Atmospheric Environment 43 (2009) 798–804

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Gas-phase chemistry of benzyl alcohol: Reaction rate constants and products with OH radical and ozone

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ARTICLE INFO

Article history:
Received 3 July 2008
Received in revised form
17 October 2008
Accepted 1 November 2008

Keywords:
OH rate constant
Ozone rate constant
Benzyl alcohol
Indoor chemistry

ABSTRACT

A bimolecular rate constant, $k_{\mathrm{OH+Benzyl\ alcohol}}$, of $(28 \pm 7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was measured using the relative rate technique for the reaction of the hydroxyl radical (OH) with benzyl alcohol, at (297 ± 3) K and 1 atm total pressure. Additionally, an upper limit of the bimolecular rate constant, $k_{\mathrm{O3+Benzyl\ alcohol}}$, of approximately 6×10^{-19} cm^3 molecule^{-1} s^{-1} was determined by monitoring the decrease in benzyl alcohol concentration over time in an excess of ozone (O_3). To more clearly define part of benzyl alcohol's indoor environment degradation mechanism, the products of the benzyl alcohol + OH were also investigated. The derivatizing agents *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) were used to positively identify benzaldehyde, glyoxal and 4-oxopentanal as benzyl alcohol/OH reaction products. The elucidation of other reaction products was facilitated by mass spectrometry of the derivatized reaction products coupled with plausible benzyl alcohol/OH reaction mechanisms based on previously published volatile organic compound/OH gas-phase reaction mechanisms.

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1. Introduction

Consumer formulations used in indoor environments for air freshening and cleaning can contain compounds that can serve as fragrance and solvent (Nazaroff and Weschler, 2004; Rogers et al., 2005; Singer et al., 2006). Many consumer product formulations contain volatile organic compounds (VOCs) such as terpenes, terpene alcohols, aldehydes, and alcohols. Locally high concentrations of these classes of VOCs can be obtained in activities such as cleaning, washing, painting, etc., and as a result of building energy-saving measures. (Carslaw, 2003; Nazaroff and Weschler, 2004). To better understand building occupant exposure investigations of the indoor gas-phase chemistry of many of these compounds can yield important insights.

Just as in the outdoor environment, gas-phase reactions between emitted VOCs and the OH radical, NO_3 radical and O_3 may occur in the indoor environment (Atkinson and Arey, 2003; Calvert et al., 2002; Forester et al., 2007; Ham et al., 2006; Weschler, 2001). In order to accurately assess the behavior of a particular VOC in the indoor environment, an investigation into the gas-phase reaction rate constants plus the identification and quantification of the reaction products are needed. Many fragrance compounds contain carbon–carbon double bonds and are expected to react very rapidly with the OH and NO_3 radicals and/or O_3 present in the indoor environment (Aschmann et al., 2002; Sarwar et al., 2002; Wells, 2005). The formation of a number of oxygenated organics such as: aldehydes, ketones, dicarbonyls, organic nitrates and particulate matter precursors have been observed (Atkinson, 1989; Atkinson, 1994; Fan et al., 2005; Yu et al., 1998).

Exposure to the reaction products described above may result in building occupant health effects (Weschler et al., 2006). Dicarbonyls, such as glyoxal and methyl glyoxal, have been observed as VOCs reaction products. These dicarbonyls have the potential to induce a respiratory response. For example, local lymph node assay (LLNA) results showed that methylglyoxal and diacetyl to be irritants and sensitizers with EC3 values ranging from 0.42 to 1.9% (Anderson et al., 2007). Diacetyl exposure has also been implicated as one of the routes responsible for bronchiolitis obliterans observed in popcorn factory workers. (Kreiss et al., 2002).

Benzyl alcohol, an aromatic primary alcohol, is used as a solvent in paint stripper and waterborne coating applications and as an intermediate for synthesis of target molecules used in pharmaceuticals, cosmetics, preservatives, and flavoring and fragrance agents. Production capacity worldwide of benzyl alcohol is estimated at 50 kT (INCHEM, 2005). Determining the kinetics and reaction products of benzyl alcohol with the reactants OH radicals and O_3 is important in assessing potential exposures of indoor occupants.

In the work presented here, the rate constants for the benzyl alcohol + OH radical reaction have been measured using the

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1352-2310/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2008.11.001

relative rate method. An upper limit for the benzyl alcohol/O_3 rate constant was also determined by monitoring the decrease in the benzyl alcohol concentration in an excess of ozone. The carbonyl products of the OH + benzyl alcohol reaction are reported using the derivatization agent *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA). The alcohol reaction products were derivatized using PFBHA with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The OH rate constant is compared to previous work cited in Atkinson. (Atkinson, 1989). The O_3 rate constant for benzyl alcohol has not been previously reported.

2. Experimental methods

2.1. Apparatus and materials

Experiments to measure the gas-phase rate constant of the OH + benzyl alcohol reaction were conducted with a previously described apparatus (Forester et al., 2007). A brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4 mm Swagelok fitting attached to a 5-mil Teflon® film bag (50–80 L) housed in a light-tight wooden chamber. The filler system was equipped with a syringe injection port facilitating the introduction of both liquid and gaseous reactants into the Teflon® bag with the flowing air stream. All reactant mixtures and calibration standards were generated using this system. Irradiations were carried out in the chamber (described above) which contained the following mix of lamps: six Philips TL40W/03; one GE F40BL; two QPANEL (Cleveland, OH) UV351 and seven QPANEL UV340. This lamp mixture approximates solar radiation from 300 to 450 nm.

