Products of the Gas-Phase Photooxidation Reactions of 1-Propanol with OH Radicals

K. AZAD, J. M. ANDINO

University of Florida, Department of Environmental Engineering Sciences, P.O. Box 116450, Gainesville, Florida 32611

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ABSTRACT: An experimental investigation of the hydroxyl radical initiated gas-phase photooxidation of 1-propanol in the presence of NO was carried out in a reaction chamber using gas chromatography mass spectrometry. The products identified in the OH radical reactions of 1-propanol were propionaldehyde and acetaldehyde, with corresponding formation yields of 0.719 ± 0.058 and 0.184 ± 0.030, respectively. Errors represent $\pm 2\sigma$. The experimental product yields were compared to predictions made using chemical mechanisms. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 810–818, 1999

INTRODUCTION

The alcohols present in ambient air are a result of both biogenic and anthropogenic sources. Anthropogenic emissions of alcohols occur through their use in fuels and as industrial solvents [1]. 1-Propanol, in particular, is widely used as a chemical solvent in the manufacturing of disk drives, computers, semiconductors, and various electronic components. 1-Propanol is also used in the esterfication of acetic acid, a common ingredient found in vinegar. Alcohols such as *tert*-butyl alcohol (TBA) [1,2–4], ethanol [4,5], and methanol [4,6] have been used in oxygenated fuels to reduce automobile emissions of carbon monoxide and hydrocarbons [7]. The addition of alcohols to fuels promotes better combustion by allowing for engine operation at a high octane rating [1,7]. Since alcohols are highly volatile compounds, significant evaporative emissions result from their use as solvents and fuel additives. Hence, it is important to determine their atmospheric degradation pathways in the troposphere.

Once emitted into the atmosphere, alcohols can react with oxidizing species such as hydroxyl radicals ($\dot{O}H$), nitrate radicals (NO_3), and ozone (O_3) [8,9] to produce a number of radicals and products, and convert NO to NO_2. The subsequent photolysis of NO_2 is the main reaction mechanism for the formation of tropospheric ozone. During daytime hours, reaction with the OH radical is the most prominent loss mechanism [8]. Kinetic studies of the OH radical reaction with alcohols have already been performed [2–4,10–15]. However, there are relatively few studies that have investigated the products from the $\dot{O}H$ initiated reactions of alcohols. Summarized in Table I are the products of the OH radical reaction of alcohols currently available in the literature. In order to accurately assess the impact of alcohols on tropospheric ozone production, a knowledge of the products of the $\dot{O}H$-initiated photooxidation of these species is needed.

In their study of the OH radical reactions of 2-butanol [17] and 2-pentanol [17], Baxley and Wells observed products that could only occur from the direct reaction of oxygen with the α-hydroxy alkyl radical. For the reactions of 2-butanol, the products observed were methyl ethyl ketone and acetaldehyde. Methyl

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Correspondence to: J. M. Andino

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Table I Products of OH Radical Reaction with Alcohols

