Kinetic Study of Gas-Phase Reactions of Pinonaldehyde and Structurally Related Compounds

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ABSTRACT: Rate constants for the reactions of OH, NO3, and O3 with pinonaldehyde and the structurally related compounds 3-methylbutanal, 3-methylbutan-2-one, cyclobutyl-methylketone, and 2,2,3-trimethyl-cyclobutyl-1-ethanone have been measured at 300 ± 5 K using on-line Fourier transform infrared spectroscopy. The rate constants obtained for the reactions with pinonaldehyde were: \( k_{\text{OH}} = (9.1 \pm 1.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), \( k_{\text{NO}_3} = (5.4 \pm 1.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), and \( k_{\text{O}_3} = (8.9 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). The results obtained indicate a chemical lifetime of pinonaldehyde in the troposphere of about two hours under typical daytime conditions.

INTRODUCTION

Monoterpenes (C10H16) from vegetation contribute an important fraction of the total nonmethane hydrocarbons emitted to the troposphere [1–4]. In the troposphere they react with OH and NO3 radicals as well as with O3, leading to the formation of a variety of products. α-Pinene is one of the most abundant monoterpenes in the troposphere [2–4], and its gas-phase oxidation reactions have been the subject of several investigations [5–8]. Pinonaldehyde (cis-4-acetyl-2,2-dimethyl-cyclobutyl-ethanal) has been found to be one of the major products in the tropospheric oxidation of α-pinene [5–8]. The tropospheric fate of pinonaldehyde is unknown, but, taking its structure into account, only photolysis and reaction with OH are expected to be of importance.

To elucidate the atmospheric degradation of pinonaldehyde we have measured rate constants for its reactions with OH, NO3, and O3 and the structurally related compounds 3-methylbutanal, 3-methylbutan-2-one, cyclobutyl-methylketone, and 2,2,3-trimethyl-cyclobutyl-1-ethanone.

EXPERIMENTAL

All the experiments were performed in purified air at 740 ± 5 torr and 300 ± 5 K in a 480 L Teflon-coated reaction chamber surrounded by photolysis lamps.
H₂O₂. A detailed description of the experimental system has been previously published [9]. The spectra were obtained with a Bruker IFS 113v at 1 cm⁻¹ nominal resolution by co-adding 20 to 50 scans.

The OH radicals were formed by photolysis of either CH₃ONO or H₂O₂. CH₃ONO was synthesized by adding H₂SO₄ (50 wt % aqueous solution) to sodium nitrite dissolved in a methanol/water mixture [10]. Pure gaseous H₂O₂ was obtained by heating a commercial Urea-H₂O₂ complex to ca. 70°C. Ozone was prepared by silent discharge of pure oxygen. NO₃ radicals were formed by thermal dissociation of N₂O₅, which was prepared in solid form according to a previously described procedure [11]. In a typical experiment the temperature was 295 ± 3 K in the beginning of an experiment; but when CH₃ONO was used as the precursor for OH radicals the temperature increased by 3–7 K due to the heating from the UV-lamps.

The rate constants for the ozone reactions were determined under pseudo-first-order conditions:

\[ A + O₃ \rightarrow \text{Products} \]  \[ k_{A} = A \exp\{-[O₃]t\} \]  \[ \ln A = \text{const.} - (\{O₃\}t) \]  \[ = \text{const.} - (k't) \]

where \( k \) is the reaction rate constant for the reaction between compound A and O₃, and \( k' \equiv k[O₃] \).

With O₃ in large excess its concentration will be approximately constant during an experiment and pseudo-first-order conditions are obtained. A plot of \( \ln A \) vs. time \( t \) will then give pseudo-first-order decay \( k' \). A plot of \( k' \) vs. \( \{O₃\} \) will subsequently give the reaction rate constant \( k \) as the slope. Typical experimental conditions during the O₃ experiments were: 50 ppmV < \( \{O₃\} \) < 400 ppmV, 1 ppmV < \( \{A\} \) < 10 ppmV, but \( \{O₃\} \) was always < 10 times \( \{A\} \).