Sampling for the benzyl alcohol/OH, benzyl alcohol/O_3 kinetics experiments and benzaldehyde yield experiments was performed using a polydimethylsiloxane/divinylbenzene solid phase microextraction (SPME) fiber (Supelco, Milwaukee, WI, 57310-U) assembly which was inserted into a 6.4 mm Swagelok (Solon, OH) fitting attached to a 50–80 L Teflon®-film bag. The SPME fiber was exposed for 45 min within the bag, and then inserted into the injector of an Agilent (Wilmington, DE) 6890 gas chromatograph with a 5975 mass selective detector (GC/MS) and Agilent ChemStation software. The GC temperature program used was: injection port was set to 250 °C, and oven temperature began at 40 °C for 6 min and was ramped 20 °C min^{-1} to 240 °C and held for 2 min.

Derivatized reaction products were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000GC/MS system operated in both the electron impact (EI) and chemical ionization (CI) modes (Yu et al., 1998). Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.32 mm i.d., 30 m long, 1 μm film thickness) column and the following GC oven parameters: 60 °C for 1 min then 20 °C min^{-1} to 170 °C, then 3 °C min^{-1} to 280 °C and held for 5 min.

Samples were injected in the splitless mode, and the GC injector was returned to split mode one minute after sample injection with the following injector temperature parameters: 60 °C for 1 min then 180 °C min^{-1} to 250 °C and held to the end of the chromatographic run (Yu et al., 1998). The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI ionization spectra were collected from m/z 40 to 650. Acetonitrile was the chemical ionization reagent used for all CI spectra. When possible, commercially available samples of the identified products were derivatized and subsequently analyzed to verify matching ion spectra and chromatographic retention times.

Hydroxyl radicals were generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of nitric oxide (NO) in air (Atkinson et al., 1981). CH_3ONO was prepared in gram quantities using the method of Taylor et al. (Taylor et al., 1980) and stored in a lecture bottle at room temperature. The CH_3ONO purity (>95%) was verified by GC/MS. Ozone was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon® bag. Aliquots of this O_3/air mixture were added to the Teflon® reaction chamber using a gas-tight syringe.

All compounds were used as received and had the following purities: from Sigma–Aldrich (Milwaukee, WI): benzyl alcohol (100%), decane (99+%), hexanal (98%), benzaldehyde (99%), *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA)(98+%), cyclohexane (99.9%), *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) (99+%); from Fisher Scientific (Fairlawn, NJ): methanol (99%). 4-Oxopentanal (4-OPA) was synthesized by Richman Chemical Inc. (Lower Gwynedd, PA) (98.84%). Nitric oxide (99+% pure) was obtained as a 4942 ppm mixture in UHP nitrogen from Butler Gases (Morrisville, PA). Helium (UHP grade), the carrier gas, was supplied by Amerigas (Sabraton, WV) and used as received. Experiments were carried out at (297 ± 3) K and 1 atmosphere pressure.

2.2. Experimental procedures

The experimental procedures for determining the benzyl alcohol + OH reaction kinetics were similar to those described previously (Wells, 2005).

$$\text{Benzyl alcohol} + \text{OH} \xrightarrow{k_{\text{OH+Benzyl alcohol}}} \text{Products} \tag{1}$$

$$\text{Reference} + \text{OH} \xrightarrow{k_{\text{Ref}}} \text{Products} \tag{2}$$

The rate equations for reactions (1) and (2) are combined and integrated, resulting in the following equation:

$$\ln\left(\frac{[\text{Benzyl alcohol}]_0}{[\text{Benzyl alcohol}]_t}\right) = \frac{k_{\text{OH+Benzyl alcohol}}}{k_{\text{Ref}}}\ln\left(\frac{[\text{Ref}]_0}{[\text{Ref}]_t}\right) \tag{3}$$

If reaction with OH is the only removal mechanism for benzyl alcohol and reference, a plot of ln([benzyl alcohol]$_0$/[benzyl alcohol]$_t$) versus ln([Ref]$_0$/[Ref]$_t$) yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_{Ref} yields $k_{\text{OH+Benzyl alcohol}}$ (Fig. 1). The OH rate constant experiments for benzyl alcohol employed the use of two reference compounds: decane and hexanal. The use of two different reference compounds with different OH rate constants ensures the accuracy of the benzyl alcohol/OH rate constant and demonstrates that other reactions are not removing benzyl alcohol.

