Organic Aerosol Formation from the Oxidation of Bornyl Acetate with Hydroxyl Radicals

Guest contribution

C. Coeur, V. Jacob, P. Foster and P. Baussand

Laboratoire GRECA (Groupe de Recherche sur l'Environnement et la Chimie Appliquée), 39-41 Bvd. Gambetta, 38000 Grenoble, France

The gas phase reaction of bornyl acetate (1,7,7-trimethyl-bicyclo[2,2,1]-heptan-2-ol-acetate), VOC emitted by Mediterranean trees (orange and mandarin trees), with hydroxyl radicals has been studied in a smog chamber. It was found that the reaction of bornyl acetate with OH radicals leads to organic aerosols. The chemical composition of the aerosol was studied. On the basis of mass spectral data, 1,7,7-trimethyl-6-acetyloxy-bicyclo[2.2.1]-heptan-2,3-dione has been identified in irradiated CH_3ONO–NO–air–bornyl acetate mixtures. The aerosol carbon yield, the fraction of the carbon initially present that is converted to aerosol, has been estimated to be ≈ 5 %.

Introduction

Terrestrial vegetation releases a variety of reactive organic compounds into the atmosphere, including isoprene, monoterpenes, sesquiterpenes, alcohols, esters, ethers, ketones, aldehydes, alkanes, alkenes and aromatics (Isidorov *et al.*, 1985; Lamb *et al.*, 1985; Winer *et al.*, 1992; Guenther *et al.*, 1995; Kesselmeier *et al.*, 1996). The total annual global emission of biogenic hydrocarbons has been estimated to be between 825 and 1150 Tg $C.yr^{-1}$ (Feshenfeld *et al.*, 1992; Guenther *et al.*, 1995).

Understanding the degradation pathways of biogenic hydrocarbons represents an important current problem in atmospheric chemistry. For example, there is substantial evidence that biogenic hydrocarbons influence the regional distribution of ozone (MacKeen *et al.*, 1991a; 1991b; Chameides *et al.*, 1992; Simpson 1995; Trainer *et al.*, 1995; Vogel *et al.*, 1995). Moreover, one of the major uncertainties of the impact of biogenic hydrocarbons on atmospheric processes is the quantitative understanding of their ability to form organic aerosols (Went 1960; Kamens *et al.*, 1981; Hooker and Westberg, 1985; Hatakeyama *et al.*, 1989, 1991; Pallen *et al.*, 1991; Pandis *et al.*, 1992; Zang *et al.*, 1992).

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The principal goal of this study, is to characterise the organic aerosols formed from the gas-phase reaction of bornyl acetate with OH radicals, and to evaluate the aerosol forming potential of this biogenic compound. Bornyl acetate was observed from emissions of a number of agricultural crops and natural vegetation. The major tropospheric loss process of this compound is expected to be the reaction with hydroxyl radical (Coeur *et al.*, in press).

Experimental description

The experiments were performed in a ≈ 2000 L evacuable wall coated Teflon smog chamber at atmospheric pressure, 294 ± 2 K and moderate relative humidity (5–10 %). Hydroxyl radicals were generated by the photolysis of methyl nitrite in air and NO was added to the reactant mixture to avoid the formation of O_3 and hence of NO_3 radicals (Atkinson *et al.*, 1981).

Aerosol formation was monitored continuously during the experiments with an optical particle counter (OPC model MPC 301X - Malverne). The OPC operated in concentration mode. This mode gives a quick calculation of the particle concentration within a defined volume of air. In selected experiments, bulk aerosol samples were collected on glass fiber filters, dissolved into ethanol and subsequently analysed by gas chromatography - mass spectrometry.

Aerosol yields

The aerosol yield from photo-oxidation of hydrocarbon can be expressed in several ways. The aerosol volume concentration, $V_{(t)}$, (expressed in $\mu m^3\ cm^{-3}$), can be used directly to calculate the aerosol volume yield per unit concentration of primary hydrocarbon, $Y_{(t)}$, (expressed in $\mu m^3\ cm^{-3}\ ppm^{-1}$), as follows :

$$Y_{(t)} = V_{(t)} / ([HC]_0 - [HC]_{(t)}) \qquad (1)$$

where $[HC]_0$ is the initial concentration of hydrocarbon, and $[HC]_{(t)}$ is the hydrocarbon concentration at reaction time *t*, expressed in ppm.

The fraction of a particular hydrocarbon that is converted to aerosol can also be expressed on a mass or carbon concentration basis. Izumi *et al.* (1988) measured the aerosol generated from photo-oxidation of various hydrocarbons, and correlated the mass concentration of aerosol organic carbon, $[AOC_{(t)}]$ (expressed in pg C cm^{-3}), to aerosol volume concentration, $V(t)$ (expressed in $\mu m^3\ cm^{-3}$), as:

$$[AOC_{(t)}] = C \times V(t) \qquad (2)$$

where $[AOC_{(t)}]$ is the mass concentration of aerosol organic carbon (expressed in pg C cm^{-3}), and C represents the aerosol carbon density which was found to be largely independent of the particular hydrocarbon ($C = 0.49 \pm 0.02$ pg C m^{-3}).

The dimensionless aerosol organic yield, Y_c, the fraction of the carbon initially present that is converted to aerosol can then be obtained from equations (1) and (2) as :

$$Y_c = [AOC_{(t)}] / \{f_c \times ([HC]_0 - [HC]_{(t)})\} \qquad (3)$$

where f_c is a constant to convert hydrocarbon concentration in ppm, into carbon mass concentration, in pg C cm^{-3}. For bornyl acetate at 1 atm and 298 K, $f_c = 5890$ (pg C $cm^{-3}.ppm^{-1}$, or μg C m^{-3} ppm^{-1}).