Compound		Principle Products		Ref.
Methanol	CH_3OH	Formaldehyde	$HCHO$	[2],[15],[16]
Ethanol	CH_3CH_2OH	Acetaldehyde	CH_3CHO	[2],[16]
2-Propanol	$CH_3CH(OH)CH_3$	Acetone	$(CH_3)_2CO$	[16]
2-Butanol	$CH_3CH_2CH(OH)CH_3$	2-Butanone	$CH_3CH_2COCH_3$	[16],[17]
		Acetaldehyde	CH_3CHO	
2-Pentanol	$CH_3CH_2CH(OH)CH_3$	2-Pentanone	$CH_3COCH_2CH_2CH_3$	[17]
		Propionaldehyde	CH_3CH_2CHO	
		Acetaldehyde	CH_3CHO	
t-Butyl Alcohol	$(CH_3)_3COH$	Acetone	$(CH_3)_2CO$	[2],[3]
		Formaldehyde	$HCHO$	
Methyl Butenol	$(CH_3)C(OH){=}CHCH_2$	Acetone	$(CH_3)_2CO$	[18],[19]
		Formaldehyde	$HCHO$	
		Glycolaldehyde	$C(OH)CH_2OH$	
		Formic Acid	$C(OH)HO$	
		Carbon Dioxide	CO_2	
		Carbon Monoxide	CO	
1-Methoxy-2-propanol	$CH_3CH(OH)CH_2OCH_3$	Methoxy Acetone	$CH_3C(O)CH_2OCH_3$	[20]
		Methyl Formate	CH_3OCHO	
		Acetaldehyde	CH_3CHO	
2,4-Dimethyl-2-pentanol	$(CH_3)_2C(OH)CH_2CH(CH_3)_2$	Acetone	$(CH_3)_2CO$	[21]
		2-Methylpropanal	$(CH_3)_2CHCHO$	
		4-Methyl-2-pentanone	$CH_3C(O)CH_2CH(CH_3)_2$	
		4-Hydroxy-4-methyl-2-pentanone	$CH_3C(O)CH_2C(OH)(CH_3)_2$	
3,5-Dimethyl-3-hexanol	$CH_3CH_2C(CH_3)(OH)CH_2CCH(CH_3)_2$	Acetone	$(CH_3)_2CO$	[21]
		2-Butanone	$CH_3CH_2C(O)CH_3$	
		2-Methylpropanal	$(CH_3)_2CHCHO$	
		4-Methyl-2-pentanone	$CH_3C(O)CH_2CH(CH_3)_2$	
		4-Hydroxy-4-methyl-2-pentanone	$CH_3C(O)CH_2C(OH)(CH_3)_2$	
2-Butoxyethanol	$CH_3CH_2CH_2CH_2OCH_2CH_2OH$	Butyl Formate	$HC(O)OCH_2CH_2CH_2CH_3$	[20],[22]
		Ethylene Glycol Monoformate	$HC(O)OCH_2CH_2OH$	
		Butoxyacetaldehyde	$CH_3CH_2CH_2CH_2OCH_2C(O)H$	
		3-Hydroxybutyl Formate	$HC(O)OCH_2CH_2CHOHCH_3$	
		Propionaldehyde	CH_3CH_2CHO	
2-Ethoxyethanol	$CH_3CH_2OCH_2CH_2OH$	Ethyl Formate	$CH_3CH_2O(O)CH$	[23]
		Ethylene Glycol Monoformate	$HC(O)OCH_2CH_2OH$	
		Ethylene Glycol Monoacetate	$CH_3C(O)OCH_2CH_2OH$	
		Ethoxyacetaldehyde	$CH_3CH_2OCH_2C(O)H$	
cis-3-Hexen-1-ol	$CH_3CH_2CHCHCH_2CH_2OH$	Propionaldehyde	CH_3CH_2CHO	[24],[25]
		Acetaldehyde	CH_2CHO	
		Methylglyoxal	CH_3COCHO	
Allyl Alcohol	CH_2CHCH_2OH	Formaldehyde	$HCHO$	[24]
		Hydroxyacetaldehyde	CH_2OHCH_2HO	
3-Buten-1-ol	$CH_2CHCH_2CH_2OH$	Formaldehyde	$HCHO$	[24]

ethyl ketone can only be formed by the $\dot{O}H$ abstraction of the α-hydrogen and the subsequent reaction of the α-hydroxy alkyl radical with O_2. To determine the role of atmospheric oxygen in its reaction with α-hydroxy alkyl radical, 2-butanol was labeled with ^{18}O. The resulting methyl ethyl ketone, $CH_3CH_2\dot{C}(^{18}O)CH_3$, was analyzed for the presence of ^{18}O. The results showed that methyl ethyl ketone contained only ^{18}O and no ^{16}O. Hence, atmospheric oxygen merely abstracts a hydrogen atom from the α-hydroxy alkyl radical and does not attach to form a peroxy radical [17]. Similar observations were made for 2-pentanol. The mechanisms proposed by Stemmler et al. in their studies of 2-butoxyethanol [22] and 2-ethoxyethanol [23] with the OH radical, also suggested that the reaction of the α-hydroxy alkyl radical with O_2 proceeds via hydrogen abstraction rather than O_2 addition. Consequently, the α-hydroxy radicals produced in the reactions of 1-propanol with H are expected to react with oxygen in a similar manner.

The structure activity relationship (SAR) [26] was used to determine the percent of $\dot{O}H$ attack on the

Table II Hydroxyl Radical Attack Sites and Estimated Alkyl Radical Distribution of 1-Propanol

Reaction	Abstraction Site & Distribution	
$CH_3CH_2CH_2OH + \dot{O}H \rightarrow CH_3CH_2CH_2\dot{O}$	Site I	2.6%
$\rightarrow CH_3CH_2\dot{C}HOH$	Site II	73.4%
$\rightarrow CH_3\dot{C}HCH_2OH$	Site III	21%
$\rightarrow \dot{C}H_2CH_2CH_2OH$	Site IV	3%

carbon centers of 1-propanol. Table II shows the possible attack sites by the OH radical. The main degradation pathway is expected to be hydrogen abstraction by the OH radical from the secondary carbon center in 1-propanol (site II), followed by the reactions of the resulting intermediate alkyl, peroxy, and alkoxy radicals [8,9,27,28].