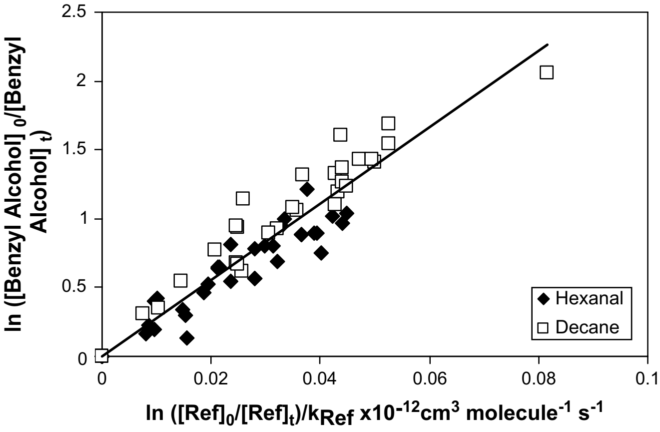

Fig. 1. Benzyl alcohol relative rate plot with hexanal (◆) and decane (□) as reference compounds. The OH + benzyl alcohol constant, $k_{\text{OH+Benzyl alcohol}}$, measured is $(27.8 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

For the benzyl alcohol/OH kinetic experiments the typical concentrations of the pertinent species in the 50–80 L Teflon® bag were 0.15–0.3 ppm ($0.4–0.7 \times 10^{13}$ molecule cm^{-3}) benzyl alcohol, 0.008–0.3 ppm ($0.02–0.7 \times 10^{13}$ molecule cm^{-3}) reference, 10 ppm (23×10^{13} molecule cm^{-3}) CH_3ONO, and 0.6 ppm (1.4×10^{13} molecule cm^{-3}) NO in air. The gas-phase mixtures were allowed to reach equilibrium before initial species concentration ($[X]_0$) samples were collected. Typically, three photolysis intervals of 15–80 s each were used on the reaction mixture for a combined total photolysis time of approximately 200 s. The total ion chromatogram (TIC) from the Agilent 6890 mass selective detector was used to determine benzyl alcohol and reference concentrations.

To determine possible chromatographic interferences from reference/OH and reaction products, both benzyl alcohol and the reference compounds were mixed and allowed to react with the OH radical in separate experiments and analyzed as described previously (Wells, 2004). No chromatographic interferences were observed. All measurements were at least duplicated. A relative standard deviation (the data set standard deviation divided by the data set average) of approximately 3.4 % was achieved with the described sampling methods utilizing the Agilent 6890/5975GC/MS system.

The experimental procedures for the determination of the benzyl alcohol + O_3 reaction kinetics were similar to those described previously (Wells, 2005).

$$\text{Benzyl alcohol} + O_3 \xrightarrow{k_{O_3+\text{Benzyl alcohol}}} \text{Products} \tag{4}$$

Benzyl alcohol was injected into a 50–80 L Teflon® bag reaction chamber as it was being filled with air. The benzyl alcohol concentration was 0.057 ppm (0.14×10^{13} molecule cm^{-3}). Cyclohexane (905 ppm) was also injected into the reaction chamber to scavenge any OH formed as a byproduct of the benzyl alcohol/O_3 reaction (Paulson et al., 1999). Background measurements were made using the SPME fiber. O_3 was injected resulting in a final concentration of 0.660 ppm (1.6×10^{13} molecule cm^{-3}) in the reaction chamber. The mixture was allowed to react for a total of 70 min. Like the OH radical experiments, the SPME fiber was exposed for 45 min within the reaction chamber, and then inserted into the injector of an Agilent 6890 gas chromatograph with a 5975 mass selective detector (GC/MS) and Agilent ChemStation software. In these series of experiments, a slight decrease ~3% in benzyl alcohol concentration was observed over the experimental time range. In order to determine an upper limit estimate for the benzyl alcohol/O_3 reaction rate constant, the measurement was repeated 3 times.

The experimental procedures for the determination of the yield of benzaldehyde from benzyl alcohol were similar to those described above for the benzyl alcohol/OH kinetics experiments, except that reference compound was excluded from the reaction mixture. The gas-phase mixtures were allowed to reach equilibrium before initial species concentration ($[X]_0$) samples were collected. Typically, two or three photolysis intervals of 5–60 s each were used on the reaction mixture for a combined total photolysis time of approximately 15–120 s.

Derivatization of the carbonyl reaction products was initiated by flowing 15–25 L of chamber contents at 3.8 L min^{-1} through an impinger containing 4 mL of acetonitrile and 250 μL of 0.02 M PFBHA in acetonitrile to derivatize the carbonyl reaction products to oximes with no effort to prevent acetonitrile evaporation during sample collection. (Yu et al., 1998). The sample was removed from the impinger and allowed to react for a 24–48 h time period in the dark. The reacted solutions were gently blown to dryness with UHP N_2, reconstituted with 100 μL of methanol, and then 1 μL of the reconstituted solution was injected onto the Varian 3800/Saturn 2000GC/MS system. The derivatization of hydroxyl groups (alcohol) was achieved by subsequent addition of 150 μL of commercially available BSTFA solution to the PFBHA oximes. These PFBHA/BSTFA solutions were heated to approximately 70 °C for 60 min to complete the silylation and then 1 μL of the solution was injected into the Varian 3800/Saturn 2000GC/MS system. Additionally, chemical ionization (CI) mass spectra using acetonitrile were also collected on the derivatized reaction products allowing the determination of the PFBHA or PFBHA/BSTFA-derivatized compound's molecular weight.

