Gas-Phase Reactions of Nopinone, 3-Isopropenyl-6-oxo-heptanal, and 5-Methyl-5-vinyltetrahydrofuran-2-ol with OH, NO₃, and Ozone

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In the troposphere, α -pinene, β -pinene, limonene, and linalool are mainly oxidized to pinonaldehyde, nopinone, 3-isopropenyl-6-oxoheptanal (IPOH), and 5-methyl-5vinyltetrahydrofuran-2-ol (MVT), respectively. The rate constant of the reactions of nopinone, IPOH, and MVT with OH, NO₃, and O₃ were determined by long path FT-IR spectroscopy, and the oxidation products from the reactions between the OH radical and pinonaldehyde, nopinone, IPOH, and MVT were investigated using GC-MS and HPLC. The reaction rate constants (k) for the reactions have been determined at 740 \pm 5 Torr and 298 \pm 5 K, and a number of reaction products were identified. The rate constants obtained for the reactions with nopinone were $k_{\rm OH} = (1.7 \pm 0.2) \times 10^{-11}$, $k_{\rm NO_3} < 2 \times 10^{-15}$, and $k_{\rm O_3} < 5 \times 10^{-21}$; for the reactions with IPOH were $k_{\rm OH} = (1.1 \pm 10^{-21})$ 0.3) × 10⁻¹⁰, $k_{\rm NO_3} = (2.6 \pm 0.8) \times 10^{-13}$, and $k_{\rm O_3} = (8.3 \pm 2.2) \times 10^{-18}$; and for the reactions with MVT were $k_{\rm OH}$ = (7.4 \pm 0.9) \times 10⁻¹¹, $k_{\rm NO_3}$ = (2.0 \pm 0.9) \times 10⁻¹⁴, and $k_{\rm O_3}$ = $(3.8 \pm 0.8) \times 10^{-18}$ (all units are in cm³ molecule⁻¹ s^{-1} , and uncertainties are given as two σ on the experimental data). From the results obtained in this investigation and previous studies, it was concluded that a typical atmospheric lifetime with respect to chemical reactions was only a few hours for pinonaldehyde, IPOH, and MVT but was much longer for nopinone with a lifetime of about 10 h.

Introduction

Emissions of natural non-methane hydrocarbons (NMHC) have been estimated to exceed anthropogenic hydrocarbons by a factor of about 10, with biogenic NMHC emissions being about 1000 Tg of C yr⁻¹, compared to anthropogenic emission of about 100 Tg of C yr⁻¹ (1-4). An important fraction of the natural NMHC is the monoterpenes ($C_{10}H_{16}$) emitted by vegetation, which contributes between 10 and 50% of the total natural NMHC emission (3, 4). In the troposphere, they react with OH and NO₃ radicals as well as with O₃, which leads to the formation of a variety of products. Some of these products are nonvolatile or semivolatile and contribute to the formation of organic aerosol mass in the troposphere (5). Further, terpene oxidation products may act as precursors for ozone (6); this is certainly the case for the very volatile

products such as formaldehyde and acetone. In the case of products with low vapor pressure such as those that have been investigated in the present work, the impact on atmospheric chemistry will depend on to what extend they react further in the gas phase and possibly contribute to ozone formation or, alternatively, are removed from the gas phase by adsorption on surfaces.

α-Pinene, β-pinene, limonene, and linalool (Figure 1) are among the most abundant terpenes emitted into the troposphere (2–4, 7, 8). Their gas-phase oxidation reactions have been the subject of several investigations (9–19), and pinonaldehyde (*cis*-3-acetyl-2,2-dimethylcyclobutylethanal) was found as the major product in the gas-phase oxidation of α-pinene, similar to nopinone (6,6-dimethylbicyclo[3.1.1]heptan-2-one) from β-pinene, 3-isopropenyl-6-oxo-heptanal (IPOH) from limonene, and 5-methyl-5-vinyltetrahydrofuran-2-ol (MVT) from linalool (see Figure 1).

