

**ANTHROPOGENIC AND BIOGENIC INFLUENCES ON
THE OXIDIZING CAPACITY OF THE ATMOSPHERE**

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SCIENTIFIC REPORT - 1997

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I. ABSTRACT

We know from the observational record that the composition of the troposphere changes, largely as a result of human activities, such as fossil fuel burning, biomass burning and land-use changes. Our main objective is to understand and to quantify these perturbations, and more specifically, to investigate how they interact with the natural environment. For that purpose, our work in this project is devoted 1/ to reduce the uncertainties in our understanding of the processes that determine the composition of the troposphere, and its oxidizing capacity in particular, and 2/ to use state-of-art models for the chemistry of the troposphere in order to estimate how the atmospheric composition has changed in the past, and will change in the future, as a result of human activities.

Both modelling and laboratory studies were conducted for these purposes.

First, the MOZART model, a new comprehensive chemistry-transport model for global tropospheric chemistry, is now operational. This model can be driven by either meteorological variables from a General Circulation Model or from analyses of observations. Two papers describing the model and its main results will be soon submitted. The next step will be now to couple this global model with an existing regional model. This task is already under way.

Anthropogenic emission distributions for the years 1850, 1990, 2015 and 2050 have been derived and used in the chemistry-transport model IMAGES, in order to investigate the possible evolution in the composition of the troposphere. The impact of the world aircraft fleet has been also estimated with the model, in the framework of the IPCC Special Assessment on Aviation. The results emphasize the growing importance of aviation on the global atmosphere, compared with the contributions of other human activities. They also show that the largest future changes in the chemical composition of the troposphere are expected to occur in the developing, tropical countries such as South and South-East Asia.

The IMAGES model has been also used to investigate the sources and sinks of important species controlling the oxidizing capacity of the atmosphere and the photochemical production of ozone. The global budgets and distributions of carbon monoxide and methane have been studied using a "tagging" technique designed to determine the impact of individual sources on the distributions of these species. A global budget of acetone has been derived using the model results and the observations. They imply a large biogenic component of its sources. The role of

acetone and of other possible "reservoirs" of odd hydrogen has been evaluated, with a special focus on the upper troposphere, in view of the large interest of this region in terms of ozone production (e.g. through the aircraft perturbation).

A major area of uncertainty in our understanding of the oxidizing capacity of the atmosphere is the role played by the of biogenic volatile organic compounds (BVOCs). 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. New laboratory studies are therefore required in order to unravel their reaction schemes. In this project, the fast-flow reactor technique has been adopted, because of its clean OH-radical source and because it makes possible to separate the terpene/OH reactions from the terpene/O₃ reactions (which occur simultaneously in the so-called smog chamber experiments). A problem encountered with this technique in the past, however, was the need for low pressures that made it difficult to extrapolate the results to real atmospheric conditions.

During 1997 the technique has been upscaled to pressures from 10 to 100 Torr by installing a new microwave discharge unit of the type Surfatron. First the efficiency of this OH-radical production source has been checked; it was found that the performance of this Surfatron is independent of the reactor pressure P_r . Secondly the influence of P_r , the oxygen concentration and the mixing of the reagents on the mass spectrometric sensitivity has been carefully investigated.

Besides this experimental work, a considerable effort has been devoted to elaborate a reaction mechanism explaining the formation of the majority of the reaction products observed in the α -pinene/OH/O₂/NO reaction. The mechanism includes 22 reactions and explains the observed product yields of pinonaldehyde, acetone, nitrogen dioxide and a number of condensables.

Finally, close interactions have been established between LPAC and IASB to derive a more comprehensive kinetic model for the photo-oxidation of α -pinene. A preliminary reaction mechanism has been incorporated in the 3-D chemical/transport model IMAGES. The model simulations show the potential significance of the terpenes in atmospheric chemistry. The possibility that the terpenes constitute an important source of acetone in the atmosphere has been investigated.

II. MOTIVATION

It is now well established from the observational record that the composition of the global troposphere changes, and that the causes for this evolution are mainly related to human activities, such as fossil fuel burning, biomass burning and land-use changes. The primary objective of this study is to understand and quantify these perturbations, and more specifically, to investigate how they interact with the natural environment. An example of these complex interactions we want to focus on is the role played by biogenic emissions in the context of the anthropogenic perturbations. Another important objective is to give some insight on how we think that the chemical composition changes can affect the climate and the biosphere, for example through the radiative impact of tropospheric ozone and methane, or through the impact of increased nitrogen deposition on the continental biosphere.