The OH and NO₃ reaction rate constants were determined by the “relative rate” method:

\[ A + OH \rightarrow \text{Products} \]  \[ B + OH \rightarrow \text{Products} \]

For these two bimolecular reactions the following expression for the ratio \( k_A/k_B \) can be obtained:

\[ k_A/k_B = \ln(A/O)/\ln(B/O) \] (6)

Thus when \( k_A \) is known, \( k_B \) can be calculated.

In the case that reactant A has an additional first-order loss process described by a rate constant \( k_A \), eq. (6) is modified as shown in eq. (7):

\[ k_A/k_B = \ln(A/O) - (k_A/\{A\})/\ln(B/O) \] (7)

A plot of \( \ln(A/O) - (k_A/\{A\}) \) vs. \( \ln(B/O) \) will give the ratio \( k_A/k_B \) as the slope (see Fig. 1). Typical experimental conditions: 10 ppmV < \( \{CH₃ONO\} \) < 30 ppmV, 5 ppmV < \( \{N₂O₅\} \) < 100 ppmV, 1 ppmV < \( \{A\} \) < 10 ppmV, and 5 ppmV < \( \{B\} \) < 25 ppmV.

Pinonaldehyde was introduced into the reaction chamber using a “double filter system” as explained below: Pinonaldehyde is difficult to evaporate, because it has a very low vapor pressure and decomposes easily when heated; thus we added 10 to 20 μl of pinonaldehyde to the first of two filters in series in a Teflon tube and a minor fraction of it was blown into the reaction chamber by a stream of air. The first filter was used to enhance the surface area of the compound and the second filter was used to prevent aerosols from being blown into the reaction chamber. Figure 2 shows an infrared spectrum of pinonaldehyde. The spectrum resembles the infrared spectrum previously published [8], which was tentatively identified as due to pinonaldehyde.

3-Methylbutanal, 3-methylbutan-2-one, cyclobutyl-methylketone, ethene, isoprene, 1,3-butadiene, and 1-butene were added in known quantities to the reaction chamber by standard manometric methods.
The spectral features from CO₂ have been removed.

EI-MS m/z H₂O was brought to pH 99(40), and 71(100). (methane) 83(100), 71(35), 69(80), and 55(56); CI-MS hyde were in accordance with those of ref. [12].: Aldrich). A solution of 0.46 g of in 40 par ed as pr e viously descr ibed [12] star ting fr om

Na₂HPO₄ and subsequentl y ad ded in small por tions

and the solution e xtr acted with methyl-

to a solution of 0.34 g of pinandiol in 6 mL tetr ah y-

to xida ti v e bond c lea v a g a solution of 0.24 g of in 40

to a solution of 0.34 g of pinandiol in 6 mL

to a solution of 0.34 g of pinandiol in 6 mL

and 55(56); CI-MS (methane) m/z 169(M⁺ + H⁺), 151(46), 107(40), 99(40), and 71(100).

2,2,3-trimethylcyclobutyl-1-ethanone was prepared as previously described [12] starting from pinonaldehyde synthesized as described above. EI-MS m/z 140(M⁺, 2), 125(10), 83(82), 71(18), 70(92), and 55(100); CI-MS (methane) m/z 141(M + H⁺, 22), 123(8), 111(12), 99(22), and 71(100).

Other chemicals used in this study were all com-
mmercial samples of p.a. quality and were used without further purification: 3-Methylbutanal (97% pure, Aldrich), 3-methylbutan-2-one (99% pure, Aldrich), cyclobutyl-methylketone (98% pure, Aldrich), ethene (≥ 99.5% pure, Air Liquide), isoprene (99% pure, Aldrich), 1,3-butadiene (99.5% pure, Ucar), and 1-
butene (99.9% pure, Ucar).

RESULTS AND DISCUSSION

In this investigation we have determined the rate constants for the reactions of OH, NO₃, and O₃ with pinonaldehyde and the structurally related compounds 3-methylbutanal, 3-methylbutan-2-one, cyclobutyl-methylketone, and 2,2,3-trimethylcyclobutyl-1-ethanone.

