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AFRL-ML-TY-TP-2000-4509

THE HYDROXYL RADICAL REACTION RATE CONSTANT AND ATMOSPHERIC TRANSFORMATION PRODUCTS OF 2-BUTANOL AND 2-PENTANOL

J. STEVEN BAXLEY
APPLIED RESEARCH ASSOCIATES
GULF COAST DIVISION
P.O. BOX 40128, BLDG 1142, MISSISSIPPI ROAD
TYNDALL AFB FL 32403

J.R. WELLS
AFRL/MLQR
139 BARNES DRIVE, STE 2
TYNDALL AFB FL 32403
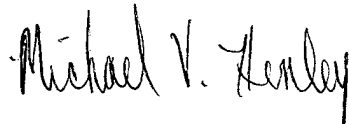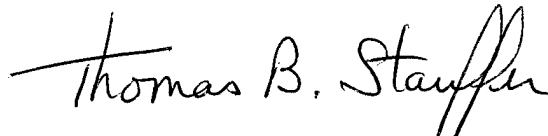
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MICHAEL V. HENLEY
Program Manager

THOMAS B. STAUFFER, PhD, DR-IV, DAF
Chief, Weapons Systems Logistics Branch

RANDY L. GROSS, Col, USAF, BSC
Chief, Air Expeditionary Forces Technologies Division

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE
The Hydroxyl Radical Reaction Rate Constant and Atmospheric Transformation Products of 2-Butanol and 2-Pentanol

5. FUNDING NUMBERS
N/A

6. AUTHORS
Baxley, Steven[1]; Wells, J.R.[2]

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
[1]ARA, Gulf Coast Division, P.O. Box 40128, Bldg 1142, Mississippi Rd, TAFB FL 32403; [2]AFRL/MLQR, 139 Barnes Drive, Ste 2, TAFB FL 32403

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFRL/MLQE
139 Barnes Drive, Ste 2
Tyndall AFB FL 32403-5323

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFRL-ML-TY-TP-2000-4509

11. SUPPLEMENTARY NOTES
AFRL/MLQE Project Manager: Dr. Joseph D. Wander   Phone: (850) 283-6240

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

12b. DISTRIBUTION CODE
A

13. ABSTRACT *(Maximum 200 words)*
The relative rate technique has been used to measure the hydroxyl radical (OH) reaction rate constant of +2-butanol (2BU, $CH_3CH_2CH[OH]CH_3$) and 2-pentanol (2PE, $CH_3CH_2CH_2CH[OH]CH_3$). 2BU and 2PE react with OH yielding bimolecular rate constants of $(8.1 \pm 2.0) \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ and $(11.9 \pm 3.0) \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$, respectively, at 297 ± 3 K and 1 atmosphere total pressure. Both 2BU and 2PE OH rate constants reported here are in agreement with previously reported values [1-4]. In order to more clearly define these alcohols' atmospheric reaction mechanisms, an investigation into the OH + alcohol reaction products was also conducted. The OH + 2BU reaction products and yields observed were: methyl ethyl ketone (MEK, $[60 \pm 2]\%$, $CH_3CH_2C(=O)CH_3$) and acetaldehyde ($[29 \pm 4]\%$ $HC(=O)CH_3$). The OH + 2PE reaction products and yields observed were: 2-pentanone (2PO, $[41 \pm 4]\%$, $CH_3C(=O)CH_2CH_2CH_3$), propionaldehyde $[14 \pm 2]\%$, $HC(=O)CH_2CH_3$), and acetaldehyde $[40 \pm 4]\%$, $HC(=O)CH_3$). The alcohols' reaction mechanisms are discussed in light of current understanding of oxygenated hydrocarbon atmospheric chemistry. Labeled (^{18}O) 2BU/OH reactions were conducted to investigate 2BU's atmospheric transformation mechanism details. The findings reported here can be related to other structurally similar alcohols and may impact regulatory tools such as ground level ozone-forming potential calculations (incremental reactivity) [5].

14. SUBJECT TERMS

15. NUMBER OF PAGES
8

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500   Computer Generated

STANDARD FORM 298 (Rev 2-89)
Prescribed by ANSI Std 239-18
298-102

PO# 98-000111

The Hydroxyl Radical Reaction Rate Constant and Atmospheric Transformation Products of 2-Butanol and 2-Pentanol

J. STEVEN BAXLEY[1], J. R. WELLS[2]

[1]Applied Research Associates, Gulf Coast Division, P.O. Box 40128, Bldg. 1142, Mississippi Road, Tyndall Air Force Base, Florida 32403

[2]Air Force Research Laboratory, AFRL/MLQR, 139 Barnes Drive, Tyndall AFB, Florida 32403-5323