Very little is known about the atmospheric fate of these terpene oxidation products. Only few rate constants of terpene oxidation products have previously been investigated, and in those studies no products were identified: Hallquist et al. (20) and Glasius et al. (21) both used a relative rate method and FT-IR as an analytical technique and found a fast rate constant for the reaction of pinonaldehyde with OH of (8.7 \pm 1.1) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ and of (9.1 \pm 1.8) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, respectively, at 298 \pm 5 K and 760 ± 20 Torr. For the reaction between pinonaldehyde and NO₃, they found k values of $(2.4 \pm 0.4) \times 10^{-14}$ and (5.4 ± 1.8) \times 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹, respectively. The rate constant for the reaction between pinonaldehyde and O_3 has only been investigated by Glasius et al. (21) where a slow value of $(8.9 \pm 1.4) \times 10^{-20}$ cm³ molecule⁻¹ s⁻¹ was determined. Atkinson and Aschmann (22) used GC-FID to study the rate constant for the reaction of nopinone with OH at 296 ± 2 K and at about 735 Torr total pressure. For the reaction between nopinone and the OH radical, a value of (1.4 \pm 0.4) \times 10 $^{-11}$ cm³ molecule⁻¹ s⁻¹ was found. No values for the reaction between nopinone and the NO₃ radical or ozone were given. Hatakeyama et al. (11) report a value of 1.5×10^{-11} cm³ molecule⁻¹ s⁻¹ for the reaction between OH and nopinone, but no experimental details were given. To our knowledge, no rate constant measurements have been published previously for the reactions of IPOH and MVT with OH, NO₃, and O₃ and no degradation product investigations have been performed with pinonaldehyde, nopinone, IPOH, or MVT.

To elucidate the atmospheric degradation pathways of these compounds, the rate constants of their reactions with OH, NO_3 , and O_3 were measured, and some of their reaction products were identified.

Experimental Section

All of the experiments were performed in purified air at 740 \pm 5 Torr and 298 \pm 5 K in a 480-L Teflon-coated reaction chamber surrounded by photolysis lamps (black lamps, $\lambda \geq$ 300 nm) and equipped with a multiple reflection mirror system for on-line fourier transform infrared spectroscopy (FT-IR) with a total optical path length of 81 m. A detailed description of the experimental system has been published previously (*23*). The spectra were obtained with a Bruker IFS 113v spectrometer at 1 cm⁻¹ nominal resolution by co-adding 20–50 scans.

The OH radicals were formed by photolysis of CH_3ONO , which was synthesized by adding H_2SO_4 (50 wt % aqueous solution) to sodium nitrite dissolved in a methanol/water mixture (24). NO₃ radicals were formed by thermal dissocia-

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FIGURE 1. Major oxidation products from the atmospheric degradation of four terpenes.



TABLE 1. Summary of Reaction Rate Constants, k, Measured in This Investigation at 298 \pm 5 K and 740 \pm 5 Torrⁱ

^{*a*} Data from Glasius et al. (*21*). ^{*b*} Measured relative to isoprene and 1,3-butadiene using $k_{isoprene + OH} = 1.01 \times 10^{-10}$ and $k_{1.3-butadiene + OH} = 6.66 \times 10^{-11}$. ^{*c*} Measured relative to 1-butene using $k_{1-butene} + NO_3 = 1.25 \times 10^{-14}$. ^{*d*} Measured relative to isobutene using $k_{isobutene + OH} = 5.13 \times 10^{-11}$. ^{*e*} Measured relative to ethene and propene using $k_{ethene + NO_3} = 2.0 \times 10^{-16}$ and $k_{propene + NO_3} = 9.45 \times 10^{-16}$. ^{*f*} Measured relative to isobutene using $k_{isobutene + NO_3} = 3.4 \times 10^{-13}$. ^{*g*} Measured relative to isobutene using $k_{isobutene + OH} = 5.13 \times 10^{-11}$. ^{*h*} Measured relative to isobutene using $k_{isobutene + O_3} = 1.21 \times 10^{-16}$. ^{*h*} Measured relative to isobutene using $k_{isobutene + O_3} = 1.21 \times 10^{-14}$. ^{*i*} Units are cm³ molecule⁻¹ s⁻¹. Uncertainties are presented with 2 *a* on the experimental data. kinetic data of pinonaldehyde is taken from Glasius et al. (*21*). The values for the reference compounds were obtained from refs *33* and *44*.

tion of N_2O_5 , which was prepared in solid form according to a previously described procedure (25). Ozone was prepared by silent discharge of pure oxygen. In a typical experiment, the temperature was 295 ± 3 K at the beginning; but when CH₃ONO was used as the precursor for OH radicals, the temperature increased by 3-5 K due to the heating from the UV lamps.