The products that are predicted to form from the $\dot{O}H$ initiated photooxidation of 1-propanol are presented in Table III. The OH radical initiated reaction of 1-propanol is expected to proceed primarily by hydrogen abstraction from the secondary carbon (site II) to form the corresponding α-hydroxy radical, which can then react with O_2 to form propionaldehyde and $H\dot{O}_2$. While there are no data available on the 1-propanol/$\dot{O}H$ reaction products, investigations of the 1-propanol/$\dot{O}H$ radical rate constant have been made [4,11–13]. The recommended 1-propanol/$\dot{O}H$ rate constant is 5.53×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [8]. Using an $\dot{O}H$ atmospheric concentration of 8.7×10^5 molecule cm^{-3} [29], the lifetime of 1-propanol is 2.4 days.

This study elucidates the atmospheric chemistry of 1-propanol. The products of the 1-propanol/$\dot{O}H$ reaction are identified and used to derive the atmospheric reaction mechanisms. The information collected in this study adds to the existing kinetic and mechanistic database of alcohols.

Table III Possible Products Formed from the OH Radical Initiated Reactions of 1-Propanol

$\dot{O}H$ Attack Site	Products
Site I —OH Group	Propionaldehyde Acetaldehyde Formaldehyde
Site II Secondary Carbon (—OH Group)	Propionaldehyde Propionic Acid Formic Acid
Site III Secondary Carbon	Hydroxyacetaldehyde Acetol Acetaldehyde Formaldehyde
Site IV Primary Carbon	Hydroxyacetaldehyde 3-Hydroxypropionaldehyde Formaldehyde

EXPERIMENTAL PROCEDURE

Apparatus and Materials

Experiments were performed in a new indoor photochemical reactor designed to study gas-phase reaction kinetics and mechanisms. The reactions were conducted in a batch reactor composed of 2 mil Tedlar® film (SKC Inc.), with a volume of approximately 100 L. The Tedlar® chamber was suspended inside a wooden cabinet. Eight fluorescent black lamps (Sylvania F40/350BL, maximum @ 350 nm) in two banks of four surrounded the chamber, and were used to initiate the chemistry. The lamps were mounted on a reflective surface to provide for uniformity in irradiation. A fan installed inside of the cabinet ensured that there was an even temperature distribution around the chamber.

The reactants were introduced into the chamber by two methods: direct syringe injection and via an evacuable glass manifold system. A 10 μL Hamilton syringe was used to inject the organic compounds into a stream of zero air (99.999% purity, Strate Welding) flowing into the chamber. The injection was made into a septum placed inside a Swagelock® union tee that was connected to the inlet of the chamber. The flowrate of air was monitored using a calibrated rotameter (Porter Instrument Co.) and a stopwatch. The chamber was filled with 78–80 liters of the air/reactant mixture. Since the final volume of the chamber, the volume of the reactant injected, the density, and the molecular weight of the reactant were known, the final concentration of the reactant inside the chamber was easily calculated.

A custom designed evacuable glass manifold system (Chemglass) was used to admit known amounts of highly volatile reactants (such as methyl nitrite and nitric oxide) to the chamber. The system contained a glass bulb and two MKS Baratron pressure gauges with a combined range of 10^{-3} to 10^3 Torr. The volume of the glass bulb was calibrated using a gravimetric method. The reactants were flushed into the chamber from the manifold using zero grade air (99.999% purity, Strate Welding). A mechanical pump (Marvac Scientific Co., Model A20) operating at 15 L/min was used to exhaust the chamber prior to and after the experiments.

The reaction chamber was interfaced to a gas chromatograph-mass spectrometer (Finnigan-MAT, GCQ Model 9001), which provided the necessary analytical tool to aid in the positive identification and quantification of the products. The GC consisted of a heated 6-port sampling valve that was kept at a constant temperature of 150°C to keep the organics in their gaseous phase, and prevent condensation. A diaphragm pump was used to extract samples from the chamber directly into the GC-MS system. The samples were drawn from the chamber through the loop at 1 lpm before being injected onto the column. A J&W Scientific DB-WAX capillary column of dimension 30 m × 0.25 mm × 0.25 μm was used to separate the organics. The GC carrier gas was helium (99.999% purity, Bitec), with a linear velocity of 45 cm/s. The temperature program started at 35°C, was held for one minute, then ramped at 10°C/min to 150°C, and held at that temperature for one minute. Mass spectral analyses were performed in positive electron ionization mode.

Methyl nitrite was used as the source of hydroxyl radicals in the reaction chamber. Hydroxyl radicals are produced from the photolysis of methyl nitrite in air via the following mechanism:

$$CH_3ONO + h\nu \longrightarrow CH_3\dot{O} + NO \qquad (1)$$

$$CH_3\dot{O} + O_2 \longrightarrow CH_2O + H\dot{O}_2 \qquad (2)$$

$$H\dot{O}_2 + NO \longrightarrow \dot{O}H + NO_2 \qquad (3)$$

Nitric oxide was added to the chamber with methyl nitrite to minimize the accumulation of ozone, and maximize the reduction of peroxy radicals to alkoxy radicals.

