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Products of the OH radical-initiated reactions of 2-propyl nitrate, 3-methyl-2-butyl nitrate and 3-methyl-2-pentyl nitrate

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ABSTRACT

In the atmosphere, alkyl nitrates formed from the reactions of alkyl peroxy radicals with NO are chemically removed by photolysis and by reaction with OH radicals. Products of the gas-phase reactions of OH radicals with 2-propyl nitrate, 3-methyl-2-butyl nitrate and 3-methyl-2-pentyl nitrate at room temperature have been investigated. The products observed and quantified were: from 2-propyl nitrate, acetone (58 ± 18%); from 3-methyl-2-butyl nitrate, acetaldehyde (113 ± 39% from gas chromatographic analyses and 70 ± 25% from FT-IR analyses), acetone (55 ± 8%), and 3-methyl-2-butanone (17 ± 2%); and from 3-methyl-2-pentyl nitrate, acetaldehyde (120 ± 26% from gas chromatographic analyses and 80 ± 21% from FT-IR analyses), propanal (≤1.1%), 2-butanone (33 ± 3%), 2-methylbutanal (≤1.1%), and 3-methyl-2-pentanone (9 ± 1%), where the percentage molar yields are given in parentheses. Using these measured product yields together with predicted reaction schemes indicates that these products account for 58 ± 18%, 86 ± 15% and 63 ± 7% of the overall reaction pathways of the 2-propyl nitrate, 3-methyl-2-butyl nitrate and 3-methyl-2-pentyl nitrate reactions, respectively. The NO_2 present in the $-ONO_2$ group in these nitrates will be released in the reaction pathways leading to the observed products.

1. Introduction

Organic nitrates ($RONO_2$) containing ≥2 carbon atoms are formed in the atmosphere by one of the two channels of the reaction of organic peroxy ($RO_2^{\bullet}$) radicals with NO (Atkinson & Arey, 2003).

$$RO_2^{\bullet} + NO(+M) \rightarrow RONO_2(+M) \quad (1a)$$

$$RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2 \quad (1b)$$

Since reaction (1a) forming the organic nitrate is a sink for NO_x and radicals, the formation of organic nitrates reduces O_3 formation which would otherwise occur from photolysis of the NO_2 formed in reaction (1b) (Carter & Atkinson, 1989). However, formation of organic nitrates may be only a temporary reservoir of NO_x, depending on the subsequent fate of organic nitrates in the atmosphere. Alkyl nitrates react with OH radicals (Atkinson, 1989; Talukdar et al., 1997a; Atkinson & Arey, 2003; IUPAC, 2010) and photolyze (Luke & Dickerson, 1988; Luke et al., 1989; Turberg et al., 1990; Clemitshaw et al., 1997; Talukdar et al., 1997b; Zhu & Ding, 1997; IUPAC, 2010). The calculated lifetimes of a series of C_2–C_5 alkyl nitrates due to photolysis are ~12–20 days at ground level at 30°N in July (Clemitshaw et al., 1997; Talukdar et al., 1997b). With a global tropospheric 24-h average OH radical concentration of 1.0×10^6 molecule cm^{-3} (Krol et al., 1998) and measured 298 K rate constants (Atkinson, 1989; IUPAC, 2010), the calculated lifetimes with respect to reaction with OH radicals range from 40 days for ethyl nitrate and 25 days for 2-propyl nitrate to ~3 days for 3-octyl nitrate. Photolysis and reaction with OH radicals therefore appear to be comparable as loss processes for the alkyl nitrates, with photolysis dominating for the smaller alkyl nitrates and reaction with OH radicals for the larger ones. Photolysis occurs to form the alkoxy radical and NO_2 (IUPAC, 2010).

$$RONO_2 \rightarrow RO^{\bullet} + NO_2 \quad (2)$$

However, the products of the reactions of alkyl nitrates with OH radicals are not understood, and it is not known whether or not NO_2 is released in the OH radical reactions. In this work, we have investigated the products formed from the reactions of OH radicals with 2-propyl nitrate [$(CH_3)_2CHONO_2$], 3-methyl-2-butyl nitrate [$CH_3CH(ONO_2)CH(CH_3)_2$], and 3-methyl-2-pentyl nitrate [$CH_3CH(ONO_2)CH(CH_3)CH_2CH_3$].