The OH, NO₃, and O₃ reaction rate constants were determined mainly with the "relative rate" method, but the O₃ + nopinone reaction was measured under pseudo-first-order conditions. Both methods have been previously described in detail (*21*). Reference compounds used in the relative rate method were isobutene, 1-butene, propene, and ethene. In the footnote of Table 1, it is written which reference compounds were used for which reaction. By the relative rate method, the ratio of the rate constants k_A/k_B are found as the slope of a plot of ln (A_0/A_t) – $k_w t$ versus ln (B_0/B_t) – $k_w t$, where A_0 and B_0 are the initial concentrations, A_t and B_t are the concentrations at time *t*, and $k_w t$ is an additional first-order loss process, if any additional loss process is present, described by rate constant k_w for *A* and *B*, respectively (see Figure 2). In purified air, nopinone showed a first-order



FIGURE 2. Plot of In {[nopinone]₀/[nopinone]₁} corrected for wall losses and photolysis vs In {[isobutene]₀/[isobutene]₁} for the decay of nopinone and isobutene during photolysis of methylnitrite, producing OH radicals; $k_w =$ losses on wall and/or by photolysis.

decay in our reaction chamber with the UV lamps turned on $(\lambda \ge 300 \text{ nm})$; this additional loss process was attributed to

wall loss and losses due to photolysis, and a value of $k_w =$ $9.5 \times 10^{-6} \ s^{-1}$ was measured for nopinone. For the other compounds, $k_{\rm w} = 1.7 \times 10^{-4} \, {\rm s}^{-1}$ for IPOH and $7.9 \times 10^{-5} \, {\rm s}^{-1}$ for MVT, but in the case of the reference compounds (isobutene, 1-butene, propene, and ethene), no additional loss process could be identified in the reaction chamber with UV light and values of $< 5 \times 10^{-6} \text{ s}^{-1}$ were assumed for k_w , which means that no data adjustment is needed for those compounds in this investigation. Without UV light, IPOH showed a first-order decay in our reaction chamber; this additional loss process was attributed to wall loss, and a value of $k_w = 5.5 \times 10^{-5} \text{ s}^{-1}$ was measured for IPOH. For the other compounds, $k_{
m w}=8.4 imes10^{-5}~{
m s}^{-1}$ for MVT, but in the case of nopinone and the reference compounds (isobutene, 1-butene, propene, and ethene), no additional loss process could be identified in the reaction chamber without UV light, and values of $<5 \times 10^{-6} \text{ s}^{-1}$ were assumed for k_w , which again means that no data adjustment is needed for those compounds in this investigation. It should be mentioned that these additional losses are relatively small because the time range for an experiment is normally between 5 and 15 min. The additional loss process (wall loss + photolysis) was always below 15% of the overall decay during an experiment for all of the experiments performed in this investigation.

For the measurements of the reactions of IPOH and MVT with O₃, cyclohexane (270 and 200 ppmV, respectively) was added to scavenge OH radicals, which are believed to be formed by the ozonolysis of these olefinic species. For the reaction of nopinone with O₃, no scavenger was used since nopinone does not contain olefinic double bonds and because these experiments were performed under pseudo-first-order conditions without a reference compound present (1 ppmV = 2.46×10^{13} molecules cm⁻³ at 298 K and 760 Torr).

The terpene oxidation products used in this investigation have a low vapor pressure and become unstable when heated. Therefore, instead of the normal manometric method, the following method was applied: Each of the compounds was introduced into the reaction chamber by applying $10-20 \mu$ L of the compound to a filter and gently blowing the vapor into the reaction chamber by a stream of air. Infrared spectra were obtained for all four compounds.

Typical initial experimental conditions were 15 ppmV < $[CH_3ONO] < 30$ ppmV, 10 ppmV < $[N_2O_5] < 100$ ppmV, 10 ppmV < $[O_3] < 300$ ppmV, and 1 ppmV < [A] < 10 ppmV (where A is one of the terpene oxidation products). The concentration of A was an estimate, based on known cross sections of similar compounds. All of the kinetics data are based on relative measurement of the decay of A and the reference compound, B; therefore, it is not necessary to know the exact concentrations. The concentrations of the reference compound [B] were in the range 4 ppmV < [B] < 25 ppmV.

