Development of Monoterpene Oxidation Mechanisms: Results from Laboratory and Smog Chamber Studies

A contribution to subproject CMD

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Introduction

The atmospheric oxidation of biogenic VOCs and especially monoterpenes is still poorly represented in atmospheric chemistry models, if at all. Partly this is simply due to the fact that the mechanistic data base for the complex reactions of these compounds is only fragmentary. Whereas rate constants for the initiating reactions of the monoterpene oxidation with OH, NO_3 and O_3 are available, only a few main products have been reported for most of these reactions (*e.g.* pinonaldehyde from α-pinene). The carbon balance seldom exceeds 50 %.

The progress reported here, concentrates on the following aspects:

1. Formation of organic nitrates from the OH-initiated oxidation of some monoterpenes
2. Products from the reaction of several monoterpenes with O_3
3. Kinetics of the reaction pinonaldehyde + OH

Experimental

The experiments were carried out in conventional photoreactors in Wuppertal, with volumes from 400 to 1080 L, as well as in the European Photoreactor (EUPHORE), located in Valencia, Spain. This outdoor smog chamber consists of two hemispherical Teflon bags each having a volume of ~ 180 m^3 and a base diameter of 9.2 m. With their steel housings closed, the chambers were also used for the investigation of the dark reactions with O_3 and some of the kinetic

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experiments described in part 3. A detailed description of the photoreactor and the analytical equipment of EUPHORE is given elsewhere [Becker, 1996].

Results and discussion

1 Monoterpenes + OH: *formation of organic nitrates*

The reaction of peroxy radicals (RO_2) with NO can proceed by two reaction channels:

$$RO_2 + NO \longrightarrow RO + NO_2 \qquad (1a)$$

$$RO_2 + NO\ (+M) \longrightarrow RONO_2\ (+M) \qquad (1b)$$

Only channel (1a) leads to the production of ozone in the troposphere, whereas the nitrate forming channel (1b) is an important chain termination reaction and radical sink. Therefore, the branching ratios of these reactions, which vary strongly for different R, are an important input in tropospheric chemistry models.

Overall yields of organic nitrates from four different terpenes were measured in a 1080 L quartz-glass reactor using H_2O_2 photolysis as the OH source. The yields were estimated from the typical nitrate IR absorption around 1670 cm^{-1} using an average integrated absorption cross section of $(2.32 \pm 0.13) \times 10^{-17}$ cm $molecule^{-1}$ (base 10) (Wängberg, 1997). Nitrate yields around 25 % were obtained for α-pinene (24 %), β-pinene (25 %), limonene (23 %), and myrcene (29 %). These yields are in general agreement with literature values for other hydrocarbons, underlining the previously observed trend that the fraction of the nitrate forming channel (1b) increases with increasing size of the peroxy radical (LeBras, 1997).

2 Products from reactions of monoterpenes with O_3

Experimental

Experiments were carried out in a 1080 l reactor in Wuppertal (W) and in EUPHORE (E); $[\text{terpene}]_0 = 0.5–1$ ppm (excess over O_3), some experiments in the presence of cyclohexane as scavenger for OH radicals.

Analytical techniques

W) FTIR; E) FTIR, GC-FID (terpenes), HPLC (DNPH derivatisation of carbonyls), ozone monitor, differential mobility analyser (aerosols)

Table 1: Product yields from the ozonolysis of monoterpenes

Terpene	Products [% molar yields]				
α-pinene	pinon aldehyde [a]	formaldehyde	acetone	formic acid [a]	cyclohexanone [b]
	init.: 48 ± 5 final: 19 ± 7	15 ± 4	7 ± 2	2–6 (dry) 3–20 (4 mbar H_2O)	14 ± 3
Δ^3-carene	caronaldehyde[a] 44–15	16	9	1–10	
β-pinene	nopinon ~ 40	70	4	2–5	8
limonene	AMCH[c]/rndolim ~ 1 each	19	~ 2	3–10	15
myrcene	hydroxyacetone 19	26	29	< 1	9

a) The yields of these products showed a pronounced trend during the reaction
b) experiments in which cyclohexane was added; c) 4-acetyl-1-methylcyclohexene

The yields reported here for the pinenes and limonene are in reasonable agreement with literature values (Hakola *et al.*, 1994; Hatakeyama *et al.*, 1989). Remarkable, in the case of α-pinene, was the high yield of pinonaldehyde at the beginning of each reaction, constantly decreasing with time and progress of the reaction. This observation was made in the absence as well as in the presence of cyclohexane, which rules out any interference from OH radical reactions. The observed simultaneous increase of the aerosol yield, as shown in Fig. 1, indicates that this could be explained by a heterogeneous loss of pinonaldehyde to the aerosol phase. Interestingly, our pinonaldehyde yield measured at the end of the reaction is in remarkable agreement with the 19 ± 4 % reported from *Hakola et al.* (1994). A similar decrease of the yield was observed for caronaldehyde from Δ^3-carene.