In purified air pinonaldehyde showed a first-order decay in our reaction chamber, which was attributed to wall loss. This wall loss varied somewhat with the condition or “history” of the cell and with temperature. On the average, the rate constant for the wall loss first-order decay of pinonaldehyde was 

k_{wall-loss} = (2.9 ± 0.3) × 10⁻³ s⁻¹ (uncertainty with 2 σ). With the external photolysis lamps turned on, λ ≥ 300 nm, the decay of pinonaldehyde was enhanced. The average photolysis and wall loss constant of pinonaldehyde in our system, J_{UV/Vis} + k_{wall}, was found to be between 1 × 10⁻³ s⁻¹ and 2 × 10⁻³ s⁻¹ (when UV-light ≥ 300 nm was used), which correspond to up to 25% of the overall decay of pinonaldehyde during an experiment with OH radicals. The reference compounds and the other compounds studied were all very stable in the cell with 

k_{wall-loss} < 1 × 10⁻³ s⁻¹, even with the photolysis lamps turned on.

The analysis of a relative rate measurement of the OH reaction with a pinonaldehyde/1,3-butadiene mixture is presented in Figure 1. In the example shown the relative concentration measurements were obtained by spectral subtraction using the C—H stretch band of pinonaldehyde at 2650–2750 cm⁻¹ and the C—H bend band of 1,3-butadiene at 850–950 cm⁻¹. The data were analyzed assuming additional first-order loss of pinonaldehyde to the cell walls and first-order photolytical degradation as discussed above. In the spectral subtraction we also included the spectral features from the products formaldehyde and acrolein. Table I lists the bands that have been used in spectral subtraction for the individual compounds.

The rate constants for the reactions of OH, NO₃, and O₃ with the different organics are presented in Table II. The rate constant for the reaction between
pinonaldehyde and OH was obtained from two series of experiments using isoprene with \( k_{\text{OH}} = 1.01 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K [13] and 1,3-butadiene with \( k_{\text{OH}} = 6.66 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K [13] as reference compounds, respectively. There is no significant difference between the rate constants obtained using the two different reference compounds and only the average value is given in Table I. The influence of a possible variation in the wall and photolysis loss of pinonaldehyde during the experiments was estimated by letting \( J_{\text{UV/Vis}} + k_{\text{wall loss}} \) for pinonaldehyde vary within its statistical 95% confidence interval; the resulting variation was less than 10% of the average rate constant. Typical plots for pinonaldehyde + NO\(_3\) and for pinonaldehyde + O\(_3\) are shown by Figures 3 and 4, respectively. These plots are corrected for wall loss, but in Figure 4 it can be seen that the slope does not intercept with \([0; 0]\). It is tentatively suggested that an additional surface reaction with ozone may be the reason.

The rate constant for the OH reaction with 3-methylbutanal has previously been measured as \((2.7 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [14] (see Table III) with the use of GC-FID as their analytical technique. As can be seen the value reported here of \((4.0 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) obtained using 1,3-butadiene as reference compound is significantly larger. No explanation for this discrepancy between the two values can be given at this time.

It was not possible to find any IR bands unique to the organic reactants in the spectra obtained from the OH reaction with 2,2,3-trimethycyclobutyl-1-ethanone, cyclobutyl-methyl-ketone and 3-methylbutan-2-one. Changes in the IR band shapes showed

<table>
<thead>
<tr>
<th>Band (cm(^{-1}))</th>
<th>Vibration</th>
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</thead>
<tbody>
<tr>
<td>Pinonaldehyde</td>
<td>2650–2750</td>
</tr>
<tr>
<td>2,2,3-Trimethylcyclobutyl-1-ethanone</td>
<td>1150–1210</td>
</tr>
<tr>
<td>3-Methylbutanal</td>
<td>2600–2850</td>
</tr>
<tr>
<td>3-Methylbutan-2-one</td>
<td>1070–1170</td>
</tr>
<tr>
<td>Cyclobutyl-methylketone</td>
<td>1125–1225</td>
</tr>
<tr>
<td>Isoprene</td>
<td>3050–3150</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>850–950</td>
</tr>
<tr>
<td>1-Butene</td>
<td>3050–3150</td>
</tr>
<tr>
<td>Ethene</td>
<td>850–1050</td>
</tr>
</tbody>
</table>

Interfering bands from products produced in the experiments, such as formaldehyde, metacrolein, and acrolein, have been taken into account by spectral subtraction.