Samples of reaction products were taken in the following ways: (a) on stainless steel adsorbent tubes (Perkin-Elmer) filled with 200 mg of Tenax-TA at a sampling flow of 150 mL min⁻¹ (sampling volume = 0.3 L); (b) on glass adsorbent tubes filled with 150 mg of Carboxen 563 at a sampling flow of 600 mL min⁻¹ (sampling volume = 12 L); (c) through an impinger filled with 15 mL of a solution of H_2O/t -BuOH (3:1) at a flow rate of 800 mL min⁻¹ (sampling volume = 12 L) (d) on 2,4-dinitrophenylhydrazine (DNPH) coated C₁₈-silica gel cartridges at a sampling flow of 1 L min⁻¹ (sampling volume = 1 L).

The analysis of the Tenax tubes was done by thermal desorption (ATD 400, Perkin-Elmer) gas chromatography (Fisons HRGC Mega 2 Series)—mass spectrometry (Fisons Trio1000) as described in detail elsewhere (*26*). The analysis of the Carboxen tubes was done by solvent extraction (dichloromethane) followed by on-column injection into a gas chromatograph (HP-5890) coupled to a mass spectrom-



FIGURE 3. Plot of In {[IPOH]₀/[IPOH]₁} vs In {[isobutene]₀/ [isobutene]₁} (**m**). Plot of In {MVT]₀/[MVT]₁} vs In {[isobutene]₀/ [isobutene]₁} (**•**). During photolysis of methylnitrite, producing OH radicals; k_{w} = losses on wall and/or photolysis.

eter (HP-5972) operated in the chemical ionization (isobutane as ionizing agent) mode. The compounds trapped in the aqueous solution of the impinger were derivatized with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine using 0.5 mL of a 1 M phosphate buffer (27) and extracted twice with solvent (first dichloromethane and then methyl *tert*-butyl ether). The analysis was carried out by chemical ionization GC-MS in the same system used to analyze the Carboxen tubes as described by Lahaniati et al. (28). The analysis of the DNPH cartridges was done by solvent extraction (acetonitrile) followed by high-performance liquid chromatography (HPLC, Kontron) with ultraviolet detection.

Chemicals. Pinonaldehyde was synthesized and identified as described previously (21). Nopinone was commercially available from Aldrich (98% pure). IPOH and MVT were synthesized as described in refs 15 and 29. IPOH, IR spectrum (gas phase, cm⁻¹): 900 (m), 1161 (m), 1367 (m), 1740 (s), 2714 (m), 2814 (m), 2945 (m), and 3081 (m). EI-MS m/z 168 (M⁺, 0), 107 (25), 67 (23), 58 (15), 55 (18), 43 (100), and 41 (32); CI-MS (methane) 169 (M + H⁺, 20), 151 (100), and 107 (26). MVT, IR spectrum (gas phase, cm⁻¹): 845 (m), 924 (m), 975 (s), 995 (s), 1036 (s), 1210 (m), 1459 (m), 2881 (m), 2935 (m), 2984 (s), 3019 (m), 3102 (m), 3650 (m). EI-MS m/z 128 (M⁺, 2), 113 (44), 110 (10), 95 (20), 71 (90), 67 (94), 55 (78), 43 (100), and 41 (53); CI-MS (methane) 127 (M + H⁺ - H₂, 3), 111 (100), 93 (36), and 81 (9). The other chemicals used in this study were all commercial samples used without further purification: isobutene (Matheson, >99% pure), 1-butene (99.9% pure, Ucar), propene (Ucar, >99.5% pure), ethene (\geq 99.5% pure, Air Liquide), synthetic air (80% N₂ and 20% O₂: mixture \geq 99.95% pure, SIO), and O₂ (\geq 99.9% pure, SIO).

Results and Discussion

Kinetic Studies. In this investigation, we have determined the rate constants for the reactions of OH, NO₃, and O₃ with nopinone, IPOH, and MVT. The values measured are presented in Table 1 together with the values for pinonaldehyde. Typical examples of the results obtained by the relative rate measurements of the OH, NO₃, and O₃ reactions with nopinone, IPOH, and MVT can be found in Figures2-6. For the relative rate measurement of the reaction between nopinone and the NO₃ radical, in the presence of the reference compounds ethene and propene, only a very small decay of nopinone could be observed, and only an upper limit for that reaction rate constant has been given; no figure is shown here. For the only pseudo-first-order measurements that were performed (nopinone $+ O_3$), no reaction could be detected, and thus only an upper limit for that reaction rate constant has been given; no figure is shown.