ABSTRACT: The relative rate technique has been used to measure the hydroxyl radical (OH) reaction rate constant of +2-butanol (2BU, $CH_3CH_2CH(OH)CH_3$) and 2-pentanol (2PE, $CH_3CH_2CH_2CH(OH)CH_3$). 2BU and 2PE react with OH yielding bimolecular rate constants of $(8.1 \pm 2.0) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} and $(11.9 \pm 3.0) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}, respectively, at 297 ± 3 K and 1 atmosphere total pressure. Both 2BU and 2PE OH rate constants reported here are in agreement with previously reported values [1–4]. In order to more clearly define these alcohols' atmospheric reaction mechanisms, an investigation into the OH + alcohol reaction products was also conducted. The OH + 2BU reaction products and yields observed were: methyl ethyl ketone (MEK, $(60 \pm 2)\%$, $CH_3CH_2C(=O)CH_3$) and acetaldehyde $((29 \pm 4)\%$ $HC(=O)CH_3$). The OH + 2PE reaction products and yields observed were: 2-pentanone (2PO, $(41 \pm 4)\%$, $CH_3C(=O)CH_2CH_2CH_3$), propionaldehyde $((14 \pm 2)\%$ $HC(=O)CH_2CH_3$), and acetaldehyde $((40 \pm 4)\%$, $HC(=O)CH_3$). The alcohols' reaction mechanisms are discussed in light of current understanding of oxygenated hydrocarbon atmospheric chemistry. Labeled (^{18}O) 2BU/OH reactions were conducted to investigate 2BU's atmospheric transformation mechanism details. The findings reported here can be related to other structurally similar alcohols and may impact regulatory tools such as ground level ozone-forming potential calculations (incremental reactivity) [5]. © 1998 John Wiley & Sons, Inc. Int J Chem Kinet 30: 745–752, 1998

INTRODUCTION

Oxygenated organic compounds are being used in fuels to promote better combustion and to increase octane without using more aromatic compounds, thereby reducing carbon monoxide and photochemically active volatile exhaust emissions. Oxygenated organics are also being used as solvents in paints and paint strippers. With the increased usage of these compounds a better understanding of their environmental impact is necessary. Several hydroxyl radical (OH) + oxygenated organic bimolecular rate constants are well known, but details pertaining to the reaction mechanisms are sparse and incomplete. Current studies of the products of OH + oxygenated organic compounds have illustrated the complexity of their atmospheric reaction mechanisms [6–10]. Re-

cently, structural reactivity, which uses factors based on neighboring molecular groups and molecular structure to predict hydroxyl radical rate constants, has become a useful tool for initially assessing molecules' complex atmospheric transformations [11].

Poorly understood atmospheric reaction mechanisms seriously affect air quality analysis and regulatory decisions. Calculation of a compound's incremental reactivity [5], tendency to generate tropospheric ozone (O_3), requires detailed knowledge of a compound's reactive and mechanistic properties. While not emitted directly, O_3 is a by-product of the photooxidation of hydrocarbons [12] and a regulated pollutant. Sources that contribute to its formation in the troposphere are also regulated. Currently, the reactivity models incorporate educated assumptions about a compound's unknown atmospheric mechanism, but in order to minimize uncertainties and to calculate a compound's incremental reactivity more accurately, the hydroxyl radical rate constant and the compound's atmospheric degradation mechanism must be well understood. As a side benefit, understanding the compounds' atmospheric mechanisms in detail can assist in chemical selection based on chemical structure. Kinetic and mechanistic investigations also expand the possibility of synthesizing new compounds incorporating environmentally and technically beneficial molecular structures. The information gained from the type of research presented here can lead to more beneficial use of organic compounds in the future.

Alcohols form a subset of oxygenated organics that are finding more widespread use. Both 2-butanol and 2-pentanol are present in coating formulations, and to date, there has been only one report of the OH/2-butanol rate constant and reaction products [4]. In the work presented here, the rate constant of OH with the alcohols was measured by the relative rate method [13] and the products of the OH + alcohols reaction are reported and used to derive the alcohols' atmospheric reaction mechanisms. This article presents information regarding the atmospheric impact of alcohols that is consistent with currently proposed transformation mechanisms.

EXPERIMENTAL METHODS

Apparatus and Materials

Experiments to measure the gas-phase rate constant of the OH + 2-butanol (2BU, $CH_3CH_2CH(OH)CH_3$) and 2-pentanol (2PE, $CH_3CH_2CH_2CH(OH)CH_3$) reactions were conducted with a previously described apparatus
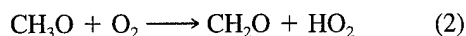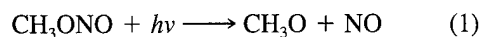
[6,14,15]. Therefore, a brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4-mm Swagelok fitting attached to ca. 100 L Teflon® film chamber. Dry compressed air was added as a diluent to the reaction chambers and measured with a 0–100 L-min^{-1} mass flow controller. The filler system was equipped with a syringe injection port facilitating the injection of both liquid and gaseous reactants into the chambers in a flowing airstream. All reactant mixtures and calibration standards were generated by this system. Irradiations were carried out in a light tight chamber using 2-mil FEP Teflon®-film bags (ca. 100 liters), and the following mix of lamps: 6-Philips TL40W/03; 1-GE F40BL; 2-QPANEL UV351 and 7-QPANEL UV340 which were shown to accurately simulate solar radiation in both frequency and intensity from 420–300 nm.

