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Investigation of the β-pinene photooxidation by OH in the atmosphere simulation chamber SAPHIR

Martin Kaminski et al.

Correspondence to: Robert Wegener (r.wegener@fz-juelich.de)

Contents

1 Additional formation of HO_2 by photolysis of β-pinene reaction products

For the addition of a primary photolytic HO_2 source an artificial species Z was introduced in the model. Every reaction of β-pinene with OH produces one molecule of Z additional to the related RO_2 species. Equivalent to an aldehyde the photolysis of Z, which is the only sink of the molecule beside dilution, produces an equal amount of HO_2 and CO. The only well investigated product species is pinonaldehyde, a main degradation product of α-pinene. As stated by Jaoui and Kamens (2003) the photolytic loss of pinonaldehyde is an important part of its overall atmospheric chemistry, accounting for as much as the loss by the reaction with OH during daytime. Nevertheless the photolysis frequency of pinonaldehyde is very similar to the photolysis frequency of formaldehyde. With regard to recent literature (Moortgat et al. (2002); Wenger (2006)), in general linear chain $C_3 - C_9$ aldehydes and formaldehyde all have very similar photolysis frequencies. In contrast to that α-branched aldehydes as well as aldehydes of substituted aromatics show significantly higher photolysis frequencies (factor of 3-20). As it is unlikely that degradation products of β-pinene form aromatic structures the photolysis frequency of formaldehyde was considered as a good first estimate for the photolysis frequency of monoterpene degradation products in general. Therefore the photolysis frequency of Z is set to the photolysis frequency of the radical pathway of the photolysis of formaldehyde. To increase the HO_2 source strength the number of HO_2 and CO molecules produced per photolysis of one molecule of Z was increased stepwise. The blue curve in Fig. 1Comparison of the measured and modeled time series of β-pinene, OH, OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: modified MCM model by Vereecken and Peeters (2012) with additional photolytic source producing HO_2, Blue: modified MCM model with additional HO_2 formation by NO independent RO_2 rearrangement reactions, Green: modified MCM model with 50 % reduced yield of organic hydroperoxides ROOH, Orange: modified MCM model by Vereecken and Peeters (2012) with additional HO_2 source from radical cleavage and photolysis of intermediatesfigure.1 shows the model run assuming a production of six HO_2 and CO molecules per molecule Z which is in terms of chemical feasibility a rather unlikely but not impossible assumption. However, even if one takes into account the possibility of a photolytical cascade, a subsequent photolysis of the photolysis products, as proposed by Jaoui and Kamens (2003) for pinonaldehyde, a production of more than three molecules of HO_2 per molecule of β-pinene is rather unlikely. Nevertheless under this assumption the modeled HO_2^* and CO agree well with the measurements for the second half of the VOC phase. At the beginning of the VOC phase HO_2^* is still strongly underestimated because during that experimental phases there is still an insufficient amount of Z being built up yet (see Fig. 1Comparison of the measured and modeled time series of β-pinene, OH, OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: modified MCM model by Vereecken and Peeters (2012) with additional photolytic source producing HO_2, Blue: modified MCM model with additional HO_2 formation by NO independent RO_2 rearrangement reactions, Green: modified MCM model with 50 % reduced yield of organic hydroperoxides ROOH, Orange: modified MCM model by Vereecken and Peeters (2012) with additional HO_2 source from radical cleavage and photolysis of intermediatesfigure.1 blue curves). Therefore the modeled OH concentration rises later than in the model run, taking measured HO_2^* as input. Other modeled time series like RO_2^*, NO, NO_2, ozone and the β-pinene products acetone and nopinone stay nearly unchanged in comparison to the model run using measured HO_2^* as model input. The temporal behavior of modeled HO_2^* and OH clearly shows that adding a photolytical HO_2 source cannot be a reasonable explanation for the missing HO_2 production in the model. Especially in the first half of the VOC phase the HO_2 production is too low to explain the measured HO_2^* levels. Increasing the HO_2 production directly after the β-pinene injection would require a further increase in the photolysis frequency to unrealistically high values. Furthermore, the assumption that one molecule of Z has to produce six molecules of HO_2 and CO to match the measured HO_2^* level at the end of the VOC phase demonstrates that a missing photolytical source cannot be the sole explanation for the disagreement between measured and modeled HO_2^* in the second half of the VOC phase.