Product Study

The typical starting concentrations of the reactants admitted into the chamber were 16–18 ppm_v of 1-propanol, 15–20 ppm_v of methyl nitrite, and 9–12 ppm_v of NO. 1-propanol. Propionaldehyde and acetaldehyde were obtained from Aldrich with stated purities of 99.5+%, 97%, and 99.5+%, respectively. 1-Propanol was introduced into the chamber without further purification. Nitric oxide was taken from a standard cylinder supplied by Liquid Carbonic. Methyl nitrite was synthesized according to the method of Taylor et al. [30]. The methyl nitrite was purified using the glass manifold system and stored at room temperature in a stainless steel lecture bottle. The purity of the methyl nitrite was verified using a Fourier Transform Infrared (FTIR) spectrometer and was found to be $>99+\%$.

Three experiments were performed in which the reactants were irradiated for 30–50 min in 3–5 min intervals. All experiments were performed at 298 ± 2 K and atmospheric pressure. Prior to each set of experiments, zero air was introduced into the chamber and photolyzed for 20 min to remove any free radicals that may have been present in the chamber. At the end of an experiment, the chamber was cleaned by flushing it several times with zero air. After flushing, GC-MS samples were taken to check for cross contamination.

The products were identified based on their retention time and mass spectra as compared to standards. Standards of all potential products identified in Table III (with the exception of formaldehyde and 3-hydroxypropionaldehyde) were injected from the chamber into the GC-MS, and full calibration curves were developed. 3-Hydroxypropionaldehyde was not commercially available, and formaldehyde could not be analyzed via the techniques employed in this study. In all cases, samples were subjected to the same temperature program used in the experiments, and the corresponding peak areas obtained. Two samples were taken for each concentration to check for internal consistency of the GC-MS. The m/z values used for quantifying 1-propanol, propionaldehyde, and acetaldehyde were 43, 57, and 43, respectively. The duplicate samples were found to have peak areas within 5% of each other. Plots of peak area versus concentration were generated, and response factors determined. These factors were then used to quantify the products during the experimental runs.

Additional studies were conducted with the organics to characterize losses due to photolysis and interaction with the walls of the chamber. Wall losses were quantified by placing the organics in the chamber and leaving them in the dark for time periods typically used in the studies. Losses due to photolysis were quantified by subjecting the organics to photolysis for time periods typically used in the actual experiments. In each case, samples were taken in 5–10 min intervals and compared to samples taken at time zero.

Secondary Product Study

Since the primary products formed in the OH radical reactions of 1-propanol also react with the OH radical, separate studies were performed to elucidate the nature and yields of secondary products. Secondary product studies were performed for propionaldehyde. Propionaldehyde was introduced into the chamber with methyl nitrite and nitric oxide using the same experimental method as the initial product study. The concentrations used in the propionaldehyde/$\dot{\mathrm{O}}\mathrm{H}$ studies were 5–6 ppm$_v$ of propionaldehyde, 20–22 ppm$_v$ of methyl nitrite, and 4–5 ppm$_v$ of NO. Propionaldehyde was injected into the chamber without further purification. The results were analyzed on the GC-MS. The primary product yields obtained for the 1-propanol/$\dot{\mathrm{O}}\mathrm{H}$ studies were corrected for interferences observed in the secondary product studies.

RESULTS AND DISCUSSION

Losses due to photolysis and interaction with the walls of the chamber were quantified, and were each within the analytical uncertainty of the GC/MS (~5%). Therefore, wall losses and losses due to photolysis were deemed negligible.

The first generation products can react with OH radicals, thus their formation yields were corrected according to the method of Atkinson [8], and using the rate constants available in the literature [8]. The correction factor, F, was calculated using Equation I. The raw molar yields were multiplied by the correction factor to obtain the true molar yields.

$$F = \left\{\frac{k_4 - k_5}{k_4}\right\} \frac{1 - \dfrac{[\text{1-Propanol}]_t}{[\text{1-Propanol}]_0}}{\left(\dfrac{[\text{1-Propanol}]_t}{[\text{1-Propanol}]_0}\right)^{\frac{k_5}{k_4}} - \dfrac{[\text{1-Propanol}]_t}{[\text{1-Propanol}]_0}} \tag{I}$$

The rate constants k_4 and k_5 are for the following reactions:

$$\text{1-Propanol} + \dot{\mathrm{O}}\mathrm{H} \longrightarrow \text{Product} \tag{4}$$

$$\text{Product} + \dot{\mathrm{O}}\mathrm{H} \longrightarrow \text{Secondary Product} \tag{5}$$