A radiatively important trace gas such as ozone is controlled in the troposphere by chemical processes involving a large number of other chemical compounds, the so-called ozone precursors (e.g. nitrogen oxides and hydrocarbons). These processes also determine the atmospheric residence time of methane, another important "greenhouse gas". An important milestone of our work is therefore the quantification of the budget of the most important ozone precursors: nitrogen oxides (NO_x), methane (CH_4), carbon monoxide (CO), and non-methane hydrocarbons (NMHC). This can be achieved by the confrontation of the results of state-of-the-art chemistry-transport models of the troposphere with available observations of these gases. It also requires a better understanding of the chemical processes involved in ozone production.

In this respect, the upper troposphere deserves a special attention. This is indeed the region of the atmosphere where ozone is most effective as a greenhouse gas. It is also a region where nitrogen oxides are particularly effective in producing ozone. These facts led to a raising concern that emissions of NO_x by aircraft could significantly perturb the chemical composition of the atmosphere and the Earth's climate. Besides the role of NO_x , however, ozone production is also determined by the supply of odd hydrogen (HO_x). Recent work has indicated that the transport of various " HO_x reservoirs" from the lower troposphere could greatly enhance the upper tropospheric HO_x levels, and therefore also the perturbation caused by aircraft emissions. Sources that have been proposed recently include the photolysis of acetone and peroxides transported from the lower troposphere. These processes, however, are currently not completely understood. The acetone budget, in particular, needs to be better quantified. Our objective include the precise quantification of the

HO_x sources in the upper troposphere and the role played by species such as acetone and other oxygenated organics.

Another major area of uncertainty is the role played by the biogenic NMHCs. While the chemistry of isoprene (the single most important of these compounds) has been the subject of many studies and is now relatively well understood, the role of the monoterpenes is largely unknown, although their global emissions are believed to outweigh the anthropogenic NMHC emissions. Our goal is to conduct both laboratory and modelling studies in order to reduce the uncertainties associated with the chemical oxidation of the terpenes in real atmospheric conditions. A major difficulty in that respect is the extrapolation of the laboratory results to the atmosphere, because of the formidable complexity of the terpenes/oxidant system and because of the difficulty to reproduce the real atmospheric conditions in the laboratory. A special focus of this study is the investigation of the possible acetone production resulting from the oxidation of terpenes.

III. METHODS AND PRELIMINARY RESULTS

1. Model developments

The development of the MOZART (Model for Ozone and Related Trace Gases) model is almost completed. MOZART is now available under two versions: a version where the transport of trace gases is driven by a General Circulation Model (the NCAR CCM), and a version where the dynamical fields (including the winds, the boundary layer and deep convection) are taken (or calculated) from an analysis of the observations (the ECMWF/NCEP winds). A module for the consistent calculation of dry deposition velocities and biogenic emissions from the meteorological variables used in MOZART has been completed. The wet deposition scheme of the model is also consistent with the meteorology used in the model, and has been validated using the radio-isotope ²¹⁰Pb. The results of MOZART for ozone and its main gaseous precursors have been validated by an extensive comparison with available observations. The overall performance of this model is found to be very good. Two papers will be soon submitted, that describe the model as well as its main results.

2. Modelling the changes in the composition of the troposphere

Geographical distribution maps for the anthropogenic emissions of trace gases in the year 2050 have been derived from the IPCC standard scenario. These future projections account for the probable increase in population and energy consumption

in the future, as well as for the expected decrease in the emissions associated with emission regulations and controls. These emissions have been fed into the tropospheric chemistry/transport model IMAGES in order to estimate the future changes in the composition of the troposphere. The results emphasize the expected large role of South East Asia and the developing world in general in the future. The radiative forcing associated with the increased ozone concentrations has been estimated to be about half the change between the pre-industrial era and the present times.

As part of the international effort to better determine the impact of aviation on the composition and the climate, we also calculated the perturbation in the ozone concentrations associated with the current fleet and with projected future (2015 and 2050) fleet. These perturbations were also compared with the changes that can be expected from the increase in the surface emissions. A remarkable result from the intercomparison exercise is a very good agreement between the different models involved. These results will be published in the forthcoming IPCC Special Assessment on Aviation.

3. Role of acetone and other organics in the upper troposphere

The emissions and chemistry of acetone has been introduced in the IMAGES and MOZART models. IMAGES has been used to derive a global budget of acetone consistent with the observations. It is found that a large biogenic source (23 Tg/yr or almost half the total source of about 55 Tg/yr) is needed to explain the observations. This source is believed to consist in primary biogenic emissions and production by the oxidation of other biogenic NMHCs, including terpenes.