3. Results

3.1. Benzyl alcohol/OH reaction rate constant

The OH rate constant for benzyl alcohol was obtained using the relative rate method described above. The use of decane ($k_{OH+\text{decane}} = 11 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) and hexanal ($k_{OH+\text{hexanal}} = 30 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) as references resulted in OH + benzyl alcohol bimolecular rate constants of (29.7 ± 0.7) and $(24.7 \pm 0.7) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively (Atkinson and Arey, 2003). The combined plot, which is a modified version of Equation (3), is shown in Fig. 1. The $\ln([\text{Ref}]_0/[\text{Ref}]_t)$ term is divided by the respective reference rate constant and multiplied by 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, resulting in a unitless number. This yields a slope that is equal to the OH/benzyl alcohol rate constant, $k_{OH+\text{Benzyl alcohol}}$, *divided by* 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. This modification allows for a direct comparison of the two reference compound/benzyl alcohol data sets. The slope of the line shown in Fig. 1 yields an OH bimolecular rate constant, $k_{OH+\text{Benzyl alcohol}}$, of $(27.8 \pm 0.6) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The data points at the origin are experimental points because pre-irradiation, $t = 0$, data showed no detectable loss of benzyl alcohol or reference. The errors in the rate constants stated above are the 95% confidence level from the random uncertainty in the slopes. Incorporating the uncertainties associated with the reference rate constants (±25% for decane and hexanal) used to derive the benzyl alcohol/OH rate constant yields a final value for $k_{OH+\text{Benzyl alcohol}}$, of $(28 \pm 7) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} which can be compared with a previously reported measurement of $(22.9 \pm 2.5) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} from Nolting, Witte, and Zetzsch, unpublished data, cited in Atkinson (Atkinson, 1989). The ratios $k_{OH+\text{Benzyl alcohol}}/k_{OH+\text{decane}}$ and $k_{OH+\text{Benzyl alcohol}}/k_{OH+\text{hexanal}}$ incorporating the uncertainties are 2.5 ± 0.6 and 0.9 ± 0.2, respectively.

3.2. Benzyl alcohol/ozone reaction rate constant

The experimental conditions, described above, to determine the benzyl alcohol/O_3 reaction rate constant yielded a first order decrease (4%) in benzyl alcohol concentration over a 70 min monitoring period. This loss is similar to the analytical uncertainty mentioned earlier. However if all of the decrease in the benzyl alcohol concentration is due solely to reaction with ozone, analysis of the data resulted in an upper limit determination of the benzyl alcohol/O_3 rate constant of 6×10^{-19} cm^3 $molecule^{-1}$ s^{-1}. The benzyl alcohol/O_3 rate constant, $k_{o_3+\text{Benzyl alcohol}}$, has not been previously reported.

3.3. Benzyl alcohol/OH reaction products

The benzyl alcohol/OH reaction products observed and positively identified based on mass spectra reaction product data and from standards: benzaldehyde, glyoxal and 4-oxopentanal. These and other observed products were determined by mass spectro metry of the derivatized reaction product coupled with plausible benzyl alcohol/OH reaction mechanisms based on previously published volatile organic compound/OH gas-phase reactions as described below (Atkinson and Arey, 2003; Hu et al., 2007; Kroll et al., 2001; Wells, 2005). The results for both the positively identified reactions products and other observed reaction products are described below.

Derivatization of nonsymmetric carbonyls using PFBHA or PFBHA/BSTFA typically resulted in multiple chromatographic peaks due to geometric isomers of the oximes. Identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak of a particular oxime are almost identical. Typically, the PFBHA-derivatized oximes' (generic structure: $F_5C_6CH_2ON{=}C(R_1)(R_2)$) mass spectra included an ion at m/z 181 ($[CH_2C_6F_5]^+$ fragment) with a large relative intensity (>40%) and a $[PFBHA\ oxime + 181]^+$ ion (due to reactions in the ion trap mass spectrometer) (Yu et al., 1998). In most cases, the m/z 181 ion relative intensity for the chromatographic peaks due to benzyl alcohol/OH reaction product oximes was either the largest or one of the largest in the mass spectrum and was used to generate selected ion chromatograms (Yu et al., 1998). The mass spectra of compounds that were additionally derivatized with BSTFA contained m/z 73 ions from the $[Si(CH_3)_3]^+$ fragments. The product data are described below.

The following chronological chromatographic retention time results and mass spectra data were observed utilizing PFBHA or PFBHA/BSTFA derivatization and the Varian 3800/Saturn 2000GC/MS system. The reaction products' chromatographic peak areas were a function of the initial benzyl alcohol concentration and were observed only after OH initiation of benzyl alcohol/methanol/methyl nitrite/NO/air mixtures. Derivatization experiments performed in the presence of benzyl alcohol, but in the absence of all other chemicals in the reaction chamber (methanol/methyl nitrite/NO/air) did not result in any of the data reported below except for small amounts (as noted by chromatographic peak areas) of benzaldehyde. However, benzaldehyde oxime peak area increased significantly, about 160 times with benzyl alcohol/OH reaction initiation, indicating that benzaldehyde is a likely product of the benzyl alcohol reaction.