2 Additional formation of HO_2 by RO_2 conversion without the involvement of NO

In the second model run, displayed in blue in Fig. 1Comparison of the measured and modeled time series of β-pinene, OH, OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: modified MCM model by Vereecken and Peeters (2012) with additional photolytic source producing HO_2, Blue: modified MCM model with additional HO_2 formation by NO independent RO_2 rearrangement reactions, Green: modified MCM model with 50 % reduced yield of organic hydroperoxides ROOH, Orange: modified MCM model by Vereecken and Peeters (2012) with additional HO_2 source from radical cleavage and photolysis of intermediatesfigure.1, the impact of some chemical sources of HO_2 on the model are shown. To simulate the influence of unimolecular RO_2 rearrangements without changing the whole degradation mechanism a modification of the so called X-mechanism published by Hofzumahaus et al. (2009) was used. An NO like species X is thereby reducing RO_2 radicals to RO radicals. The rate constants applied for these reactions are the same as the rate coefficients of NO with the corresponding RO_2 radical. Contrary to the X-mechanism of Hofzumahaus et al. in case of β-pinene X is not reacting with HO_2 radicals. For the model run, shown in Fig. 1Comparison of the measured and modeled time series of β-pinene, OH, OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: modified MCM model by Vereecken and Peeters (2012) with additional photolytic source producing HO_2, Blue: modified MCM model with additional HO_2 formation by NO independent RO_2 rearrangement reactions, Green: modified MCM model with 50 % reduced yield of organic hydroperoxides ROOH, Orange: modified MCM model by Vereecken and Peeters (2012) with additional HO_2 source from radical cleavage and photolysis of intermediatesfigure.1 a constant concentration of 300 ppt of X was assumed during the VOC phase. The comparison of the modeled HO_2^* time series with the measurements shows that both time series are much better in agreement now, the measured HO_2^* is underestimated less than 25 %. With the increase of modeled HO_2^* also the modeled OH concentration increases and so agrees better with the measurements. In parallel the introduction of the new RO_2 loss pathway leads to a substantial decrease of the modeled RO_2^* concentration. The measured RO_2^* is now slightly underestimated by the model. Furthermore the new RO_2 loss pathway has a strong influence on the modeled time series of NO and NO_2. Both time series overestimate the measurements by up to 50 %. The reason for that is the reduction of organic nitrate formation. As the yield of organic nitrates is strongly depending on the carbon number (Koppmann, 2008) monoterpenes have relatively high nitrate yields, 18-26 % were reported for α-pinene (Nozière et al., 1999; Rindelaub et al., 2014). If one adds fast NO independent RO_2 rearrangement reactions to the model these reactions compete with the NO reaction of RO_2 radicals and thus with the organic nitrate formation. With the X-mechanism the organic nitrate formation is reduced by about a factor of two compared to the base model of Vereecken and Peeters. Another effect is a slightly increased nopinone formation in the model. Again the comparison of the measured time series with the model shows the limited applicability of unimolecular RO_2 reactions acting as HO_2 source. In contrast to a photolytic source fast unimolecular rearrangement reactions are able to partially explain the measured HO_2^* levels at the beginning of the VOC phase, but their influence on the organic nitrate yield leads to inconsistencies with the measured nitrogen oxide data.

3 Influence of a reduced rate constant for the $RO_2 + HO_2$ reaction on the modeled HO_2 concentration

The third sensitivity study (see the green curves in Fig. 1Comparison of the measured and modeled time series of β-pinene, OH, OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: modified MCM model by Vereecken and Peeters (2012) with additional photolytic source producing HO_2, Blue: modified MCM model with additional HO_2 formation by NO independent RO_2 rearrangement reactions, Green: modified MCM model with 50 % reduced yield of organic hydroperoxides ROOH, Orange: modified MCM model by Vereecken and Peeters (2012) with additional HO_2 source from radical cleavage and photolysis of intermediatesfigure.1) investigates the models response on a lower organic hydroperoxide yield. In the MCM 3.2 and the model of Vereecken and Peeters the ROOH formation is nearly exclusively determined by the rate constant $k_{RO_2+HO_2}$ which is applied to the majority of all RO_2 + HO_2 reactions. For the presented experiment $k_{RO_2+HO_2}$ was on average about 20.0 x $10^{-12}\,cm^3s^{-1}$. This value is in good agreement with rate coefficients for $RO_2 + HO_2$ reactions of hydroxy alkyl peroxy radicals generated from α-pinene, d-limonene and γ-terpinene. Boyd et al. (2003) reported k-values of (19.7 -21.1) x $10^{-12}\,cm^3s^{-1}$ with an uncertainty of 7 - 20 %. For biogenic RO_2 species in general Orlando and Tyndall (2012) proposed an average uncertainty of a factor of two for the rate constants of $RO_2 + HO_2$ reactions. In the present sensitivity study the rate constant was therefore reduced by 50 %. As a result the modeled HO_2^* concentration increases by 30 %, but HO_2^* is still underestimated by the model. Similar to HO_2^* also the modeled OH concentration slightly increases. The measured RO_2^* concentration is overestimated by a factor of two by the model. A reduction of the organic hydroperoxide formation pathway also leads to a good model description of the measured time series of NO and NO_2. The reason for this is that a reduction of $k_{RO_2+HO_2}$ automatically yields in an increased production of organic nitrates which act as a temporary or permanent sink for nitrogen oxides. The influence of the reduced ROOH formation on other model species is small. Acetone formation is still over predicted by the model by 20 %, nopinone formation is slightly overpredicted as well as the k(OH) decay. The measured time series of β-pinene and ozone are reproduced well. A reduction of the ROOH production may help to reduce the discrepancy between the modeled and measured HO_2^* concentration, but cannot solely explain the deviations between model and measurements.