The major oxidation product of linalool (4-hydroxy-4methyl-5-hexenal) is a γ -hydroxyaldehyde (15, 18) and exists



FIGURE 4. Plot of In {[IPOH]₀/[IPOH]₁} corrected for wall losses vs In {[isobutene]₀/[isobutene]₁} for the decay of IPOH and isobutene during reaction with the NO₃ radical.



FIGURE 5. Plot of In {MVT] $_0/[MVT]_t$ } corrected for wall losses vs In {[isobutene] $_0/[isobutene]_t$ } for the decay of MVT and isobutene during reaction with NO₃.



FIGURE 6. Plot of In {[IPOH]₀/[IPOH]_l} vs In {[isobutene]₀/ [isobutene]_l} (**m**). Plot of In {MVT]₀/[MVT]_l} vs In {[isobutene]₀/ [isobutene]_l} (**o**). During reaction with O₃ in the presence of cyclohexane; k_w = losses on wall.

therefore in equilibrium with its cyclic form MVT (5-methyl-5-vinyltetrahydrofuran-2-ol), a thermodynamically favored lactol (in this section under Products Studies, the two forms can be seen in Figure 8). MVT is mentioned in the literature also as lavender lactol (*30*). Shu et al. (*18*) suggested on the basis on FT-IR data that the compound must be present entirely in the cyclic form. We confirm the observation done by Shu et al. (*18*), because we observed a very weak carbonyl signal in the FT-IR and ¹H NMR spectra, indicating the presence of the open chain form. On the basis of the integration of the aldehyde signal and the single hydrogen of the vinyl group in the ¹H NMR spectrum of MVT, a ratio of 18:1 of closed to open chain form was estimated. This equilibrium is of particular interest when discussing the reaction pathways of MVT.

Only a few rate constants of terpene oxidation products have previously been investigated: Hallquist et al. (20) and Glasius et al. (21) both used a relative rate method and FT-IR as the analytical technique and found a rate constant for the reaction of pinonaldehyde with OH of (8.7 \pm 1.1) \times 10⁻¹¹ and of $(9.1 \pm 1.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, respectively, at 298 \pm 5 K and 760 \pm 20 Torr. As can be seen, the two values are in good agreement. For the reaction between pinonaldehyde and NO₃, they found a *k* value of $(2.4 \pm 0.4) \times 10^{-14}$ and of $(5.4 \pm 1.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, which is about a factor of 2 difference. The relatively high value obtained for the reaction between pinonaldehyde and the NO₃ radical is in agreement with a recent study, where for aliphatic aldehydes an increasing rate constant with an increasing number of carbon atoms was observed (31). The reaction rate constant for the reaction between pinonaldehyde and O₃ has only been investigated by Glasius et al. (21) where a value of $(8.9 \pm 1.4) \times 10^{-20}$ cm³ molecule⁻¹ s⁻¹ was determined. The reaction of O₃ with aldehydes is believed to be very slow (32), which is in agreement with the value obtained.

Atkinson and Aschmann (22) used GC-FID to study the rate constant for the reaction of nopinone with OH at 296 \pm 2 K and at about 735 Torr total pressure. For the reaction between nopinone and the OH radical, a value of $(1.4 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ was found, which is in good agreement with our value of $(1.7 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The reactions of ketones with NO₃ radicals are very slow (*33*), and the reactions of ketones with O₃ are believed to be below a measurable rate (*22*). Both statements are in agreement with the values obtained in this investigation for the rate constants of the reactions of nopinone with NO₃ and with O₃ (see Table 1).

To our knowledge, no rate constants measurements have been published previously for the reactions of IPOH and MVT with OH, NO₃, and O₃ (Table 1), but the *k* values are similar to those obtained from alkene reactions (*33, 34*).

It has been suggested that the reactivity of the OH radical toward organics, including the oxygenated hydrocarbons presently studied, may be estimated from a simple structurereactivity relationship (35). This incremental reactivity method predicts a rate constant for the OH reaction of 2.4 imes 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for pinonaldehyde, of 4.6 imes 10⁻¹² cm³ molecule⁻¹ s⁻¹ for nopinone, of 7.8×10^{-11} cm³ molecule⁻¹ s⁻¹ for IPOH, and of 7.4×10^{-11} cm³ molecule⁻¹ s⁻¹ for MVT as shown in Table 2, which also includes the predicted rate constants for these reactions obtained by applying a structure-reactivity method based upon molecular orbital calculations (36-38). As seen in Table 2, the agreement between the measured values and those estimated by the incremental reactivity method (35) is acceptable in the case of MVT and reasonable in the case of IPOH, but in the case of pinonaldehyde and nopinone, the estimated value is about 3-4 times lower than the measured one. There is no obvious explanation for this discrepancy, but the fact that disagreement is found only for the two molecules that contain a 1,1-dimethylcyclobutane skeleton suggests that more data concerning the reactivity of such compounds are needed. For the structure-reactivity method based upon molecular orbital calculations (36-38), there is a good agreement in the case of nopinone + OH, but for the other three reactions the predicted rate constants are a factor of 2-3 lower than the measured ones.