A typical evolution of the number aerosol concentration is depicted in Fig. 1.

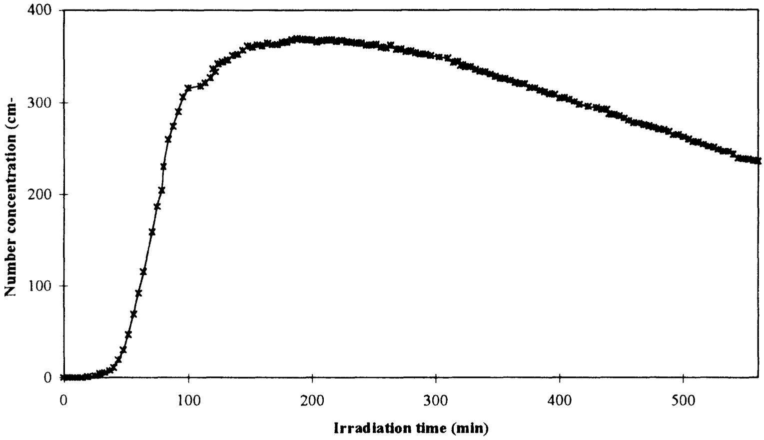
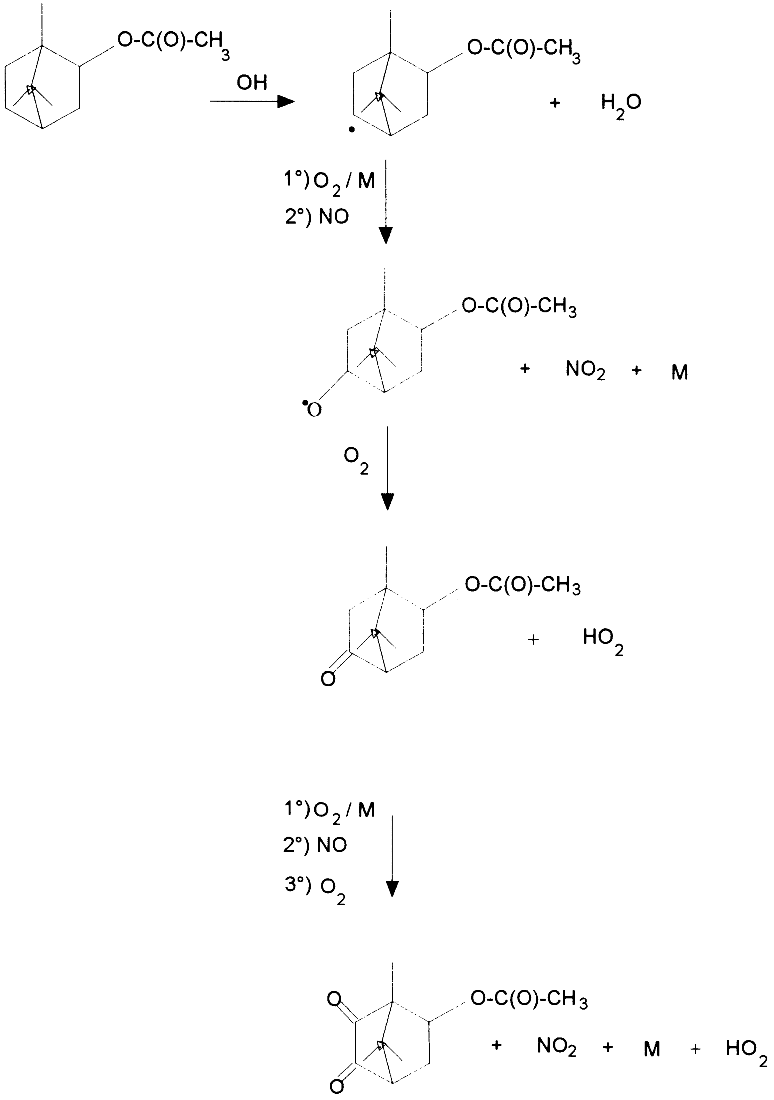


Fig. 1: Number concentration of aerosol versus the irradiation time.

The yield is initially zero, as condensable material is produced and accumulates in the gas phase. After 20 min of reaction, the concentration of condensable material reaches a critical supersaturation and nucleation begins. The yield reaches a maximum value and starts declining after 3 hours due to wall losses. The aerosol carbon yield for that experiment remains under 5% and is reached after 0.17 ppmv of bornyl acetate has reacted.

Aerosol characterisation

The GC-MS analysis of an aerosol generated from the gas-phase reaction of OH radical with bornyl acetate shows the presence of a variety of products, the majority of which could not be clearly identified. However, 1,7,7-trimethyl-6-acetyloxy-bicyclo[2.2.1]-heptan-2,3-dione has been identified as bornyl acetate aerosol. For the justification of its formation, a reaction scheme is proposed in Fig. 2.



1,7,7-trimethyl-6-acetyloxy-bicyclo[2.2.1]-heptan-2,3-dione

Fig. 2: Reaction scheme explaining the formation of 1,7,7-trimethyl-6-acetyloxy-bicyclo[2.2.1]-heptan-2,3-dione.

Conclusions

Aerosol formation has been studied in the bornyl acetate/CH_3ONO/NO/air systems in a smog chamber. The aerosol carbon yield remained under 5 % for initial concentration of bornyl acetate as high as 200 ppb. The measured bornyl acetate aerosol yield can be explained by the formation of condensable species with relatively low vapour pressure. 1,7,7-trimethyl-6-acetyloxy-bicyclo[2.2.1]-heptan-2,3-dione has been identified as bornyl acetate aerosol.

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