Yields from the ozonolysis of myrcene are to our knowledge reported for the first time. Formaldehyde and acetone are two of the expected carbonyls, formed from decomposition of the primary ozonides. A possible mechanism for the formation of hydroxyacetone would involve either rearrangement or decomposition (followed by peroxy radical reactions) of the $(CH_3)_2COO$ Criegee intermediate.

Considerable yields of acetone, between 2 and 9 %, were observed also from the other terpenes investigated. This is of interest, as it might indicate a relevant source of acetone in the atmosphere. The global acetone budget is currently under discussion, as photolysis of acetone might be an important radical source in the free troposphere.

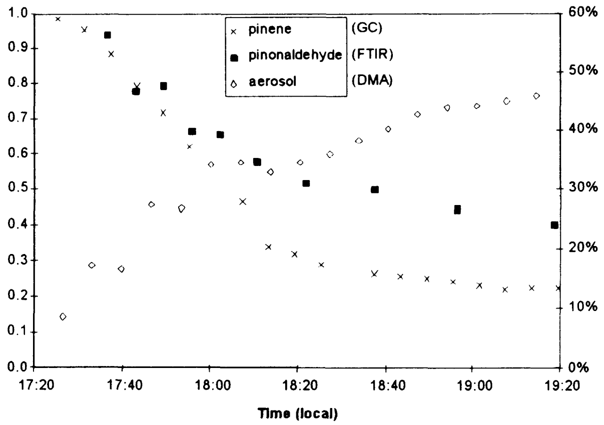

Fig. 1: Ozonolysis of 1000 ppb α-pinene in EUPHORE: Parallel decrease of gas-phase pinonaldehyde and increase of aerosol yield with reaction time

3 *Kinetic study of the reaction pinonaldehyde* + OH

Pinonaldehyde is the main product from the reactions of α-pinene with OH, NO_3 as well as O_3 (see Table 1). Further reaction of this important terpene oxidation product in the atmosphere will most likely occur via OH. We measured the rate constant of the reaction pinonaldehyde + OH → products (2) using two different experimental approaches, both relative rate methods.

a) Experiments in photoreactors in Wuppertal using conventional, photolytic OH-sources (CH_3ONO or H_2O_2), detection by long-path FTIR.

From experiments with different reference compounds (cyclohexane, isoprene, 1,3-butadiene) a value of $k_2 = (4.3 \pm 1.5) \times 10^{-11}$ cm^3 s^{-1} was obtained.

b) Experiments in EUPHORE using a dark source of OH, the ozonolysis of 2,3-dimethyl-2-butene (DMB).

The new OH-source had been tested in experiments in a 1080 l quartz reactor with a pair of hydrocarbons having well-known OH rate constants, cyclohexane and toluene. The relative rate constants from all experiments lay within 10 % of the ratio of the recommended rate constants

(k(toluene) / k(cyclohexane) = 0.83 (Atkinson, 1997).

In addition to the advantage of avoiding interferences from photolysis of pinonaldehyde (which was found to be fast in the experiments with the photolytic OH sources), both, pinonaldehyde and the reference compound cyclohexane were monitored by two independent analytical methods:

* FTIR and HPLC (DNPH-derivatisation) for pinonaldehyde

* FTIR and GC-FID for cyclohexane.

The relative decay curves monitored with the different methods agreed remarkably well. Values measured in three experiments ranged from 3.8–4.4 × 10^{-11} cm^3 s^{-1} with an average error (2σ) of ±1.3 × 10^{-11} cm^3 s^{-1} including all analytical methods.

Thus a combined value of $k_2 = (4.2 \pm 1.5) \times 10^{-11}$ cm^3 s^{-1} can be given from this study, in contrast to ~ 9 × 10^{-11} cm^3 s^{-1} published recently by two other groups (Glasius *et al.*, 1997; Hallquist *et al.*, 1997).

A possible explanation for the unusually high rate constant measured in these previous investigations could be an additional loss of pinonaldehyde to the aerosol phase as indicated in Fig. 1. In contrast, aerosol formation possibly had less influence in the present investigations, because they were carried out at much lower concentrations. Nevertheless, considerable aerosol formation was observed even at the very low concentrations used in EUPHORE.

Conclusions

* Organic nitrate yields of ~25 % from the OH-initiated oxidation of several monoterpenes
* Pinonaldehyde yields (from α-pinene + O_3) possibly underestimated before, due to loss on aerosols
* First products reported from myrcene + O_3
* Acetone (2–10 %) formed in the ozonolysis of all terpenes investigated
* Rate constant for pinonaldehyde + OH: $(4.2 \pm 1.5) \times 10^{-11}$ cm^3 s^{-1} (293 ± 6 K) (~ factor 2 lower than reported previously)

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