Product Study

Analysis of irradiated $\mathrm{CH_3ONO}$-NO-1-propanol-air mixtures indicated the formation of propionaldehyde and acetaldehyde. The yields were corrected for secondary reactions with the OH radical. The calculated ranges of the correction factors for propionaldehyde and acetaldehyde were 1.1–2.7 and 1.1–2.1, respectively. The formation of acetaldehyde was also observed in the propionaldehyde/$\dot{\mathrm{O}}\mathrm{H}$ reactions with a molar yield of 0.585 ± 0.049. Hence, the acetaldehyde yield obtained from the 1-propanol/$\dot{\mathrm{O}}\mathrm{H}$ reactions was corrected for the secondary source. The corrected molar formation yields for propionaldehyde and acetaldehyde were 0.719 ± 0.058 and 0.184 ± 0.030, respectively. The errors are two least-squares standard deviations.

The corrected yields for propionaldehyde and acetaldehyde account for about 85 ± 8% of the reacted carbon. Hence, almost all of the reacted carbon is accounted for. Some of the remaining carbon may be present as other carbonyl compounds, but none were observed within the detection limits of the GC-MS. GC-MS characteristics of acetol, hydroxyacetaldehyde, propionic acid, and formic acid, obtained from the injections of standards from the chamber into the GC were not observed in the 1-propanol/$\dot{\mathrm{O}}\mathrm{H}$ chromatograms. 3-Hydroxypropionaldehyde could not be analyzed since it was not commercially available.

Propionaldehyde may form as a result of hydrogen abstraction by $\dot{\mathrm{O}}\mathrm{H}$ from site I or site II (see Table II). Acetaldehyde is expected to form as a result of hydrogen abstraction by $\dot{\mathrm{O}}\mathrm{H}$ from any of the possible sites, except for abstraction from the primary carbon (site IV). Hydrogen abstraction from site I forms the alkoxy radical, $\mathrm{CH_3CH_2CH_2\dot{O}}$, which can react with $\mathrm{O_2}$ to yield propionaldehyde and $\mathrm{H\dot{O}_2}$ (Reaction 6), or decompose to produce formaldehyde and an acetyl radical, $\mathrm{CH_3\dot{C}H_2}$ (Reaction 7),

$$\mathrm{CH_3CH_2CH_2\dot{O}} + \mathrm{O_2} \longrightarrow \mathrm{CH_3CH_2CHO} + \mathrm{H\dot{O}_2}, \tag{6}$$

$$\mathrm{CH_3CH_2CH_2\dot{O}} \xrightarrow{\text{Decomposition}} \mathrm{CH_3\dot{C}H_2} + \mathrm{HCHO}. \tag{7}$$

Oxygen rapidly reacts with the acetyl radical to form an acetyl peroxy radical, which continues to react with NO to either yield peroxy acetyl nitrate (PAN) or the corresponding acetyl alkoxy radical and $\mathrm{NO_2}$. The alkoxy radical can react with oxygen to form acetaldehyde or decompose to form formaldehyde. Hydrogen abstraction by $\dot{\mathrm{O}}\mathrm{H}$ from site II, estimated by the SAR technique as the most probable hydrogen abstraction site, forms the α-hydroxy alkyl radical, $\mathrm{CH_3CH_2\dot{C}HOH}$, which is expected to yield propionaldehyde in a direct reaction with oxygen (Reaction 8),

$$CH_3CH_2\dot{C}HOH + O_2 \longrightarrow CH_3CH_2CHO + H\dot{O}_2 \quad (8)$$

Our results indicate the absence of propionic and formic acids. Thus, the competing reaction of the α-hydroxy alkyl radical to form the α-hydroxyperoxy radical (Reaction 9), and eventually propionic and formic acids is negligible.

$$CH_3CH_2\dot{C}HOH + O_2 \longrightarrow CH_3CH_2CH(O\dot{O})OH. \quad (9)$$

The results obtained here are consistent with the results obtained in similar studies involving the production of the intermediate α-hydroxy alkyl radicals [15–17,20–23]. Previous studies of the reactions of 2-butanol [17] and 2-pentanol [17] with the OH radical indicated that the major products observed were formed due to the OH radical hydrogen abstraction from the secondary carbon. Initial estimates by the SAR also predicted that $\dot{O}H$ attack on 1-propanol at the secondary carbon containing the alcohol group was the most probable site. With a recovery of 71.9 ± 5.8% of the reacted carbon as propionaldehyde in the 1-propanol/$\dot{O}H$ reactions and the absence of propionic and formic acids, this study confirms that the main reaction pathway (at the secondary carbon site of 1-propanol) involves hydrogen abstraction by O_2 from the α-hydroxy alkyl radical (Reaction 8), rather than O_2 addition (Reaction 9). The formation of acetaldehyde at a smaller yield indicates that other reaction pathways for OH abstraction from 1-propanol will occur, but are less important.