3.4. Benzaldehyde ($(C_6H_5)C({=}O)H$)

The peaks for the oxime observed at 17.6 min were observed as a reaction product of the benzyl alcohol/OH reaction and had ions at m/z (relative intensity) 181 (100%), 271 (38%) and 302 (20%). The m/z 301 ion is the result of a PFBHA derivatization indicating a reaction product with a molecular weight of 106. Using acetonitrile for chemical ionization, an $M+1$ ion of m/z of 302 was observed for the PFBHA-derivatized sample. The PFBHA-benzaldehyde oxime was synthesized to confirm this chromatographic assignment.

3.5. Glyoxal ($HC({=}O)C({=}O)H$)

The peaks for the oxime observed at 24.1 and 24.4 min were observed as a reaction product of the benzyl alcohol/OH reaction and had ions at m/z (relative intensity) 181 (100%), and 265 (20%). The m/z 448 ion is the result of a PFBHA double derivatization indicating a reaction product with a molecular weight of 58. Using acetonitrile for chemical ionization, an $M+1$ ion of m/z of 449 was observed for the PFBHA-derivatized sample. The PFBHA-gyloxal oxime was synthesized to confirm this chromatographic assignment (Forester et al., 2007).

3.6. 4-Oxopentanal ($HC({=}O)(CH_2)_2C({=}O)CH_3$)

The peaks for the oxime observed at 29.5, 29.9 and 30.1 min were observed as a reaction product of the benzyl alcohol/OH reaction and had ions at m/z (relative intensity) 181 (100%), and 279 (18%). The m/z 490 ion is the result of a PFBHA double derivatization indicating a reaction product with a molecular weight of 100. Using acetonitrile for chemical ionization, an $M+1$ ion of m/z of 491 was observed for the PFBHA-derivatized sample. The PFBHA-4-oxopentanal oxime was synthesized to confirm this chromatographic assignment.

3.7. Oxime at retention time 30.7 and 31.2 min

The peaks for the oxime observed at 30.7 and 31.2 min were observed as a reaction product of benzyl alcohol/OH reaction and had ions at m/z (relative intensity) 181 (100%), and 281 (11%). The m/z 478 ion is the result of a PFBHA double derivatization indicating a reaction product with a molecular weight of 88. Using acetonitrile for chemical ionization, an $M+1$ ion of m/z of 479 was observed for the PFBHA-derivatized sample. The dual PFBHA/BSTFA derivatization method described above yielded a chromatographic peak with retention times of 30.7 and 31.2 min and a mass spectrum m/z 550. The peaks for the oxime observed at 30.7 and 31.2 min were observed as a reaction product of the benzyl alcohol/OH reaction and had ions at m/z (relative intensity) 181 (100%), 73 (70%), 255 (32%), 353 (25%) and 369 (15%). The m/z 550 ion could be the result of a PFBHA double derivatization and single BSTFA derivatization indicating a reaction product with a molecular weight of 88. Additionally, the PFBHA/BSTFA m/z 550 ion is 72 amu larger than the m/z 478 ion observed in the PFBHA only derivatization sample. Using acetonitrile for chemical ionization, an $M+1$ ion of m/z of 551 was observed for the PFBHA/BSTFA-derivatized sample as seen in Fig. 2. A proposed benzyl alcohol + OH reaction product assignment of 3-hydroxy-2-oxopropanal *(HO)*$CH_2C({=}O)C({=}O)H$) was made based upon the observed data.

3.8. Oxime at retention time 32.8 and 33.2 min

The peaks for the oxime observed at 32.8 and 33.2 min were observed as a reaction product of the benzyl alcohol/OH reaction and had ions at m/z (relative intensity) 181 (100%) and 282 (12%). The m/z 474 ion could be the result of a PFBHA double derivatization indicating a reaction product with a molecular weight of 84. Using acetonitrile for chemical ionization, an $M+1$ ion of m/z of 475 was observed for the PFBHA-derivatized sample as seen in Fig. 3. A proposed benzyl alcohol + OH reaction product assignment

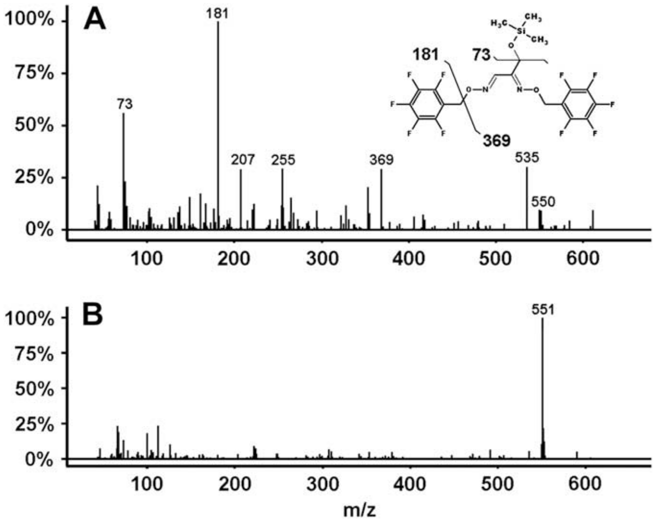

Fig. 2. PFBHA/BSTFA derivatized product of benzyl alcohol (30.7 min) A) electron ionization spectrum B) acetonitrile chemical ionization spectrum.