All samples (ca. 100 mL) were quantitatively monitored using an Hewlett–Packard (HP) gas chromatograph (GC) 5890 with a flame ionization detector (FID) and HP series Chem Station software. Gas samples for GC analysis were cryogenically collected on a Hastelloy C sample loop (ca. 1.3 mL) and injected onto the GC column (Restek Rtx 200 column (0.53 mm i.d., 30-m, 1.0 μm film thickness)) with a heated rotary valve [16]. The GC oven temperature program used was as follows: 35°C for 5 min then ramped temperature up 10°C/min to 210°C and held for two min. Helium (UHP grade) supplied by Air Products, was passed through drying and hydrocarbon traps before use.

Product identification experiments were also performed and sampled as described above except the chromatographic sample volume was up to twice as large (ca. 200mL) and analyzed with an HP 5890 Series II Plus GC/HP 5971 mass selective detector/HP 5965B infrared detector (GC/MS/FTIR) system. Compound separation was achieved using a Restek Rtx 200 (0.53 mm i.d., 30-m length, 1.0-μm film thickness) column.

Carbonyl compounds produced by gas-phase reactions were measured by sampling the contents of the reaction chamber through a 2,4-dinitrophenylhydrazine (DNPH) cartridge or impinger. Hydrazones formed by derivatization were separated and quantitatively measured by HPLC (HP 1050) using a three component gradient solvent program as described previously [17].

OH, the primary oxidizing radical in the atmosphere, was generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of nitric oxide (NO) in air [13].
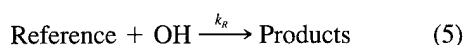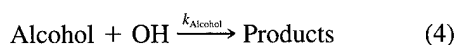
$$CH_3ONO + hv \longrightarrow CH_3O + NO \qquad (1)$$

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \qquad (2)$$

$$HO_2 + NO \longrightarrow \mathbf{OH} + NO_2 \qquad (3)$$

CH_3ONO was prepared in gram quantities using the method of Taylor et al. [18] and stored in a lecture bottle at room temperature. The CH_3ONO purity ($>95\%$) was verified by GC/MS/FTIR.

2-Pentanol was obtained from Theta Corporation and used as received. 2-Butanol, methyl ethyl ketone, 2-pentanone, propionaldehyde, dodecane, n-nonane, and heptane (all 99%+) were used as received from Aldrich Chemical. Methanol and acetonitrile, HPLC grade, were used as received from Aldrich Chemical. The water was distilled, deionized to 18 megaohm, and filtered using a Milli-Q® filter system. 2,4-Dinitrophenylhydrazine (DNPH) standards were used as received from Radian Corporation. The nitric oxide (NO) (0.662% in N_2) was obtained from Matheson Gases and used as received. Nitric oxide was added to facilitate the generation of OH and to minimize ozone (O_3) and NO_3 formation therefore preventing other possible radical reactions. The ^{18}O labeled 2-butanol (98+%) was synthesized by Cambridge Isotope Laboratories, Inc. and used as received. Experiments were carried out at 297 ± 3 K at about 1 atmosphere.

Experimental Procedures

The experimental procedures for determining the OH + alcohols reaction kinetics were similar to those described previously [14,15].

$$\text{Alcohol} + \text{OH} \xrightarrow{k_{Alcohol}} \text{Products} \qquad (4)$$

$$\text{Reference} + \text{OH} \xrightarrow{k_R} \text{Products} \qquad (5)$$

The rate equations for reactions 4 and 5 are combined and integrated resulting in the following equation:

$$\ln\left(\frac{[\text{Alcohol}]_0}{[\text{Alcohol}]_t}\right) = \frac{k_{Alcohol}}{k_R} \ln\left(\frac{[R]_0}{[R]_t}\right) \qquad \mathbf{(I)}$$

If reaction with OH is the only removal mechanism for the alcohol and reference, a plot of $\ln([\text{Alcohol}]_0/[\text{Alcohol}]_t)$ vs. $\ln([R]_0/[R]_t)$ yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_R yields $k_{Alcohol}$. The OH rate constant experiments employed the use of the reference compounds n-nonane (2BU), dodecane (2BU

and 2PE), and hexane (2PE). The use of two different reference compounds with different OH rate constants more definitively assured the accuracy of the alcohol/OH rate constant.

