Product Formation from the Gas-Phase Reactions of OH Radicals and O_3 with a Series of Monoterpenes

HANNELE HAKOLA¹, JANET AREY²*, SARA M. ASCHMANN, and ROGER ATKINSON²
Statewide Air Pollution Research Center, University of California, Riverside, CA 92521, U.S.A.

(Received in final form: 14 April 1993)

Abstract. The formation yields of nine carbonyl products are reported from the gas-phase OH radical-initiated reactions (in the presence of NO_3) and the O_3 reactions with seven monoterpenes. The products were identified using GC/MS and GC-FTIR and quantified by GC-FID analyses of samples collected on Tenax solid adsorbent cartridges. The identities of products from camphene, limonene and β-pinene were confirmed by comparison with authentic standards. Sufficient quantities of products from the 3-carene, limonene, α-pinene, sabinene and terpinolene reactions were isolated to allow structural confirmation by proton NMR spectroscopy. The measured total carbonyl formation yields ranged from non-detectable for the OH radical reaction with camphene and the O_3 reactions with 3-carene and limonene to ~0.5 for the OH radical reaction with limonene and the O_3 reaction with sabinene.

Key words. Monoterpenes, OH radical reactions, O_3 reactions, carbonyl products.

1. Introduction

A large number of individual organic compounds, including a series of C_{10}H_{16} monoterpenyl hydrocarbons, are emitted into the atmosphere from vegetation (see, for example, Rasmussen, 1972; Zimmerman, 1979; Tingey et al., 1979, 1980; Evans et al., 1982; Isidorov et al., 1985; Lamb et al., 1985; Arey et al., 1991a, b, c; Guenther et al., 1991; Corchnoy et al., 1992; Winer et al., 1992). Although there are many uncertainties in the overall biogenic non-methane organic emissions inventory (Lamb et al., 1987), the monoterpenyl hydrocarbons are known to be an appreciable fraction of the biogenic emissions (Lamb et al., 1987; Zimmerman et al., 1988). Estimates of the origins of the nonmethane organic compounds present in the atmosphere have suggested that in the U.S.A. biogenic emissions are comparable to anthropogenic sources (Lamb et al., 1987), and worldwide greatly exceed inputs from human activities (Logan et al., 1981; WMO, 1992).

* Author to whom correspondence should be addressed.
¹ Visiting Scientist; present address: Air Quality Department, Finnish Meteorological Institute, SF-00810 Helsinki, Finland.
² Also Department of Soil and Environmental Sciences, University of California, Riverside, CA 92521, U.S.A.
The monoterpenes are highly reactive towards OH and NO₃ radicals and O₃, and rate constants at room temperature for these reactions are now available for 14 common monoterpenes (Atkinson, 1989, 1991, 1994). However, there are less data available concerning the products of these reactions and the reaction mechanisms under atmospheric conditions (Gäb et al., 1985; Yokouchi and Ambe, 1985; Hatakeyama et al., 1989; 1991; Jay and Stieglitz, 1989a; Kotzias et al., 1989, 1991; Arey et al., 1990; Barnes et al., 1990; Becker et al., 1990; Hewitt and Kok, 1991; Pandis et al., 1991; Simonaitis et al., 1991; Grosjean et al., 1992; Hakola et al., 1993). To date, the only quantitative product yield data arise from the studies of Hatakeyama et al. (1989, 1991) concerning the reactions of OH radicals and O₃ with α- and β-pinene, Arey et al. (1990) for the reactions of the OH radical with α- and β-pinene, 3-carene, limonene, myrcene, sabinene and terpinolene, and Hakola et al. (1993) for the reactions of the OH radical and O₃ with β-phellandrene. Carbonyl compounds were the major products observed (Hatakeyama et al., 1989, 1991; Arey et al., 1990; Hakola et al., 1993), although several of those observed by Arey et al. (1990) were tentative identifications based on mass spectral data because of the lack of commercially available standards. Moreover, the reported carbonyl formation yields from the OH radical reactions of α- and β-pinene show significant discrepancies (Arey et al., 1990; Hatakeyama et al., 1991; Atkinson, 1994).

Recently, we developed and tested an experimental technique which allows sufficient amounts of the products formed in these reactions to be collected and purified for proton NMR identification (Hakola et al., 1993). In this work, we have extended our previous product study of the gas-phase reactions of β-phellandrene with OH radicals and O₃ (Hakola et al., 1993) to include the products formed from α- and β-pinene, limonene, 3-carene, camphene, sabinene and terpinolene.

2. Procedure

The reactions of the monoterpenes with OH radicals and O₃ were carried out in a 6400 liter all-Teflon chamber equipped with two parallel banks of blacklamps for irradiation (Arey et al., 1990; Hakola et al., 1993). All reactions were carried out at 297 ± 2 K and at 740 Torr total pressure of pure air. As detailed below, combined gas chromatography-mass spectrometry (GC/MS) was used to confirm the identity of the products quantified by gas chromatography with flame ionization detection (GC-FID) from the OH radical and O₃ reactions and also to verify that the products when purified for analysis by ¹H NMR were unchanged.

2.1. Product Quantification from Small Volume Samples

As described previously (Arey et al., 1990; Hakola et al., 1993), OH radicals were generated by the photolysis of methyl nitrite (CH₃ONO) in air at wavelengths >300 nm,