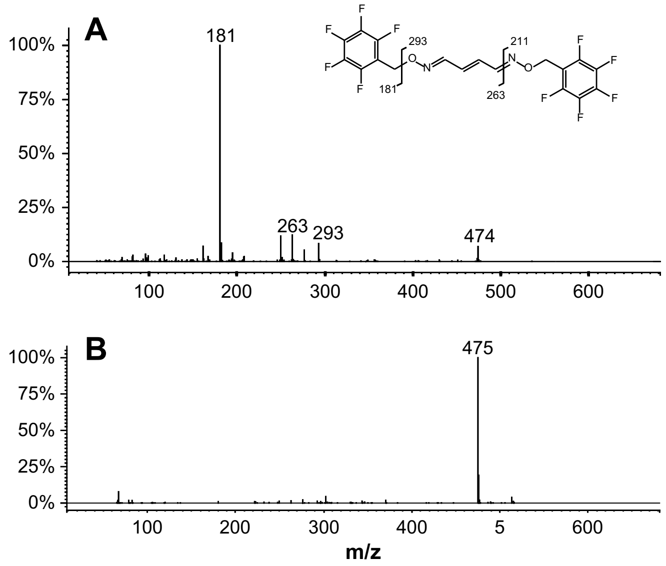

Fig. 3. PFBHA-derivatized product of benzyl alcohol (33.2 min) A) electron ionization spectrum B) acetonitrile chemical ionization spectrum.

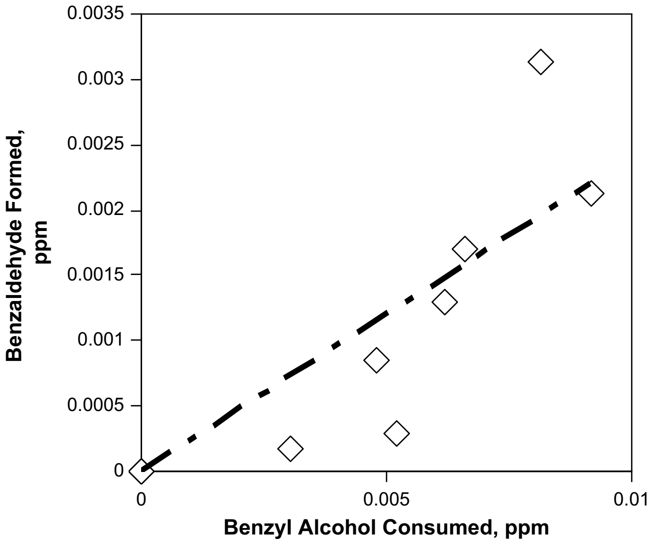

Fig. 4. Plot of benzaldehyde formed, corrected for benzaldehyde/OH reaction, versus benzyl alcohol reacted. The dashed line slope of the linear least squares analysis with a 95% confidence interval is 0.24 ± 0.03.

of but-2-enedial *(HC(=O)CH=CHC(=O)H)* was made based upon the observed data.

3.9. Benzaldehyde yield from benzyl alcohol/OH reaction

The benzaldehyde yield for the benzyl alcohol/OH reaction was investigated. While benzaldehyde concentrations increased as benzyl alcohol concentrations decreased during the course of the reaction, the relationship between benzaldehyde formed and benzyl alcohol consumed is not linear (Fig. 4). This was unexpected since the only anticipated mechanism for benzaldehyde formation is OH hydrogen abstraction on the methylene group attached to the benzene ring. This upward curvature was observed in yield experiments over a wide range of initial benzyl alcohol concentrations (0.3–0.008 ppm). Because benzaldehyde could react with OH radicals, its concentration was corrected using a previously described method (Atkinson, 2003; Smith et al., 1992). The rate constant for benzaldehyde/OH (12×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) has been measured previously (Atkinson and Arey, 2003). The average [Benzaldehyde] correction factor was 21% (maximum correction 35%). The dashed line in Fig. 4 is the linear regression of the data set which results in an approximate yield of (24 ± 3)%. This value is only approximate because the plot is clearly non linear.

4. Discussion

4.1. Benzyl alcohol/OH and benzyl alcohol/O_3 reaction kinetics

OH reacts with benzyl alcohol by H-atom abstraction or OH addition to the carbon–carbon double bonds in the benzene ring. (Atkinson, 1989). The benzyl alcohol/OH value reported here is $(28 \pm 7) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. This result compares favorably, i.e. is within experimental error of the rate constant of $(22.9 \pm 2.5) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} from Notling, Witte, and Zetzsch, unpublished data, previously cited (Atkinson, 1989). The H-atom abstraction and OH addition contribute approximately 99%, to the calculated benzyl alcohol/OH rate constant of 8.25×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (EPA, 2000) which is about 3 times slower, than the measured value reported above.

It is possible that the CH_2OH group may disturb the pi electron cloud of the benzene ring resulting in distinct pockets of electron density to facilitate OH radical addition and enhance stabilization of the alkoxy radical on the benzene ring (Atkinson, 2007; Johnson and Marston, 2008). Specifically, the CH_2OH group is an activating group; its presence causes the benzene ring on the benzyl alcohol molecule to be more susceptible to OH radical attack (Kwok and Atkinson, 1995).