The typical concentrations of the pertinent species in the 100 liter Teflon® chamber were 3–5 ppm alcohols, 2–4 ppm reference, 10 ppm CH_3ONO, and 1 ppm NO in air. These mixtures were allowed to stand for 30–60 min before background chamber samples were collected. The samples were collected. The samples were collected on a cryogenic ($-65°C$) sample loop (described above) for 4 min at 25 mL min^{-1} and then flash injected (260°C) onto the GC column [16]. Typically, 15–30 s irradiation intervals were used on the reaction mixture for a combined total photolysis time of approximately 90 s. The flame ionization detector (FID) signal was used to determine alcohols and reference concentrations.

Alcohols + OH reaction product experimental methods and component concentrations were similar to those for reaction rate experiments, except that the reference compound was excluded from the reaction mixture. For the GC/MS/FTIR measurements the mixture was irradiated for timed (10, 30, 50 s) intervals followed by two separate sample collections. The mass selective detector was tuned using perfluorotributylamine (FC-43). Full scan electron impact ionization spectra were collected from 25 to 220 mass units. The infrared detector of GC/MS/FTIR system was operated at eight cm^{-1} resolution with each four scans averaged to give a single IR spectrum every 1.5 s. Preliminary compound identifications from the GC/MS/FTIR data sets were made by searching the Wiley/NBS Mass Spectra Library and the EPA vapor library. Pure samples of the identified products were obtained to check for matching spectra (MS and FTIR) and retention time.

The loss of the parent alcohols was plotted against the formation of products yielding a linear relationship with a slope equal to the product yield. Product quantification was performed using similar GC, elution parameters, and column described for the reaction rate determination with the column effluent analyzed by an FID. Pure samples of identified products were obtained to check for matching retention times and to generate a quantitative calibration curve.

All measurements were at least duplicated. A relative standard deviation (the data set standard deviation divided by the data set average) of approximately 2.5% was achieved with the described sampling method. All compounds were tested for chromatographic interferences and photolytic stability. Methyl nitrite, NO, reference, and alcohols were injected into
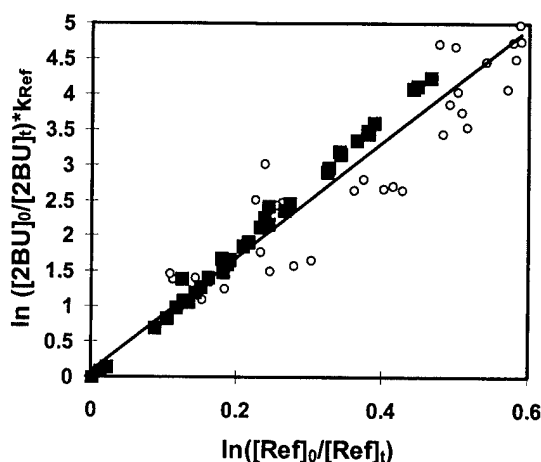
Figure 1 Relative rate data for 2 butanol with both n-nonane (■) and dodecane (○) as reference compounds. The OH + 2BU rate constant, k_{2BU}, measured is $(8.09 \pm 0.36) \times 10^{12}$ cm^{3}molecule^{-1}s^{-1}.
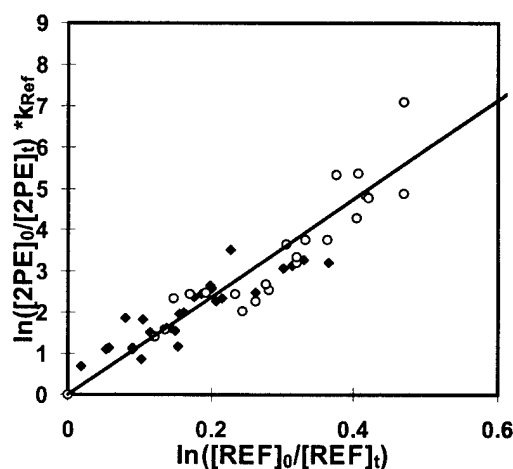

Figure 2 Relative rate data for 2 pentanol with both heptane (◆) and dodecane (○) as reference compounds. The OH + 2PE rate constant, k_{2PE}, measured is $(11.89 \pm 0.66) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}.

the bag and left for a minimum of 6 h to determine stability. None of these preliminary experiments yielded observable wall losses, chromatographic peak overlaps, chemical photolysis, or observable losses due to dark reactions. At the end of each run, the Teflon® bag was cleaned by flushing the bag a minimum of 6 times with zero-air. Measurements of an air-filled bag showed no cross contamination between runs.

