OH} \rightarrow \text{MACR}/\text{MVK} + \text{HO}_2 + \text{CH}_2O \]

where MACR/MVK – methacrolein, methyl vinyl ketone and other C4 carbonyls. At the given scheme, there is the essential part of the MACR/MVK yield associated with interaction of ISOPOOH and OH.

In the MOZART scheme of the WRF-CHEM model (Emmons et al. 2010) via the HO_2-pathway both IEPOX (SOA), and MVK/MACR species were not predicted. The corresponded equations are below:
\[ \text{ISOPO} + \text{OH} \rightarrow \text{ISOPO2} \]
\[ \text{ISOPO2} + \text{HO}_2 \rightarrow \text{ISOPOOH} \] \hspace{1cm} (S10)
\[ \text{ISOPOOH} + \text{OH} \rightarrow 0.5 \text{XO2} + 0.5 \text{ISOPO2} \]

where XO2 is HOCH2C(OO)CH3CH(OH)CHO – peroxy radical from OH+HYDRAILD. At the reaction of an interaction of ISOPOOH with OH there is a recurrence on ISOPO2.

In the CIS scheme of the GEOS-CHEM (Paulot et al. 2012) the equations via the HO_2 pathway are:
\[ \text{ISOPO} + \text{OH} \rightarrow \text{ISOPO2} \] \hspace{1cm} (S11)
\[\text{ISOPOOH} + \text{OH} \rightarrow \text{IEPOX} + \text{OH}\]

The MVK and MACR yields via the HO\textsubscript{2}-pahway were only 7.3 % and 4.7 %, respectively (Paulot et al. 2012). The ISOPOOH yields via SOA (IEPOX) pathway was 88%.

S3. Rate constants and lifetimes for biogenic VOCs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Constants, cm\textsuperscript{3} molec.\textsuperscript{-1} s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>\text{k}_{\text{OH}} \times 10^{12}</td>
</tr>
<tr>
<td>Isoprene</td>
<td>101</td>
</tr>
<tr>
<td>Methyl vinyl ketone</td>
<td>18.8</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>33.5</td>
</tr>
</tbody>
</table>

\textsuperscript{1} All rate constants are taken from (Atkinson 1994).

References