4 Interference of alkene-derived RO_2 radicals

The interference of alkene-derived RO_2 radicals on the HO_2 measurements by LIF instruments is a well known measurement uncertainty in the determination of the HO_2 concentration (Fuchs et al., 2011; Nehr et al., 2011; Whalley et al., 2013). Before the monoterpene measurement campaign the Jülich LIF instrument was carefully characterized with regard to this interference. There average interference of primary RO_2 radicals formed by the reaction of monoterpenes with OH was determined to be 25 ± 10 % on average. This interference was incorporated in the displayed model curves for HO_2^* and RO_2^* in the modified MCM model (see the red curves). To exclude an impact of the RO_2 interference on the proposed missing HO_2 source a sensitivity study was carried out. For that the previously determined interference for primary RO_2s was doubled and applied on every RO_2 species in the model. The result of this sensitivity study is displayed in the blue model curves in Fig. 2Comparison of the measured and modeled time series of β-pinene, OH, OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: MCM 3.2, Blue: modified MCM model by Vereecken and Peeters (2012) with changed product yields, Green: modified MCM model by Vereecken and Peeters (2012) assuming an RO_2 interference of 50 % for the HO_2 measurementsfigure.2 . As one can see the enhanced RO_2 interference leads to 50 % increase in HO_2^*. But HO_2^* is still underestimated by 20-30 % in the model. Caused by the measurement principle of the LIF, determining the RO_2 concentration by subtraction of the HO_x from the RO_x signal, an increase in the modeled HO_2^* leads necessarily to a decrease in the modeled RO_2^* concentration. In comparison to the base run of the model of Vereecken and Peeters the modeled RO_2^* level drops by 50 % and the model now underestimates the measured RO_2^* concentration.

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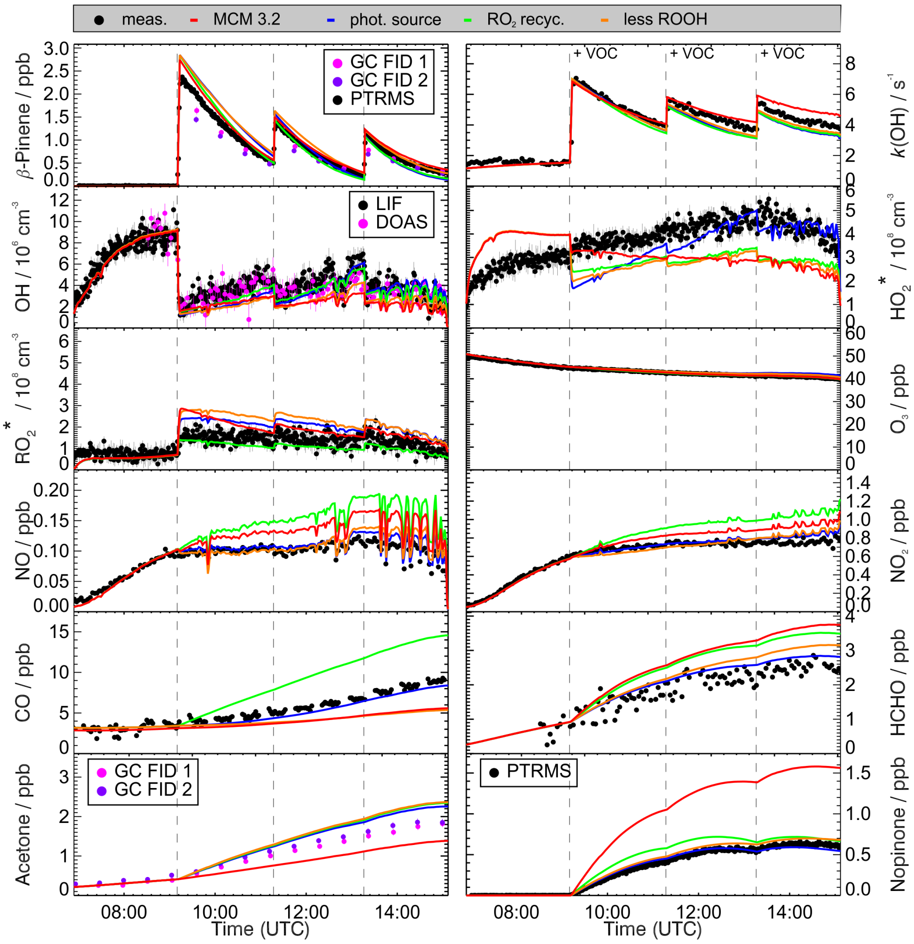