RESULTS

Hydroxyl Radical/Alcohol Reaction Rate Constant

The OH rate constants for 2-butanol (2BU, $CH_3CH_2CH(OH)CH_3$) and 2-pentanol (2PE, $CH_3CH_2CH_2CH(OH)CH_3$) were obtained using the relative rate method described above. Typically five experimental runs were conducted on each alcohol/reference pair. The plots of a modified version of eq. (I) are shown in Figures 1 (2BU) and 2 (2PE). The $\ln([Alcohol]_0/[Alcohol]_t)$ term is multiplied by the respective recommended reference rate constant (dodecane $(14.2 \pm 3.6) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} and n-nonane $(10.2 \pm 2.6) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} and heptane $(7.15 \pm 1.79) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}) [19] and divided by 10^{-12} cm^{3}molecule^{-1}s^{-1} resulting in a unitless number and yielding a slope that is equal to the hydroxyl radical/alcohol rate constant, $k_{Alcohol}$, divided by 10^{-12} cm^{3}molecule^{-1}s^{-1}. This modification allows for simultaneous comparison of the two reference compound/alcohol data sets to demonstrate data consistency.

Hydroxyl Radical/Alcohols Reaction Rate Constant (k_{2BU} and k_{2PE})

The individual alcohol/reference data sets yielded the following hydroxyl radical rate constant results: 2-butanol/n-nonane = $(9.26 \pm 0.14) \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}, 2-butanol/dodecane = $(8.14 \pm 0.47) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}, 2-pentanol/heptane = $(9.93 \pm 1.21) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}, and 2-pentanol/dodecane = $(12.46 \pm 0.88) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}. The combination of both alcohol/reference data sets are shown in Figures 1 (2BU) and 2 (2PE). The slopes of the lines in Figures 1 and 2 yield an hydroxyl radical bimolecular rate constants of $(8.09 \pm 0.36) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} and $(11.89 \pm 0.66) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} for 2-butanol, k_{2BU}, and for 2-pentanol, k_{2PE}, respectively. The data points at the origin are experimental points because preirradiation, $t = 0$, data showed no detectable loss of 2BU, 2PE or references. The error in the rate constant stated above is the 95% confidence level from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate constants used ($\pm 25\%$) yields final values for k_{2BU} of $(8.1 \pm 2.0) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} and k_{2PE} of $(11.9 \pm 3.0) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} which are within experimental error of the individual alcohol/reference data set results. Assuming an OH concentration of 1×10^6 molecules cm^{-3}, the atmospheric ($1/e$) lifetimes calculated for 2BU and 2PE are 34 and 23 hours, respectively. The 2BU/OH rate constant, k_{2BU}, has been previously measured, using the relative rate method, by Chew et al. [4] yielding a value of

$(9.2 \pm 2.4) \times 10^{-12}$ cm³molecule⁻¹s⁻¹, within error limits of our reported value. Wallington et al., using flash-photolysis resonance fluorescence, reported a k_{2PE} of $(11.8 \pm 0.8) \times 10^{-12}$ cm³molecule⁻¹s⁻¹, also within error limits of our reported value [1]. Using structure reactivity, the calculated k_{2BU} of 9.8×10^{-12} cm³molecule⁻¹s⁻¹ and k_{2PE} of 11×10^{-12} cm³molecule⁻¹s⁻¹ are within error limits of our and the previously reported values. [11]

OH/Alcohols Reaction Products

The observed OH/alcohol reaction products are consistent with previously observed hydroxyl radical atmospheric chemistry reaction mechanisms for organic compounds [6–9]. For 2BU and 2PE, the major OH/alcohol reaction products observed were ketones of the same length as the alcohol and the carbonyl group in the same position as the hydroxyl group of the parent alcohol. The specific product results for each alcohol are described in separate sections below. The reported yields are based on the slopes of the alcohol reacted versus product formed plots (Figure 3). The reported error in the product yield is the 95% confidence level from the random uncertainty in the slope of these plots.

Because the OH/alcohol reaction products could subsequently react with OH, the observed product concentrations had to be corrected for OH + reaction product reactions. This correction has been described in detail [7,20] and has the following form:
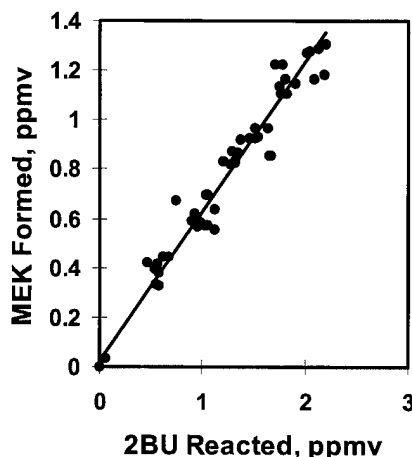
$$F = \frac{(k_{Alcohol} - k_P)}{k_{Alcohol}} \times \frac{1 - \dfrac{[Alcohol]_t}{[Alcohol]_0}}{\left(\dfrac{[Alcohol]_t}{[Alcohol]_0}\right)^{k_P/k_{Alcohol}} - \dfrac{[Alcohol]_t}{[Alcohol]_0}} \quad \textbf{(II)}$$

F, the correction factor, was multiplied by the product concentration data; $k_{Alcohol}$ is the OH + alcohol rate constant, and k_P is the rate constant for the reaction of OH with reaction product. The value for k_P reported in ref. [19] was used. It should be noted that all of the products exhibited linear concentration profiles; the lack of curvature strongly suggests no unusual side reactions that generate or remove primary reaction products. For completeness, the k_P values are presented with the respective product in Table I.