Mechanism Predictions

The reaction mechanisms for the $\dot{O}H$ initiated photooxidation of 1-propanol were developed and implemented using the SAPRC Atmospheric Photochemical Mechanism Preparation Program [31]. The mechanisms did not include secondary reactions of products since the experimental raw yields were corrected for secondary reactions. Hence a direct comparison of predicted and experimental yields was made.

The rate constants for the individual OH radical initiated abstraction steps were determined using the SAR technique and the recommended overall OH radical rate constant. The rate constants for the 1-propyl radical reaction with O_2 [8] was used as an estimate for the rate constant of O_2 addition to the $\cdot CH_2CH_2CH_2OH$ radical. Except for the alkoxy radical reactions, the rate constants for all the other reactions were directly obtained from Atkinson [8]. The rate constant for the alkoxy radical decomposition and O_2 reactions were determined by calculating the enthalpies of reaction using the NIST Structures and Properties Database Estimation Program [32] in combination with the estimation technique of Atkinson [9]. The rate constants for alkoxy radical decomposition, k_d, were determined using Equation II,

$$k_d = A_d e^{-E_d/RT}\ s^{-1}, \quad (II)$$

$$\text{where } A_d = 2 \times 10^{14}\ d\ s^{-1}, \quad (III)$$

$$E_d = a + 0.36\Delta H_d, \quad (IV)$$

A_d is the pre-exponential factor, d is the reaction path degeneracy, R is the ideal gas constant, T is the temperature in Kelvin, ΔH_d is the decomposition enthalpy in kcal mol^{-1}, and E_d is the activation energy in kcal mol^{-1}. The activation energy is dependent on the alkyl leaving-group, represented in Equation IV by parameter *a*. Reported [9] values of *a* (in kcal mol^{-1}) are: methyl, 15.5; primary alkyl, $R\dot{C}H_2$, 11.1; secondary alkyl, $R_1R_2\dot{C}H$, 9.3; tertiary alkyl, $R_1R_2R_3\dot{C}$, 7.9; and $\dot{C}H_2OH$, 10.0. The rate constant for the reaction of the alkoxy radical with O_2 is calculated using Equation V:

$$k_{O_2} = 4.0 \times 10^{-19}\ n e^{(-0.28\Delta H_{O_2})}, \quad (V)$$

where k_{O_2} is the rate constant for the alkoxy radical reaction with O_2 in cm^3 molecule^{-1} s^{-1}, n is the number of abstractable hydrogen atoms in the alkoxy radical, and ΔH_{O_2} is the enthalpy of the alkoxy radical reaction with O_2. The completed mechanisms were implemented into the Carter modeling program [31], and time-concentration profiles were generated. Predicted product yields were determined by calculating the ratio of product concentration to the change in the concentration of the reactant species, and were compared to experimental yields. Presented in Table IV are the predicted and experimental yields of the products.

Table IV Measured and Predicted Product Yields for the Gas-Phase Reactions of 1-Propanol with OH Radicals

	Yield	
Product	Experimental[a]	Predicted[b]
Propionaldehyde	0.719 ± 0.058	0.757
Acetaldehyde	0.184 ± 0.030	0.177

[a] Indicated errors are 2 least-squares standard deviations.

[b] Predicted as described in text.