IMAGES was also used in order to quantify the sources of odd hydrogen (HO_x) in the upper troposphere. Although the photolysis of ozone, followed by reaction of O^1D with water vapor is the largest source of HO_x in many areas (30-70% in the regions where most aircraft fly), other sources such as acetone oxidation and the transport and oxidation of lower tropospheric peroxides and aldehydes are also important. An interesting finding is the unexpected importance of aldehydes over most tropical regions.

4. Kinetic model for the α -pinene/OH/O₂/NO reaction

Since the oxidation of terpenes cannot be studied in situ, atmospheric conditions are simulated in a fast-flow reactor where hydroxyl radicals are generated by means of a microwave induced plasma. This technique has the major advantage that it allows to investigate terpene/hydroxyl radical reactions without interference of ozone reactions. Initial hydroxyl radical concentrations are a factor 10^5 higher than in the

atmosphere but this is compensated for by a much shorter reaction time in the order of milliseconds. Before the reaction product yields derived by this technique can be applied and used in atmospheric chemistry models, the reaction conditions have to be checked and the reaction rates must be related to those occurring under real atmospheric circumstances.

A reduced model has now been developed explaining to a large extent the observed product yields of the α -pinene+OH reaction (except for CO and CO₂). The reaction scheme is shown in Table I. The essential features of the mechanism (see Table I) are the following:

1. A pinonaldehyde yield of 30% as calculated (Vinckier et al., 1997) can only be achieved when the isomerisation of the PIN.OH.O₂-adduct directly leads to the formation of pinonaldehyde with regeneration of a hydroxyl radical. This path does not involve NO-reactions and thus corresponds to atmospheric conditions in remote areas and "smog chamber" experiments in the absence of NO. Here also a pinonaldehyde yield of $31.5 \pm 6\%$ has recently been determined (Nozière et al., 1997). In addition pinonaldehyde is a very reactive compound and can be treated under steady state conditions which allows lumping of a number of reactions.
2. Isomerisation reactions of the PIN.OH-adduct followed by a H-atom abstraction reaction may result in the formation of pinocamphone, campholene aldehyde and carvotan acetone, major condensable species determined in this study.
3. Mutual peroxyradical RO₂ reactions are too slow to influence the product yields.
4. The importance of RO₂ + HO₂ reactions which are known to form hydroperoxides RO₂H are too slow under our experimental conditions when a rate constant of the order of 10^{-11} molecule⁻¹ cm³ s⁻¹ is adopted.
5. The nitrogen dioxide yield of 0.13 is very low which is in agreement with the low ozone formation potential recently observed in smog chamber experiments (Hjort et al., 1997).

Table I

	rate constants (cm ³ molecule ⁻¹ sec ⁻¹)
(1) H + NO ₂ → OH + NO	1.3E-10
(2) OH → wall	1.5E+01 (sec ⁻¹)
(3) OH + OH → H ₂ O + O	1.8E-12
(4) O + OH → H + O ₂	3.3E-11
(5) H → wall	8 (sec ⁻¹)
(6) C ₁₀ H ₁₆ + OH → PINOH	5.7E-11
(7) C ₁₀ H ₁₆ + O → PINO	2.8E-11
(8) PINOH + O ₂ → HO ₂ + carvotan acetone	5E-12
(9) PINOH + O ₂ → HO ₂ + pinocamphone	5 E-12

(10) PINOH + O ₂ → HO ₂ + camfolenealdehyde	5E-12
(11) PINOH + O ₂ → PINALD + OH	3E-11
(12) PINOH + O ₂ → CO + CO + PROD1	1E-11
(13) PINOH + O ₂ → CO ₂ + PROD2	3E-11
(14) PINALD + OH → C ₁₀ H ₁₅ O ₂ + H ₂ O	9.1E-11
(15) C ₁₀ H ₁₅ O ₂ + NO → NO ₂ + PROD3	9E-12
(16) C ₁₀ H ₁₆ → wall	3 (sec ⁻¹)
(17) CO + OH → CO ₂ + H	2.4E-13
(18) PINOH + O ₂ → PINOHO ₂ '	5E-11
(19) PINOHO ₂ ' + NO → NO ₂ + acetone + PROD4	6E-11
(20) PINOH + O ₂ → PINOH.O ₂	3E-12
(21) PINOH.O ₂ + NO → NO ₂ + PINOH.O	9E-12
(22) PINOH.O + O ₂ → HO ₂ + PINALD	7.5E-15

In Table I no combination reactions of RO₂ radicals with NO or NO₂ have been taken into account. Part of the missing carbon though in the overall carbon balance might be due to the formation of peroxy nitrates but these compounds could not be detected by GC-MS. It should also be pointed out that the observed acetone yield of 0.18 indicates that a direct path is required for its formation not involving the pinonaldehyde as an intermediate. In order to calculate the yields of CO and CO₂ the further degradation paths of the PROD1 to PROD4 have to be elaborated.