2-Butanol/OH Reaction Product Results

Two major products were observed from the 2-butanol/OH reaction: methyl ethyl ketone (MEK) and acetaldehyde. Quantification of MEK yields (Figure 3) was achieved with GC/FID and DNPH derivatization was used to quantify acetaldehyde yields. The product results data are summarized in Table I.

The large correction for acetaldehyde was due mainly to the large value of $k_{Acetaldehyde}$ relative to k_{2BU}.

2-Pentanol/OH Reaction Product Results

Three major products were observed from the 2-pentanol/OH reaction: 2-pentanone, propionaldehyde, and acetaldehyde. Quantification of both 2-pentanone and propionaldehyde yields was achieved with GC/FID and DNPH derivatization was used to quantify acetaldehyde yields. The product results data are summarized in Table I.

The large corrections for propionaldehyde and acetaldehyde were due mainly to the large value of $k_{Product}$ relative to k_{2PE}.

DISCUSSION

OH reacts with alcohols by H-atom abstraction and both 2BU and 2PE are molecules with several possible abstraction sites. However, the products of the reaction of OH with alcohols strongly suggest that the OH abstracts hydrogen principally from the alcoholic carbon. This is consistent with the reaction "hot spot" pro-
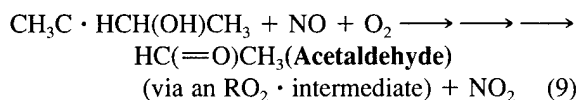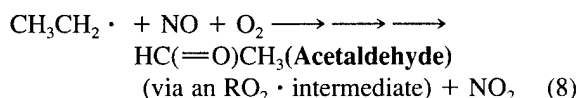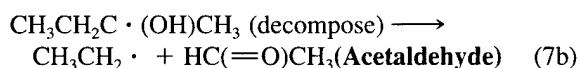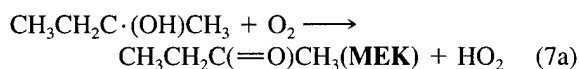

Figure 3   MEK yield (determined from slope of plot) from reaction of OH with 2BU. Yield data are corrected for reaction of OH with MEK. A yield of 0.60 ± 0.02 was observed.
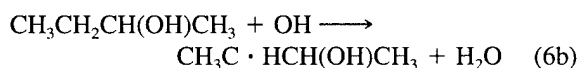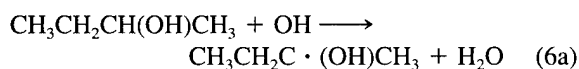
Table I   2-Butanol/OH and 2-Pentanol/OH Reaction Product Data and Correction Factors

Product	Structure	Yield %	$k_{Product}$ (Units of 10^{-12} molecule^{-1}s^{-1})	F_{avg} %	$F_{Maximum}$ %
2-Butanol					
Methyl Ethyl Kentone	$CH_3C(=O)CH_2CH_3$	60 ± 2	1.15 [19]	1.8	3.6
Acetaldehyde	$HC(=O)CH_3$	29 ± 4	15.8 [19,21–23]	41	127
2-Pentanol					
2-Pentanone	$CH_3C(=O)(CH_2)_2CH_3$	41 ± 4	4.9 [19]	7	12
Propionaldehyde	$HC(=O)CH_2CH_3$	14 ± 2	19.6 [19]	30	86
Acetaldehyde	$HC(=O)CH_3$	40 ± 4	15.8 [19,21–23]	24	67

$k_{Product}$ is the OH/product reaction bimolecular rate constant, F_{avg} is the average correction factor calculated using eq. (**II**) for the yield data set, and $F_{Maximum}$ is the largest correction factor calculated using Eq. (**II**) for the yield data set.

posed by structure reactivity analysis of both 2BU and 2PE. [11] Also, the agreement between the calculated vs. the measured $k_{Alcohols}$ supports these "reactive site" assignments. However, the structure reactivity calculated MEK and 2-pentanone yields were 84% and 76%, respectively. The lower observed ketone yields, 60% (MEK) and 41% (2-pentanone), reported here and in ref. [4] suggests the —OH activating effects are less than assumed by structure reactivity calculations and/or due to competition for acetaldehyde and propionaldehyde formation.