If ozone reacts with benzyl alcohol, it would be by addition to the aromatic ring. An upper limit of 6×10^{-19} cm^3 $molecule^{-1}$ s^{-1} was determined for $k_{O_3+\text{Benzyl alcohol}}$. For comparison, an estimated rate constant for the ozone/benzene reaction, $k(\text{calc})_{O_3+\text{benzene}}$, of 1.7×10^{-22} cm^3 $molecule^{-1}$ s^{-1} can be determined from a published Arrhenius expression (Toby et al., 1985).

4.2. Benzyl alcohol/OH reaction products

For the benzyl alcohol/OH reaction the experimental parameters were set to minimize other side reactions, such as peroxy radical reactions, and highlight the primary OH hydrogen abstraction and OH addition step.

4.3. Benzaldehyde

Benzaldehyde was the product with the largest peak area observed in the PFBHA derivatization experiments from the benzyl alcohol/OH reaction. The radical $(C_6H_5)CH\bullet(OH)$ is formed by hydrogen abstraction of the alkyl hydrogen. This then reacts with O_2 to give $C_6H_5C(=O)H$ and HO_2. As may be expected from the poor agreement of the EPA (2000) estimated rate constant for the OH radical reaction, the predicted benzaldehyde yield of 40% is also in poor agreement with the approximate yield of benzaldehyde of 24% (EPA, 2000).

4.4. Glyoxal, Oxime at retention time 30.7 and 31.2 min, Oxime at retention time 32.8 and 33.2 min

These three carbonyl compounds were observed in the PFBHA derivatization experiments from the benzyl alcohol/OH reaction. The radical $(C_6H_5)\bullet(OH)(CH_2(OH))$ is formed by hydroxyl radical addition to carbon C4 of the aromatic/benzene ring (see Fig. 5). This then reacts with oxygen to form the peroxybicyclicradical, $\bullet(OO(C_6(OO)H_5)(OH))(CH_2(OH))$. This can react with NO to form NO_2 and

(•O(C_6(OO)H_5)(OH))(CH_2(OH) (“A” in Fig. 5). As shown in Fig. 5 this radical can decompose to form glyoxal and (2E)-2-(hydroxy methyl)but-2-enedial. Similar reaction mechanisms can be proposed for OH addition to C2 or C3 leading to the formation of 3-hydroxy-2-oxopropanal ($HOCH_2C(O)C(O)H$, proposed oxime at 30.7 and 31.2 min), and but-2-enedial (HC(O)CH=CHC(O)H, proposed oxime at 32.8 and 33.2 min) or the formation of glyoxal and (2E)-6-hydroxy-5-oxohex-2-enal, respectively.

4.5. 4-Oxopentanal

4-Oxopentanal was a product observed in the PFBHA derivatization experiments from the benzyl alcohol/OH reaction. The radical (C_6H_5)•(OH)(CH_2(OH)) is formed by hydroxyl radical addition to carbon C2 of the aromatic/benzene ring. The exact steps of this reaction product maybe surface dependent and proposal of a potential mechanism would be difficult to suggest based on conventional gas-phase OH/VOC mechanisms.

Unfortunately, neither (2E)-2-(hydroxymethyl)but-2-enedial or (2E)-6-hydroxy-5-oxohex-2-enal were observed as reaction products. They would be expected to be doubly derivatized by PFBHA (similar to glyoxal) with m/z’s of 504 and 518, respectively. These reaction products would also be expected to be derivatized by BSTFA with m/z’s of 577 and 591, respectively. These masses are well within the capabilities of the mass spectrometer used for these experiments. A thorough search of the EI and CI mass spectral data

