



The α -Pinene Reaction with Hydroxyl Radicals: from Laboratory Measurements to the Application in the 3-D Model IMAGES

A contribution to subproject CMD

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Introduction

A major area of uncertainty in tropospheric chemistry is the role of the biogenic volatile organic compounds. In particular, the role of the terpenes is largely unknown, although their global emissions are believed to outweigh the anthropogenic emissions of non-methane hydrocarbons. While it is well established that the terpenes react initially with hydroxyl radicals, ozone and nitrate radicals, their further reaction paths still need to be elucidated in laboratory experiments.

Here a fast-flow reactor technique with its clean OH-radical source has been selected to investigate the α -pinene/OH reaction, because it allows to separate the α -pinene/OH reactions from the α -pinene/O₃ reactions. A reaction mechanism will be given explaining the formation and yields of the products formed. In addition, a more comprehensive mechanism for α -pinene oxidation has also been derived for use in a global 3-D model, in order to investigate the global impact of the terpenes. This mechanism which needs to be further developed attempts to describe the α -pinene degradation in terms of known reaction steps for smaller hydrocarbons.

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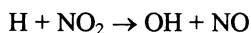
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Results and discussion

Fast-flow reactor experiments

The experimental conditions are as follows: the source of OH radicals is the reaction :



pressure range: 2–8 Torr He; time scale: 5–30 ms;

α -pinene: $(3\text{--}4) \times 10^{11}$ molec. cm^{-3} ; O_2 : $(0.26\text{--}7.9) \times 10^{16}$ molec. cm^{-3} ;
OH and NO: $(5\text{--}500) \times 10^{11}$ molec. cm^{-3} .

The experimentally determined product yields R of CO_2 , CO, NO_2 , acetone, pinonaldehyde, condensables are shown in Table 1. A reduced model including 23 reactions has been constructed to explain to a large extent the observed product yields (except for CO and CO_2).

Table 1: Product yields R of CO_2 , CO, NO_2 , acetone, pinonaldehyde condensables*.

	R(CO_2)	R(CO)	R(NO_2)	R(acetone)	R(pinald)	R(cond)
experiment	2.0 ± 0.4	1.8 ± 0.3	0.13 ± 0.1	0.18 ± 0.02	0.12 ± 0.6	n.m
calculated	0.12	0.17	0.16	0.15	0.29	0.09

* Condensable products: carvotanacetone, pinocamphone and campholenealdehyde

The essential features of the mechanism are the following:

- 1) The calculated yield for pinonaldehyde of 29% which falls within the error range of 31 ± 15 % reported previously (Vinckier *et al.*, 1998) can only be achieved when the isomerisation of the PIN.OH. O_2 -adduct directly leads to the formation of pinonaldehyde with regeneration of a hydroxyl radical. This path does not involve NO reactions. A pinonaldehyde yield of 31.5 ± 6 % has recently been determined by Nozière *et al.*, 1997 at NO_x -free conditions.
- 2) Mutual peroxy radical RO_2 reactions are too slow to influence the product yields.
- 3) The $\text{RO}_2 + \text{HO}_2$ reactions which are known to form hydroperoxides are too slow under the experimental conditions.

The extrapolation of the flow reactor results to atmospheric conditions should take into account the following restrictions:

- 1) Concerning the high hydroxyl concentrations, the only important condition to be fulfilled is that the initially formed α -pinene-OH adduct must react with molecular oxygen and that subsequent reactions of the adduct with hydroxyl radicals or nitric oxide are negligible.
- 2) The initial nitric oxide concentrations are of the same magnitude as the hydroxyl concentrations. In terms of atmospheric concentrations, this corresponds to tens of ppb which is unrealistically high for atmospheric conditions. However the fact that the measured product yields shown in Table 1 were not influenced by the nitric oxide concentrations indicates that at the time scale of milliseconds, nitric oxide reactions were too slow to be important or were rather leading to the formation of nitrite compounds.
- 3) A major difference between our flow reactor conditions and the atmosphere is the low oxygen concentration and reactor pressure. This implies for the oxygen that the alkoxy radicals formed in the $\text{RO}_2 + \text{NO}$ reaction mainly isomerise or decompose and that their reaction with oxygen can only account for a few percent of their destruction. The pressure effect is related to the stabilisation of the initially formed PINOH-adducts and the intermediate alkoxy radicals. Experiments at higher oxygen concentration and pressure are planned in the near future to check their effect on the measured product yields.