5. Fast-flow reactor study

In the past the microwave discharge technique, used to produce hydrogen atoms as precursors for the hydroxyl radicals, could only operate in a pressure range from 0.5 to 12 Torr. This limitation was a major drawback of the fast-flow reactor technique since the results had to be relevant for atmospheric conditions. Therefore, a specially designed microwave cavity Surfatron that can operate at pressures up to 100 Torr had first to be installed and tested. Before studying the reaction between α -pinene and OH-radicals at higher pressures, the dissociation yield of the new microwave discharge had to be measured. Secondly the influence of several experimental or instrumental parameters (reactor pressure, oxygen concentration, mixing of the reagents) on the mass spectrometric sensitivity and the detection limits had to be determined.

2.a. Yield of the microwave discharge

It was seen that compared to pyrex, a fused quartz tube carrying the Surfatron cavity enhanced the dissociation yield with more than an order of magnitude. Below a

reactor pressure P_r of 50 Torr, the power of the microwave discharge had no effect and only at 100 Torr the dissociation yield increased from 50 % at 30 Watt to 80 % at 70 Watt. Finally the importance of the hydrogen atom loss on the reactor wall could be verified by following its concentration as a function of the axial distance d : only a small loss was observed between $d=5$ and 35 cm. In this case the OH-concentration is independent of the axial location where the radicals are produced.

2.b. Mass spectrometric sensitivity

Various parameters having an influence on the ion signal intensities and sensitivities had also to be checked. As is logical it was found that ion signal ($m/z = 93$) of the dominant α -pinene fragmentation peak is directly proportional with the He flow sent across the α -pinene vessel. Also the sensitivity of α -pinene remained constant within 15 % when P_r was varied between 2 and 50 Torr.

2.c. Calibration

In this project a quantitative determination of the volatile products formed in the reaction has to be carried out. The components α -pinene, NO_2 , CO_2 , CO and acetone were followed on-line by means of mass spectrometric detection. Generally, an experiment consists of 4 main steps :

- 1) In a blank experiment a mass scan is performed when all the reagents (α -pinene, NO_2 , O_2 and bath gas helium) except for H_2 were present with the discharge turned on.
- 2) Next, this procedure was repeated in the presence of H_2 . So OH-radicals can be formed and the reaction with α -pinene can start and the signals of the compounds formed can be measured. Calibration factors are needed to convert these signals into concentrations. After correction for the background, the net product yields can be calculated being the ratio of the concentration of the product formed to the amount of α -pinene reacted.
- 3) In a third step, the discharge was turned off and H_2 was removed. The signals of α -pinene and NO_2 were then followed in order to determine their calibration factors.
- 4) Since for both compounds also a blank is needed, the flows of α -pinene and NO_2 were turned off in a last step (only O_2 and He present).

It was seen that the sensitivity remained nearly constant over the entire pressure range between 2 and 100 Torr which confirms the results mentioned sub 2.b.

Another parameter deals with the effect of the oxygen concentration on the sensitivity. Almost independent of P_r , the sensitivity decreased with about 50 % when increasing the oxygen fraction from 0.32 to 20 %.

2.d. Detection limits and interference's

Impurities in the reagents may lead to two problems. When the carrier gas He contains traces of O_2 , it leads to O-atom formation in the discharge and thus unwanted O-atom reactions. In addition high blank signals for CO were observed

indicating interference of N_2 at the same m/z . To get rid of both problems He with a purity of 99.996 (N56) will be used in the future.

2.f. Product yields

A series of product yield determinations have been carried out for acetone, CO, CO_2 and NO_2 at the pressures of 2, 10, 20, 50 and 100 Torr. Apparently the initial OH-concentrations were not well established which resulted in a poor reproducibility and large fluctuations in the day to day measurements.

6. Role of terpenes in atmospheric chemistry

The role of α -pinene in the atmosphere has been tentatively studied using the IMAGES model. A reduced chemical mechanism for its oxidation by OH, O_3 and NO_3 has been derived from the (limited) available laboratory data and from the SAR (Structural Activity Technique) method, as part of a collaboration with Pr. J. Peeters of the K.U.Leuven (Laboratory of Physical and Analytical Chemistry). Although the derived mechanism should be considered with caution, it is a useful starting point for future studies. Its implementation in the IMAGES model indicate a large importance of organic hydroperoxides formation in the oxidation of terpenes. The model results also suggests that terpenes generally deplete both ozone and hydroxyl concentrations. More importantly, the simulations indicate that a potentially large production of acetone might result from the oxidation of α -pinene in the atmosphere.

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