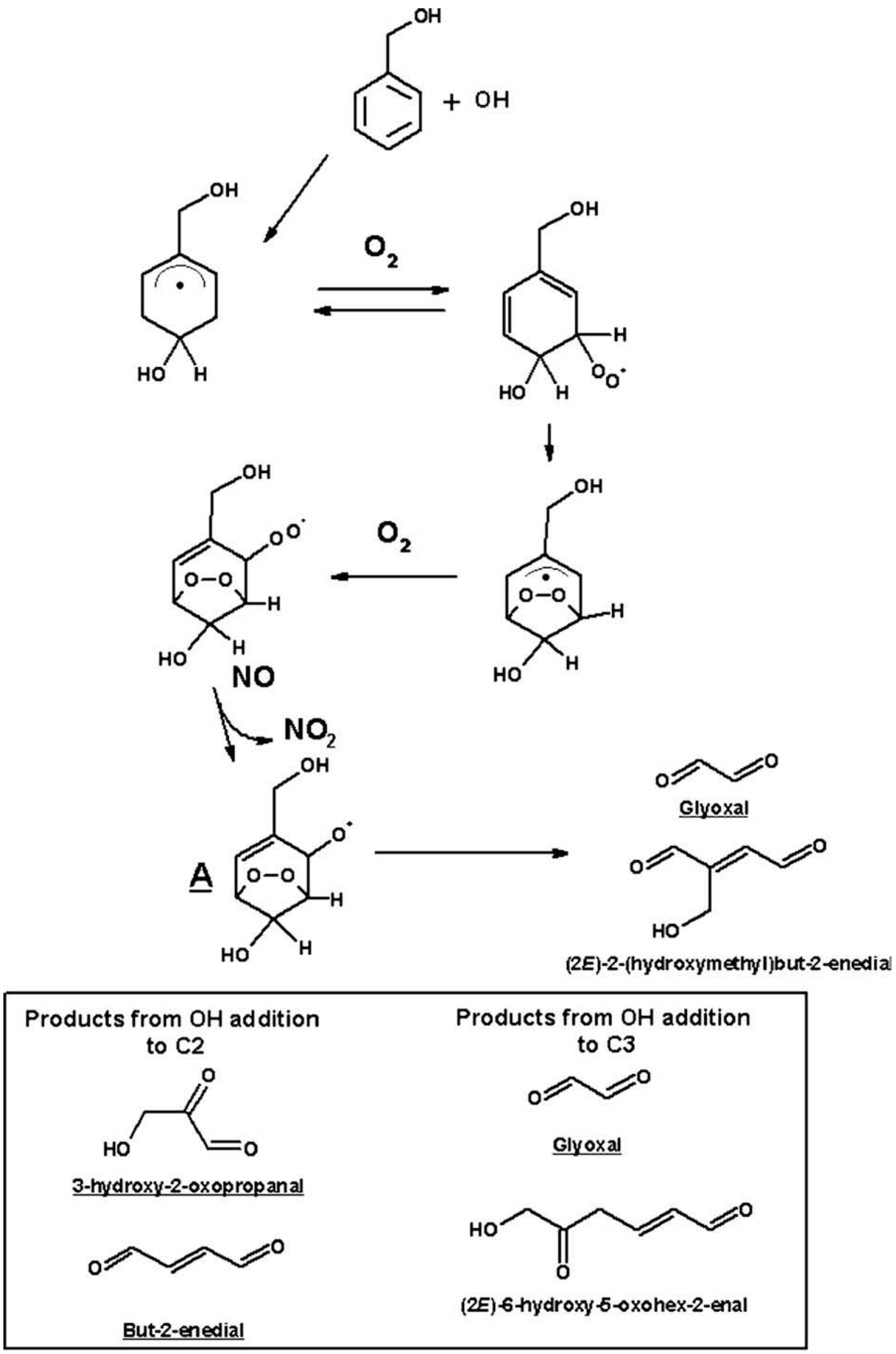

Fig. 5. Proposed reaction mechanism for benzyl alcohol + OH showing formation of products. Structures with names underlined were observed from PFBHA derivatization.

of both the PFBHA and PFBHA/BSTFA data sets did not yield any reaction products with these stated m/z's. The anticipated reaction products could adhere to the chamber walls and be removed from the gas-phase.

The benzaldehyde yield (Fig. 4) from the benzyl alcohol/OH reaction appears to have an upward curve rather than a linear relationship with benzyl alcohol consumed. This trend was observed at varying benzyl alcohol initial concentrations (0.3 ppm and 0.008 ppm). Again, benzaldehyde interacting with the chamber walls may play a role in this non-linear pattern. Another possibility is that benzaldehyde could be formed through some other intermediate from OH addition to the benzene ring.

5. Conclusions

In order to investigate the detailed gas-phase chemistry of benzyl alcohol, the hydroxyl (OH) radical reaction rate constant, ozone reaction rate constant, and respective reaction mechanisms were investigated. The OH radical reacts by hydrogen abstraction or addition to the aromatic/benzene ring of benzyl alcohol. A bimolecular rate constant, $k_{\mathrm{OH+Benzyl\ alcohol}}$, of $(28 \pm 7) \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ was measured using the relative rate technique. Ozone is expected to add to the benzene ring of the benzyl alcohol. An upper limit of $6 \times 10^{-19}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ was determined for $k_{\mathrm{O_3+Benzyl\ alcohol}}$.

The identification of the benzyl alcohol/OH reaction products was facilitated by the use of derivatizing agents PFBHA or BSTFA. The major reaction products: benzaldehyde, glyoxal and 4-oxopentanal of the benzyl alcohol/OH reaction was proposed based on mass spectral data from the PFBHA derivatization experiments and confirmed using standards. Other derivatization techniques could identify additional products such as hydroperoxides. While other benzyl alcohol/OH reaction products were simply proposed based on observed experimental data and previously published VOCs/OH reaction mechanisms.

Approximate indoor environment concentrations of the hydroxyl radical (1×10^5 molecules cm^{-3}) and ozone (5×10^{11} molecules cm^{-3}) have been previously estimated by Sarwar et al. (2002). Using the benzyl alcohol/OH and benzyl alcohol/O_3 rate constants reported here pseudo-first order rate constants of $0.012\ \mathrm{h}^{-1}$ and $0.0011\ \mathrm{h}^{-1}$ were determined, respectively. Comparing these values to a typical indoor air exchange rate of $0.6\ \mathrm{h}^{-1}$, room air exchange is expected to be the most likely indoor environment loss mechanism for benzyl alcohol (Wilson et al., 1996).

Disclaimer: The findings and conclusions in this report are those of the author(s) and do not necessarily represent the official position of the Centers for Disease Control and Prevention/the Agency for Toxic Substances and Disease Registry.

Acknowledgement

The authors would like to thank the reviewers for helpful suggestions and comments which were incorporated into the manuscript.

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