Product Studies. *Reaction between Pinonaldehyde and OH.* Norpinonaldehyde (*cis*-3-acetyl-2,2-dimethylcyclobutylmethanal, [I] in Figure 7) was identified by CI–GC–MS (methods b and c in the Experimental Section). In addition, acetone and a carbonyl compound, tentatively identified as methylglyoxal, were identified as their hydrazones by HPLC (method d). Norpinonaldehyde has previously been observed as a product from the reaction between α-pinene and O₃ (*9, 39*). The formation of norpinonaldehyde results from known reaction mechanisms as shown in Figure 7, and a rear-



FIGURE 7. Reaction scheme proposed for the reaction between pinonaldehyde and the OH radical.

FIGURE 8. Reaction scheme proposed for the reaction between MVT and the OH radical.

rangement of the intermediate cyclobutyl radical (40) could explain the formation of acetone. Other formation pathways to acetone could be hydrogen abstraction from either of the two tertiary C–H sites and further reactions of the cyclic radical formed.

Reaction between nopinone and OH. 6,6-Dimethylbicylco-[3.1.1]heptan-2,3-dione [II] and 3,7-dihydroxy-6,6-dimethylbicylco[3.1.1]heptan-2-one [III] (see Chart 1) were identified, and 6,6-dimethyl-3-hydroxybicylco[3.1.1]heptan-2-one [IV] was identified in traces by CI-GC-MS (method b). 6,6-Dimethylbicylco[3.1.1]heptan-2,3-dione was identified by GC-MS [method a: 152 (M⁺, 1), 124 (26), 109 (80), 81 (63), 68 (84), and 55 (100)] and 3,7-dihydroxy-6,6-dimethylbicylco[3.1.1]heptan-2-one as its oxime (method c). Acetone

^a The units are in cm³ molecule⁻¹ s⁻¹. Numbers in parentheses are reference numbers. An asterisk (*) means that the values were calculated by the authors using the method described by Kwok and Atkinson (*35*). The number sign (#) means that the values were calculated by Klamt and Lohrenz (*38*) using the method described in refs *36* and *37*.

CHART 1

was observed as its hydrazone by HPLC (method d). 6,6-Dimethylbicylco[3.1.1]heptan-2,3-dione and 6,6-dimethyl-3-hydroxybicylco[3.1.1]heptan-2-one have previously been observed as products from the reaction between α -pinene and O₃ (*7*, *39*), and their formation can be explained by the well-known chemistry of alkyl peroxy and oxy radicals. The formation of 3,7-dihydroxy-6,6-dimethylbicylco[3.1.1]heptan-2-one can be understood if a 1,5 hydrogen transfer takes place after the formation of a 3-oxy or 7-oxo radical intermediate in the oxidation of nopinone.

Reaction between IPOH and OH. 2-Isopropenyl-5-oxohexanal was identified by CI–GC–MS (methods b and c).

Reaction between MVT and OH. 4-Oxopentanal ([V] in Figure 8) was unambiguously identified by CI–GC–MS (methods b and c) by comparison with an authentic standard synthesized in the laboratory (*37*). 4-Oxopentanal has been incorrectly identified in a previous study as 4-hydroxypentanal (*14*). 5-Methyl-5-vinyltetrahydrofuran-2-one and a

hydroxycarbonyl with mass 142, which we attributed to 5-methyl-4-oxo-5-vinyltetrahydrofuran-2-ol, were observed in small amounts by GC–MS and CI–GC–MS (methods a and b). The formation of 4-oxopentanal can be better understood if a fast equilibrium of MVT with its open form 4-hydroxy-4-methyl-5-hexenal is supposed, see Figure 8. 4-Oxopentanal could be readily formed together with hydroxyacetaldehyde following the mechanism described in Figure 8.