Modelling Study

Most current models of atmospheric chemistry either ignore the terpenes, or treat their chemistry in a very simplified way. This is partly attributable to the complexity and uncertainties associated with their emissions and chemistry. Furthermore, the recent estimate of their global emissions makes them *a priori* unlikely to play a significant role at the global scale, with less than 150 Tg/yr or about 11 % of the global source of biogenic hydrocarbons (Guenther *et al.*, 1995). Here we attempt to combine kinetic information obtained from recent laboratory studies with the Structural Activity Relationship (SAR) method to derive a new oxidation mechanism for α -pinene. Although our focus here is on the OH-initiated oxidation, the ozone and nitrate radical reactions were also considered. Our mechanism and results are still preliminary, as they are part of an on-going research. The primary objective at this stage is to identify the largest gaps and uncertainties in the mechanism in the perspective of its application in a 3-D model.

The first step is the derivation of an explicit mechanism for α -pinene oxidation, involving more than 35 chemical species in its current version. Regarding the OH-initiated oxidation, the main experimental data it is based on are the following:

- 1) Kinetic rate constants for α -pinene and pinaldehyde reactions with OH, O₃, NO₃ (Atkinson, 1994; Martinez *et al.*, 1997; Jensen *et al.*, 1997).
- 2) Photolysis cross section of pinaldehyde (Hallquist *et al.*, 1997).
- 3) The observation of pinaldehyde as a major product, with a yield on the order of 30–70% (Vinckier *et al.*, 1998; Hakola *et al.*, 1994; Hatakeyama *et al.*, 1991).
- 4) The observation of low aerosol yields in atmospheric conditions (*e.g.* Hoffmann *et al.*, 1997).
- 5) The observed formation of a stable PAN-like compound resulting from the OH and NO₃ initiated oxidation of pinaldehyde (Wängberg *et al.*, 1997).
- 6) The observation of acetone as a possible product (this study; Grosjean *et al.*, 1992)

The other constants and yields were derived using the SAR method and analogies with oxidation of lighter olefins. The resulting explicit mechanism is not robust for low-NO_x conditions, when hydroperoxide formation dominates the fate of peroxy radicals. These peroxides are considered, but the products of their OH reaction were assumed to consist primarily in species produced in high-NO_x conditions, an assumption that will require further investigation in the future. Another hypothesis is that, in contrast with the mechanism proposed above for the laboratory results, the α -pinene-OH adduct does not isomerise.

In a second step, the explicit mechanism was reduced by usual lumping procedures in order to fit into the mechanism of an existing 3-D model for tropospheric chemistry, the IMAGES model (Müller and Brasseur, 1995).

The emissions inventory of Guenther *et al.* (1995) is used in the model. The terpenes emissions are assumed to consist entirely of α -pinene. Dry deposition is considered for pinaldehyde, α PPN, and all hydroperoxides. The possible aerosol sink for these compounds has been neglected. The model was run for two years, with and without terpenes emissions, in order to investigate the possible impact of terpenes on the global tropospheric composition. The most relevant results are summarised below:

- 1) Average contributions to α -pinene sink: OH: 36 %, O₃: 50 %, NO₃: 14 %.
- 2) Average yield of pinonaldehyde: 35 %.
- 3) Global production of acetone: 13 Tg/year.
- 4) Impact on NO_x (= NO + NO₂): between –25 % (boreal PBL and tropical upper troposphere) and +15 % (remote tropical ocean and polar lower troposphere).

- 5) Impact on night-time NO_3 : -70 to -95 % in the summertime PBL over the emission areas, -50% over other continental areas.
- 6) maximum impact on surface O_3 : -15 % .

OH is calculated to be the main α -pinene oxidant over boreal forests, while ozone is by far more important than OH over Tropical forests. The calculated acetone yield might be overestimated, because of simplifications in the oxidation mechanism. Although the impact on globally averaged ozone and OH is small, α -pinene is seen to play a large role in the Planetary Boundary Layer (PBL) and even in the upper troposphere above the emission areas. The impact on NO_x is two-fold: a reduction in the vicinity of the emissions and an increase over remote areas, resulting from the formation of PAN-like compounds in the emission region. Finally, α -pinene is estimated to have a dramatic impact on night-time NO_3 concentrations.

Acknowledgements

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