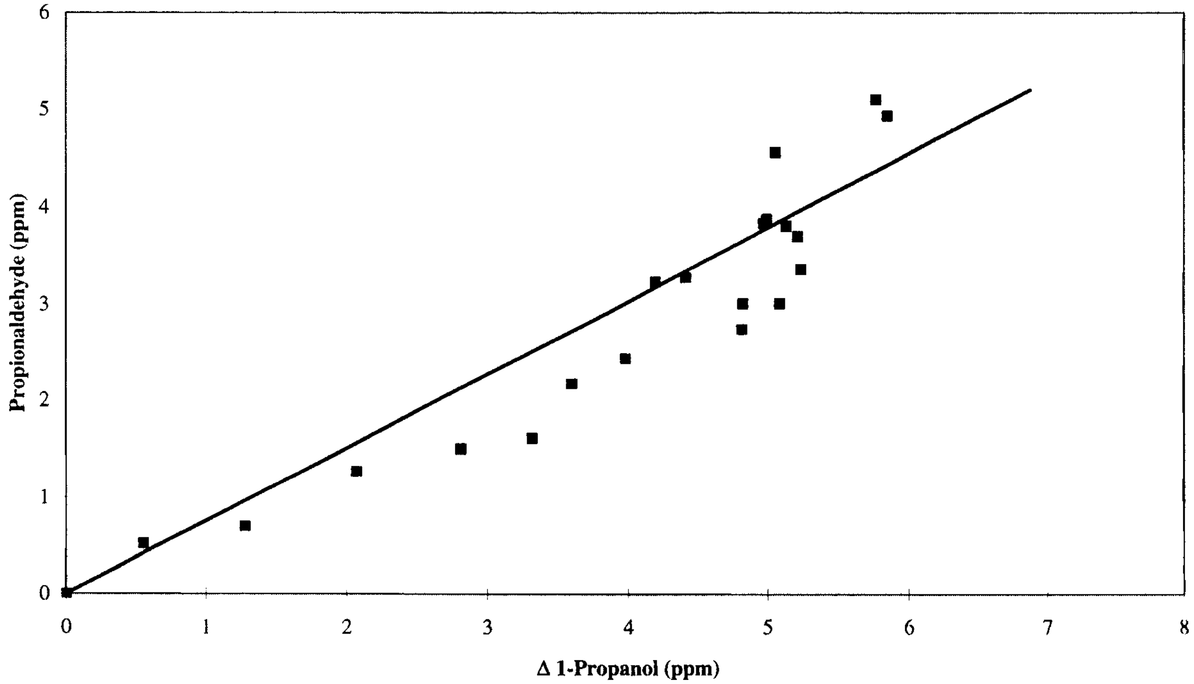

Figure 1 Amount of propionaldehyde formed, corrected for reaction with the OH radical, against the amount of 1-propanol reacted. Data points (■) represent experimental values. The dashed line represents the predicted yield.

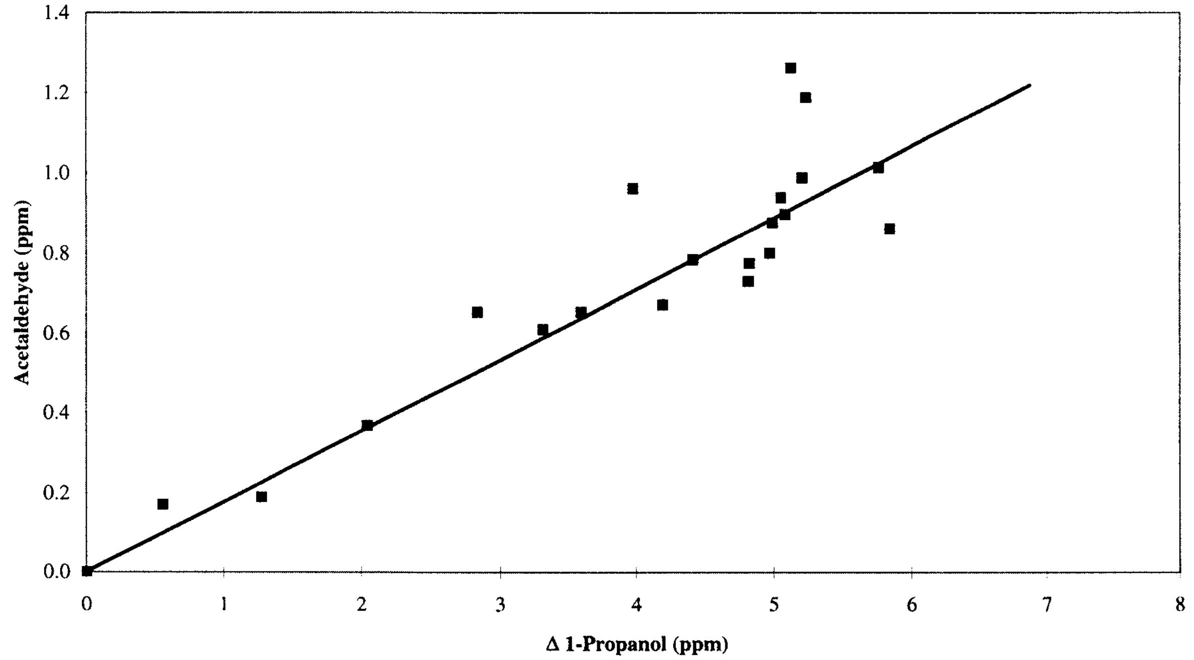

Figure 2 Amount of acetaldehyde formed, corrected for reaction with the OH radical, against the amount of 1-propanol reacted. Data points (■) represent experimental values. The dashed line represents the predicted yield.