Figure 1: Comparison of the measured and modeled time series of β-pinene, OH, OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: modified MCM model by Vereecken and Peeters (2012) with additional photolytic source producing HO_2, Blue: modified MCM model with additional HO_2 formation by NO independent RO_2 rearrangement reactions, Green: modified MCM model with 50 % reduced yield of organic hydroperoxides ROOH, Orange: modified MCM model by Vereecken and Peeters (2012) with additional HO_2 source from radical cleavage and photolysis of intermediates.

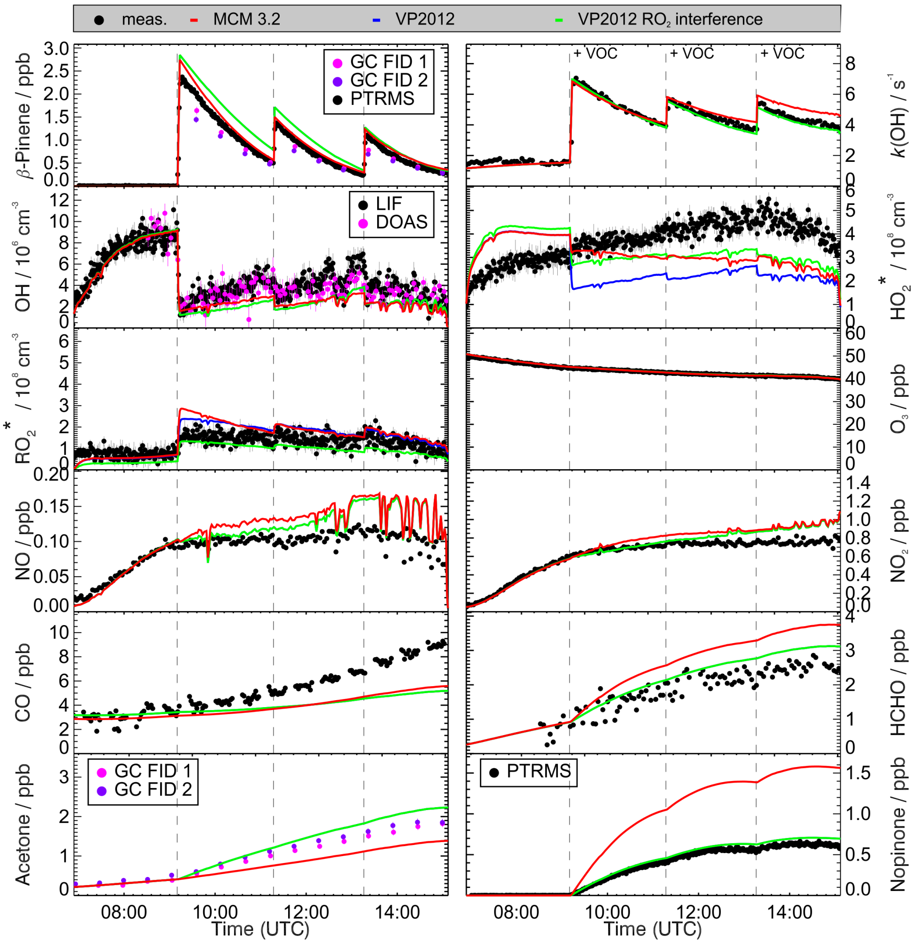

Figure 2: Comparison of the measured and modeled time series of β-pinene, OH, OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: MCM 3.2, Blue: modified MCM model by Vereecken and Peeters (2012) with changed product yields, Green: modified MCM model by Vereecken and Peeters (2012) assuming an RO_2 interference of 50 % for the HO_2 measurements.