**Table I** Bands used for Spectral Subtraction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Band (cm(^{-1}))</th>
<th>Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinonaldehyde</td>
<td>2650–2750</td>
<td>C–H(_{e}) stretch</td>
</tr>
<tr>
<td>2,2,3-Trimethylcyclobutyl-1-ethanone</td>
<td>1150–1210</td>
<td>C–C(_{a}) stretch</td>
</tr>
<tr>
<td>3-Methylbutanal</td>
<td>2600–2850</td>
<td>C–H(_{a}) stretch</td>
</tr>
<tr>
<td>3-Methylbutan-2-one</td>
<td>1070–1170</td>
<td>C–H(_{a}) stretch</td>
</tr>
<tr>
<td>Cyclobutyl-methylketone</td>
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<td>1,3-Butadiene</td>
<td>850–950</td>
<td>&gt;=C–H out-of-plane bend</td>
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<td>1-Butene</td>
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</tr>
<tr>
<td>Ethene</td>
<td>850–1050</td>
<td>&gt;=C–H out-of-plane bend</td>
</tr>
</tbody>
</table>

**Table II** Rate Constants Determined at 740 ± 5 torr and 300 ± 5 K (Units in cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) in this Investigation

<table>
<thead>
<tr>
<th>( R )</th>
<th>Pinonaldehyde</th>
<th>3-Methylbutanal</th>
<th>2,2,3-T trimethylcyclobutyl-1-ethanone</th>
<th>Cyclobutylmethylketone</th>
<th>3-Methylbutan-2-one</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t )</td>
<td>9.1 ± 1.8 \times 10^{-14}</td>
<td>4.0 ± 0.7 \times 10^{-11}</td>
<td>n.d. (^b)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>( a )</td>
<td>5.4 ± 1.8 \times 10^{-14}</td>
<td>1.2 ± 0.3 \times 10^{-14}</td>
<td>&lt;5 \times 10^{-16}</td>
<td>&lt;5 \times 10^{-16}</td>
<td>&lt;5 \times 10^{-16}</td>
</tr>
<tr>
<td>( n )</td>
<td>8.9 ± 1.4 \times 10^{-20}</td>
<td>3.9 ± 0.6 \times 10^{-20}</td>
<td>&lt;5 \times 10^{-21}</td>
<td>&lt;5 \times 10^{-21}</td>
<td>6.3 ± 1.3 \times 10^{-21}</td>
</tr>
</tbody>
</table>

The uncertainties are given as 2 times the standard deviation.

\(^a\) For this reaction two reference compounds were used and we obtained the following results: When isoprene was used as reference compound the ratio \((0.896 \pm 0.260)\) was obtained, corresponding to \( k_{\text{isoprene + O}_3} = (9.05 \pm 2.62) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) \([13]\) and with 1,3-butadiene as reference compound the ratio \((1.37 \pm 0.19)\) was obtained, corresponding to \( k_{\text{1,3-butadiene + O}_3} = (9.18 \pm 2.15) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) \([13]\).

\(^b\) n.d.: Not determined, see text.
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logees of acetaldehyde [16] our values lie well within the trend of increasing rate constants by increasing carbon atom number. The present knowledge about the mechanism of the NO₃ radical reaction with aldehydes gives no satisfactory explanation for this trend.

The reaction between ozone and 3-methyl-butano-2-one is somewhat faster than those of ozone with 2,2,3-trimethylcyclobutyl-1-ethanone and cyclobutylmethylketone, and the observed loss of organic is apparently reasonably well correlated with the ozone concentration in the reaction chamber.