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2. Experimental methods

Experiments were carried out in a ~7000 L Teflon chamber, equipped with two parallel banks of black lamps for irradiation, at 296 ± 2 K and 735 Torr total pressure of dry purified air, and in a 5870 L Teflon-coated evacuable chamber at 298 ± 1 K and 740 Torr total pressure of dry synthetic air (80% N_2 + 20% O_2), with irradiation provided by a 24-kW xenon arc lamp filtered through a 6 mm thick Pyrex pane to remove wavelengths <300 nm. Both chambers contain Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber, and the 5870 L evacuable chamber is equipped with a multiple reflection optical system interfaced to a Mattson Galaxy 5020 Fourier Transform Infrared (FT-IR) spectrometer. Hydroxyl radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in the presence of air at wavelengths >300 nm, and NO was included in the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals.

2.1. Analyses by gas chromatography

Experiments with analyses by gas chromatography with flame ionization detection (GC–FID) were carried out in the ~7000 L Teflon chamber, with initial reactant concentrations (molecule cm^{-3}) of: CH_3ONO, ~2.4×10^{14}; NO, ~2.4×10^{14}; and alkyl nitrate, $(4.36–4.96) \times 10^{13}$. Irradiations were carried out at a light intensity corresponding to an NO_2 photolysis rate of 0.137 min^{-1} for up to 60 min, resulting in up to 4% reaction of 2-propyl nitrate, up to 14% reaction for 3-methyl-2-butyl nitrate, and up to 21% reaction for 3-methyl-2-pentyl nitrate.

The concentrations of the alkyl nitrates and selected carbonyl products (acetaldehyde, propanal, acetone, 2-butanone, 2-methylbutanal and 3-methyl-2-butanone) were measured during the experiments by GC–FID. Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~205 °C onto a 30 m DB-1701 megabore column, initially held at −40 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. Acetaldehyde has a very low GC–FID response and hence its quantification is subject to significant uncertainties, and this is reflected in the measurement uncertainties. Because of this, experiments were also carried out with in situ FT-IR analyses to confirm the GC–FID data (see below).

Additional analyses for the 3-methyl-2-butyl nitrate and 3-methyl-2-pentyl nitrate reactions were carried out by combined gas chromatography–mass spectrometry (GC–MS), using solid phase microextraction (SPME) fibers pre-coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) for on-fiber derivatization (Reisen et al., 2005). Samples were collected by exposing a 65 μm polydimethylsiloxane/divinylbenzene SPME fiber pre-coated with PFBHA to the chamber contents for 15 min, with the chamber mixing fan on. The samples were then thermally desorbed and analyzed by positive chemical ionization GC–MS (PCI GC–MS) using methane as the CI gas in an Agilent 5975 Inert XL Mass Selective Detector with a 60 m DB-5 capillary column (250 μm i.d., 0.25 μm phase) operated in the scanning mode. Each carbonyl group derivatized to an oxime adds 195 mass units to the compound's molecular weight. Methane–CI gives protonated molecules $[M + H]^+$ and smaller adduct ions at $[M + 29]^+$ and $[M + 41]^+$.