The proposed OH reaction mechanisms for 2BU and 2PE are shown below. Depending on the nature of the radical formed in Reaction (4): For 2BU:
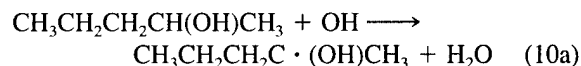
$$CH_3CH_2CH(OH)CH_3 + OH \longrightarrow$$
$$CH_3CH_2C \cdot (OH)CH_3 + H_2O \quad (6a)$$

$$CH_3CH_2CH(OH)CH_3 + OH \longrightarrow$$
$$CH_3C \cdot HCH(OH)CH_3 + H_2O \quad (6b)$$

$$CH_3CH_2C \cdot (OH)CH_3 + O_2 \longrightarrow$$
$$CH_3CH_2C(=O)CH_3(\textbf{MEK}) + HO_2 \quad (7a)$$

$$CH_3CH_2C \cdot (OH)CH_3 \ (\text{decompose}) \longrightarrow$$
$$CH_3CH_2 \cdot + HC(=O)CH_3(\textbf{Acetaldehyde}) \quad (7b)$$

$$CH_3CH_2 \cdot + NO + O_2 \longrightarrow \longrightarrow \longrightarrow$$
$$HC(=O)CH_3(\textbf{Acetaldehyde})$$
$$(\text{via an } RO_2 \cdot \text{ intermediate}) + NO_2 \quad (8)$$

$$CH_3C \cdot HCH(OH)CH_3 + NO + O_2 \longrightarrow \longrightarrow \longrightarrow$$
$$HC(=O)CH_3(\textbf{Acetaldehyde})$$
$$(\text{via an } RO_2 \cdot \text{ intermediate}) + NO_2 \quad (9)$$

The major product of the OH/2BU reaction was methyl ethyl ketone (MEK (60 $\pm$ 2)%). From the

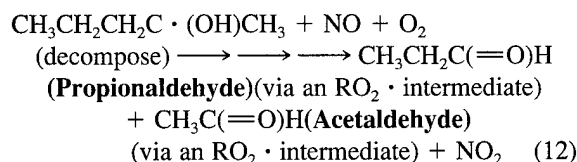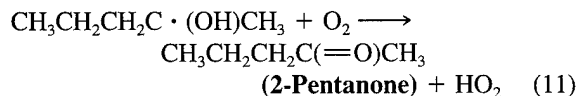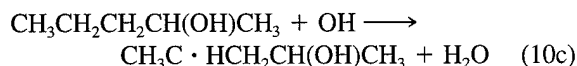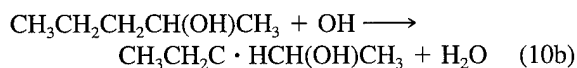mechanism proposed, MEK is a product of the hydrogen abstraction from the alcoholic carbon. Using ^{18}O labeled 2BU and mass spectral analysis of OH + 2BU reaction products, insights into the details of the $CH_3CH_2C \cdot (^{18}OH)CH_3$ radical reaction pathway could be investigated. The MEK product from reaction 7a was pure ^{18}O labeled. This result confirms retention of the alcoholic oxygen in the product and means that atmospheric oxygen (mainly $^{16}O_2$) does not play a role in the reaction mechanism. If atmospheric oxygen was involved in MEK formation, the MEK product would either be mixed $^{18}O/^{16}O$ or pure ^{16}O, neither of which was observed. This finding is instructive for assessing the incremental reactivity (ozone-forming potential) of 2BU and possibly other aliphatic alcohols. Tropospheric ozone is a by-product of the oxidation of volatile organic compounds (VOCs) [12]. The ^{18}O experiment provides definitive evidence that the $CH_3CH_2C \cdot (OH)CH_3$ radical/atmospheric oxygen reaction does not yield a tropospheric ozone-forming $RO_2 \cdot$ type radical. [12] To our knowledge, this is the first direct confirmation of the retention of the alcoholic oxygen in the reaction product.

The other reaction product, acetaldehyde, was observed by DNPH derivatization. The acetaldehyde could have come from decomposition (Reactions 7b and 9) and reaction of the $CH_3CH_2 \cdot$ radical (Reaction 8). The detection method used could not distinguish between different acetaldehyde pathways.

2-Pentanol (2PE) more than likely has similar mechanistic pathways as 2BU discussed above.