It has been suggested that the reactivity of the OH radical towards organics, including the oxygenated hydrocarbons presently studied, may be estimated from a simple structure-reactivity relationship [17]. This incremental reactivity method predicts a rate constant for the OH reaction of 2.4 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for both pinonaldehyde and 3-methylbutanal, which is significantly lower than our values of 9.1 and 4.0 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, respectively (see Table III). The rate constants for the OH reaction with the three ketones investigated are estimated by the same method to range between 1.5 and 3 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, i.e., an order of magnitude lower than for pinonaldehyde and 3-methylbutanal. All of the structure elements in pinonaldehyde and 3-methylbutanal are included in the database used in the derivation of the structure-reactivity relationship [17]. The incremental reactivity method is claimed to be reliable within a factor of 2 for ca. 90% of organic compounds belonging to the classes used in the database development, but pinonaldehyde may very well belong to the 10% “ill-behaving” molecules. Table III also includes the predicted OH rate constants for a structure-reactivity method based upon molecular orbital calculations [18–20]: The values for the aldehydes, 2.6 × 10⁻¹¹ and 2.2 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for pinonaldehyde and 3-methylbutanal, respectively, are similar to those calculated by the incremental reactivity method, showing however, a trend towards a faster reaction for pinonaldehyde. For the ketone, 2,2,3-trimethylcyclobutyl-1-ethanone, a rate constant of 1.4 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ is predicted, which is about one order of magnitude higher than the rate constant obtained by the incremental reactivity method.

CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

This study shows that the chemical lifetime of pinonaldehyde in the atmosphere is essentially determined
by the reaction with the OH radical. The reaction with the NO₃ radical is only of minor importance even in polluted areas, whereas the reaction with O₃ is of no importance. The present results indicate an atmospheric chemical lifetime of pinonaldehyde of about two hours, assuming [OH] = 1.6 × 10⁶ molecules cm⁻³ [21].

It is concluded from the results shown in Table II and from the estimates of the OH radical reaction rates in Table III, that the reactivity of pinonaldehyde with the NO₃ radical and with O₃ is mainly linked to the aldehyde group, because the reactions rates of structurally similar compounds without the aldehyde group are significantly slower as shown by Table II. For the reactions of pinonaldehyde with OH radicals other sites like the two tertiary H-atoms could be of importance, see Table III under Klamt [18–20], who does not calculate a significant difference between the rates of the reaction of pinonaldehyde with OH and that of the structurally similar compound with OH.

To our knowledge, pinonaldehyde has only been tentatively identified at low pptV levels in ambient air [22]. This is somewhat puzzling considering that laboratory studies have shown pinonaldehyde to be a major product from oxidation of α-pinene [5–8]. Hence, we have estimated the daytime steady-state concentration of pinonaldehyde in the atmosphere using k(OH+pinonaldehyde) obtained in this study, and assuming that photolysis and heterogeneous losses are unimportant sinks. Pinonaldehyde is formed by the oxidation of α-pinene by OH radicals with a yield of approximately 60% in an NOₓ-containing atmosphere [7]. The yield of pinonaldehyde from the ozonolysis of α-pinene is not known so we consider the two extreme cases where the yield is 0% and 100%, respectively. By equating sources and sink terms of pinonaldehyde (i.e., applying the steady-state assumption) and using k(OH + α-pinene) = 5.37 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ [13], k(O₃ + α-pinene) = 8.5 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ [23], [OH] = 1.6 × 10⁶ molecules cm⁻³, and O₃ = 1.2 × 10¹² molecules cm⁻³ (50 pptV), ratios of [pinonaldehyde]/[α-pinene] of 0.35 and 1.05, respectively, are obtained. This means that under typical ambient conditions, pinonaldehyde should be detected at low pptV levels and not at low pptV levels [22]. From the simple estimate given, we conclude that other effective atmospheric sinks for pinonaldehyde, like heterogeneous losses or photolytic degradation, probably exist.

It should be mentioned that other terpenes in the atmosphere are also oxidized to keto-aldehydes like pinonaldehyde [8,24] and therefore the fate of pinonaldehyde may give an indication of the fate of other keto-aldehydes in the troposphere.

Further work on the atmospheric lifetime and fate for other terpene oxidation products is in progress.

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BIBLIOGRAPHY

2. A. Guenther, C. N. Hewitt, D. Erickson, R. Fall, C.
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