Conclusions and Atmospheric Implications

Typical chemical lifetimes in the troposphere for the terpene oxidation products (pinonaldehyde, nopinone, IPOH, and MVT) have been estimated (Table 3) by applying the values of the reaction rate constants from Table 1. Reaction with the OH radical seems to be the dominant reaction pathway in the troposphere for these compounds, reaction with the NO₃ radical is only of minor importance, whereas reaction with O₃ is negligible. The present results indicate a typical atmospheric lifetime with respect to chemical reactions of about 1-2 h for pinonaldehyde, IPOH, and MVT and about 9 h for nopinone.

From the available kinetic information, the ratios between the concentrations of these terpene oxidation products and their parent compounds in ambient air can be estimated, taking only gas-phase chemical reactions into account. Such TABLE 3. Estimated Chemical Lifetimes of Oxidation Products in the Troposphere under Typical Tropospheric Conditions^a

^a An asterisk (*) indicates that the concentration of OH used is considered to be a typical daytime value (45), while that of NO₃ is assumed to be a characteristic continental nighttime concentration (46). The concentration given for O₃ is a 24-h average (47).

a calculation requires knowledge not only about the relevant rate constants but also about the yields of the oxidation products. For daytime conditions, the NO₃ radical concentration can be considered as being negligible, and thus only OH and ozone are taken into consideration. For this calculation, the OH and ozone concentrations shown in Table 3 (0.07 pptV and 30 ppbV, respectively) have been used together with the rate constant values presented in Table 1 and the rate constants for the OH and ozone reactions with α -pinene, β -pinene, limonene, and linalool given by Atkinson (*34*) and by Atkinson et al. (*42*). Assuming steady-state conditions, i.e., that the formation rates equals the removal of the terpene oxidation product A:

$$\begin{aligned} k1_{\rm OH} [\rm OH] [\rm terpene] \alpha + k1_{\rm ozone} [\rm O_3] [\rm terpene] \beta = \\ k2_{\rm OH} [\rm OH] [\rm A]_{\rm ss} + k2_{\rm ozone} [\rm O_3] [\rm A]_{\rm ss} \end{aligned}$$

where α an β are the fractional yields of A, and the ratio between the concentration of the terpene and its oxidation product A ([A]_{ss}/[terpene]) can be calculated. The reaction of A with ozone is negligible in the cases of pinonaldehyde and nopinone. The steady-state assumption is best in the case where a 'box model' approach can be used and not good in the cases where transport and dispersion are likely to be important. However, it does give an insight into the concentration levels of these compounds that should be expected in a forest area. If α and $\bar{\beta}$ are set equal to 1, the following ratios are obtained: [pinonaldehyde]/[α -pinene] = 1.0, [nopinone]/[β -pinene] = 5.1, [IPOH]/[limonene] = 2.2, and [MVT]/[linalool] = 4.7. These ratios must then be modified according to the yields of these oxidation products (i.e., α and β), which are not known precisely; however, laboratory experiments indicate that pinonaldehyde, nopinone, and MVT are formed in high yields, i.e., in the range from 20 to more than 50% on a molar basis, by the oxidation of their parent compounds by reaction with OH radicals or ozone (9, 11, 13, 18).

Very few field measurements of these terpene oxidation products are available; results of measurements performed in Italy and Spain, reported by Calogirou et al. (43), show ratios between oxidation products and parent compounds that are lower than those calculated here even when yields (α and β) as low as 0.2 are used for the calculation. More field measurements of these compounds in ambient air will show if atmospheric sinks other than gas-phase reactions with OH are of importance.

A number of reaction products could be identified, part of which have been previously detected as products from their parent terpene. It is, however, clear from this and other product studies of the atmospheric terpene degradation that the mechanisms are not fully clarified. The present product is of only qualitative character, and additional analytical techniques are needed to give a more detailed reaction mechanism.

Further work should clarify the importance of other tropospheric sinks of these terpene oxidation products and their degradation products. The importance of photolysis and heterogeneous losses should be investigated. Recent results indicate that the typical lifetime of pinonaldehyde with respect to photolysis under clear sky conditions is 3.3 h at 50° N in July and 22 h at 50° N in January (*20*), when a photolysis quantum yield of 1 was assumed. By comparing these lifetime values with the values in Table 3, it can be concluded that photolysis could be an important degradation mechanism for pinonaldehyde in the atmosphere.

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