For 2PE:

$$CH_3CH_2CH_2CH(OH)CH_3 + OH \longrightarrow$$
$$CH_3CH_2CH_2C \cdot (OH)CH_3 + H_2O \quad (10a)$$

$$CH_3CH_2CH_2CH(OH)CH_3 + OH \longrightarrow$$
$$CH_3CH_2C \cdot HCH(OH)CH_3 + H_2O \quad (10b)$$

$$CH_3CH_2CH_2CH(OH)CH_3 + OH \longrightarrow$$
$$CH_3C \cdot HCH_2CH(OH)CH_3 + H_2O \quad (10c)$$

$$CH_3CH_2CH_2C \cdot (OH)CH_3 + O_2 \longrightarrow$$
$$CH_3CH_2CH_2C(=O)CH_3$$
$$\textbf{(2-Pentanone)} + HO_2 \quad (11)$$

$$CH_3CH_2CH_2C \cdot (OH)CH_3 + NO + O_2$$
$$(\text{decompose}) \longrightarrow \longrightarrow \longrightarrow CH_3CH_2C(=O)H$$
(Propionaldehyde)(via an $RO_2 \cdot$ intermediate)
$$+ CH_3C(=O)H\textbf{(Acetaldehyde)}$$
(via an $RO_2 \cdot$ intermediate) $+ NO_2$ (12)

$$CH_3CH_2C \cdot HCH(OH)CH_3 + NO + O_2(\text{decompose})$$
$$\longrightarrow \longrightarrow \longrightarrow CH_3CH_2C(=O)H$$
(Propionaldehyde) (via an $RO_2 \cdot$ intermediate)
$$+ CH_3C(=O)H \textbf{ (Acetaldehyde)}$$
(via an $RO_2 \cdot$ intermediate) $+ NO_2$ (13)

$$CH_3C \cdot HCH_2CH(OH)CH_3 + NO + O_2$$
$$(\text{decompose}) \longrightarrow \longrightarrow \longrightarrow CH_3C(=O)H$$
(Acetaldehyde) (via an $RO_2 \cdot$ intermediate)
$$+ NO_2 + \text{unobserved products} \quad (14)$$

The major product, 2-pentanone, is expected to be formed the same way as the MEK product in the 2BU mechanism above. The smaller yield of 2-pentanone, compared to structure reactivity calculations, could be due in part to the multiple reaction/decomposition pathways for the $CH_3CH_2CH_2C \cdot (OH)CH_3$ radical and more OH reactive sites on 2PE. The multiple radical pathways leading to product are probably due to the stability of this larger radical. The same implication regarding the effect of ketone yield data on incremental reactivity that was made for 2BU above can be made for 2PE.

The pathways for propionaldehyde and acetaldehyde formation are not as straightforward as 2-pentanone's. The combination of acetaldehyde and propionaldehyde carbon structures yields a five carbon backbone like 2PE. At first inspection, the yields of acetaldehyde and propionaldehyde might be expected to be the same if both were formed from decomposition of the same 2PE molecule. However, the yields of propionaldehyde ((14 ± 2)%) and acetaldehyde ((40 ± 4)%) are significantly different to suggest each product may have multiple formation routes. As the carbon backbone lengthens the possibility of isomerization increases. [24, 25] The primary radical can self abstract hydrogen and open the door to several alter-native reaction paths resulting in products that are not simple straight chain aldehydes and ketones such as cyclic compounds, diols and others. As can be seen from the mechanism proposed, there are several routes for propionaldehyde and acetaldehyde formation. More labeling experiments to sort these transformation pathways are needed to clarify these mechanisms. Also, experiments to determine nitrate reaction product transformation pathways are needed to more fully understand organic compounds' atmospheric mechanisms.

CONCLUSION

The OH radical abstracts hydrogen principally from the alcoholic carbon on aliphatic alcohols. The 2BU/OH and 2PE/OH bimolecular rate constants, k_{2BU} and k_{2PE}, were measured using the relative rate technique. The values for k_{2BU} ((8.1 ± 2.0) $\times$ 10^{-12} $cm^3 molecule^{-1}s^{-2}$) and k_{2PE} ((11.9 ± 3.0) $\times$ 10^{-12} $cm^3 molecule^{-1}s^{-1}$) are consistent with the single previously measured values for each alcohol; using an OH radical concentration of 1×10^6 molecules cm^{-3} the atmospheric ($1/e$) lifetimes for 2-butanol and 2-pentanol are approximately 34 and 23 h, respectively.

The identification and quantification of the 2BU/OH and 2PE/OH reaction products allowed a tentative development of atmospheric reaction mechanisms for these alcohols. For 2BU, the observed yields for methyl ethyl ketone and acetaldehyde were (60 ± 2)% and (29 ± 4)%, respectively. For 2PE, the observed yields for 2-pentanone, acetaldehyde, and propionaldehyde were (41 ± 4)%, (40 ± 4)%, and (14 ± 2)%, respectively.

Using ^{18}O labeled 2BU, transformation product experiments led to the verification that the alcoholic oxygen is retained in the principal ketone product. This finding coupled with product yield information has potential impact on the incremental reactivity (ozone forming potential) calculations of this class of compounds. However, as more methylene groups are added to the carbon backbone isomerization pathways that result in ringed, multi carbonyl, or other oxygenated reaction products become more likely. More investigations into the detailed atmospheric transformation chemistry of alcohols are needed to more accurately describe the air quality impact of these volatile organic compounds.

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