2.2. Analyses by in situ fourier transform infrared (FT-IR) spectroscopy

Irradiations of CH_3ONO – NO – 3-methyl-2-butyl nitrate (or 3-methyl-2-pentyl nitrate) – air mixtures were carried out in the evacuable chamber, with initial concentrations (molecule cm^{-3}) of: CH_3ONO, $(2.46–2.71) \times 10^{14}$; NO, 2.46×10^{14}; and 3-methyl-2-butyl nitrate, 4.25×10^{14}, or 3-methyl-2-pentyl nitrate, $(3.63–5.88) \times 10^{14}$. Irradiations were carried out for up to 60–70 min for 3-methyl-2-butyl nitrate and for up to 57–90 min for 3-methyl-2-pentyl nitrate, resulting in up to 5.7–7.3% consumption of 3-methyl-2-butyl nitrate and 12–19% consumption of 3-methyl-2-pentyl nitrate. The quantitative analysis of products and reactants by FT-IR spectroscopy was carried out by a subtractive procedure. Components were successively subtracted from the spectrum of the mixture using calibrated spectra of the gaseous reactants and known products, which had been recorded previously with the same instrument and identical spectral parameters. As routinely carried out, the absorption bands of CH_3ONO and NO and of their irradiation products NO_2, HCHO, CH_3ONO_2, HNO_3, and HONO were subtracted first to reveal more clearly the products from the main reactant.

2.3. Chemicals

The chemicals used, and their stated purities, were: acetaldehyde (99.5+%), 2-methylbutanal (95%), 3-methyl-2-butanone (99%), 3-methyl-2-pentanone (99%) and propanal (99+%), Aldrich; 3-methyl-2-pentyl nitrate and 3-methyl-2-butyl nitrate, Fluorochem, Inc.; 2-propyl nitrate, Eastman; acetone (HPLC grade) and 2-butanone (99.5%), Fisher; and NO (99.0%), Matheson Gas Company. Methyl nitrite was prepared as described by Taylor et al. (1980) and stored at 77 K under vacuum.

3. Results

3.1. GC analyses

Replicate pre-reaction analyses of the alkyl nitrates in the chamber agreed to within 1% in all experiments, showing no evidence of dark losses of the alkyl nitrates. GC–FID analyses of irradiated CH_3ONO – NO – alkyl nitrate – air mixtures showed the presence of acetone from 2-propyl nitrate, acetaldehyde, acetone and 3-methyl-2-butanone from 3-methyl-2-butyl nitrate, and acetaldehyde, 2-butanone and 3-methyl-2-pentanone from 3-methyl-2-pentyl nitrate. GC–MS analyses using a coated SPME fiber confirmed these carbonyl products from the 3-methyl-2-butyl nitrate and 3-methyl-2-pentyl nitrate reactions. Although no other product peaks were observed from the GC–FID analyses of Tenax samples or from GC–MS analyses of exposed SPME fibers, without authentic standards it is not known whether or not the procedures used would have been suitable for the analysis of the multifunctional products predicted to account for the remaining carbon balance (see Section 4). The observed products also react with OH radicals, and their measured concentrations were corrected for reaction with OH radicals as described previously (Atkinson et al., 1982), using rate constants (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) of: 2-propyl nitrate, 0.29 (IUPAC, 2010); 3-methyl-2-butyl nitrate, 1.59 (Atkinson, 1989; re-evaluated using the current IUPAC, 2010 recommendation for the reference compound); 3-methyl-2-pentyl nitrate, 2.79 (Atkinson, 1989; re-evaluated using the current IUPAC, 2010 recommendation for the reference compound); acetaldehyde, 15 (Atkinson & Arey, 2003; IUPAC, 2010); acetone, 0.18 (IUPAC, 2010); propanal, 20 (Atkinson & Arey, 2003; IUPAC, 2010); 2-butanone, 1.1 (IUPAC, 2010); 2-methylbutanal, 33 (Atkinson & Arey, 2003); 3-methyl-2-butanone, 2.9 (Le Calvé et al., 1998); and 3-methyl-2-pentanone, 6.4 (Tuazon et al., 2003; re-evaluated using the current recommendation (Atkinson & Arey, 2003) for the reference compound).

The multiplicative correction factors, *F*, increase with increasing extent of reaction and with the rate constant ratio *k*(OH + product)/