Observed and predicted concentrations of propionaldehyde and acetaldehyde are presented in Figures 1 and 2, respectively. Clearly, the exclusion of reactions leading to the formation and subsequent reaction of the α-hydroxyperoxy radical produces a propionaldehyde yield that is in excellent agreement with the experimental yield. The experimental yield of acetaldehyde is also in excellent agreement with current estimates. A tabulation of the 1-propanol reactions appears in Table V. Note that methyl nitrite, methyl radical, and NO_x reactions were also included in the overall mechanism used for modeling.

Table V 1-Propanol Mechanisms (in cm^3, molecule, s units)

Rxn No.	k (298 K)	Reaction	Source
		1-Propanol Reactions	
P1)	1.44×10^{-13}	PROP + $HO\cdot$ = $CH_3(CH_2)_2O\cdot$ + H_2O	26,8
P2)	4.06×10^{-12}	PROP + $HO\cdot$ = CH_3CH_2CHOH + H_2O	26,8
P3)	1.16×10^{-12}	PROP + $HO\cdot$ = CH_3CHCH_2OH + H_2O	26,8
P4)	1.66×10^{-13}	PROP + $HO\cdot$ = $CH_2CH_2CH_2OH$ + H_2O	26,8
		Site I Hydrogen Abstraction	
P5)	8.24×10^{-15}	$CH_3(CH_2)_2O\cdot$ + O_2 = PROPIONALDEHYDE + $HO_2\cdot$	32,9
P6)	3.8×10^{-11}	$CH_3(CH_2)_2O\cdot$ + NO = NITRITE	8
P7)	3.8×10^{-11}	$CH_3(CH_2)_2O\cdot$ + NO_2 = NITRATE	8
P8)	1.04×10^{3}	$CH_3(CH_2)_2O\cdot$ = CH_3CH_2 + FORMALDEHYDE	32,9
P9)	7×10^{-12}	CH_3CH_2 + O_2 = $CH_3CH_2O_2\cdot$	8
P10)	8.82×10^{-12}	$CH_3CH_2O_2\cdot$ + NO = $CH_3CH_2O\cdot$ + NO_2	8
P11)	8×10^{-14}	$CH_3CH_2O_2\cdot$ + NO = NITRATE	8
P12)	4.4×10^{-11}	$CH_3CH_2O\cdot$ + NO = NITRITE	8
P13)	2.8×10^{-11}	$CH_3CH_2O\cdot$ + NO_2 = NITRATE	8
P14)	9.5×10^{-15}	$CH_3CH_2O\cdot$ + O_2 = ACETALDEHYDE + $HO_2\cdot$	8
P15)	3.36×10^{-1}	$CH_3CH_2O\cdot$ = FORMALDEHYDE + $\cdot CH_3$	32,9
		Site II Hydrogen Abstraction	
P16)	26.1×10^{-12}	CH_3CH_2CHOH + O_2 = PROPIONALDEHYDE + $HO_2\cdot$	8
		Site III Hydrogen Abstraction	
P17)	11.6×10^{-12}	CH_3CHCH_2OH + O_2 = $CH_3CH(O_2\cdot)CH_2OH$	8
P18)	8.45×10^{-12}	$CH_3CH(O_2\cdot)CH_2OH$ + NO = $CH_3CH(O\cdot)CH_2OH$ + NO_2	8
P19)	4.5×10^{-13}	$CH_3CH(O_2\cdot)CH_2OH$ + NO = NITRATE	8
P20)	3.8×10^{-11}	$CH_3CH(O\cdot)CH_2OH$ + NO = NITRITE	8
P21)	3.8×10^{-11}	$CH_3CH(O\cdot)CH_2OH$ + NO_2 = NITRATE	8
P22)	1.16×10^{-14}	$CH_3CH(O\cdot)CH_2OH$ + O_2 = ACETOL + $HO_2\cdot$	32,9
P23)	4.7×10^{5}	$CH_3CH(O\cdot)CH_2OH$ = ACETALDEHYDE + CH_2OH	32,9
P24)	6.22	$CH_3CH(O\cdot)CH_2OH$ = HYDROXYACETALDEHYDE + $\cdot CH_3$	32,9
P25)	9.4×10^{-12}	$\cdot CH_2OH$ + O_2 = FORMALDEHYDE + $HO_2\cdot$	8
		Site IV Hydrogen Abstraction	
P26)	8×10^{-12}	$\cdot CH_2CH_2CH_2OH$ + O_2 = $\cdot OO{-}CH_2CH_2CH_2OH$	Estimate[a]
P27)	8.72×10^{-12}	$\cdot OO{-}CH_2CH_2CH_2OH$ + NO = $CH_2CH_2CH_2OH{-}O$ + NO_2	8
P28)	1.8×10^{-13}	$\cdot OO{-}CH_2CH_2CH_2OH$ + NO = NITRATE	8
P29)	3.8×10^{-11}	$\cdot O{-}CH_2CH_2CH_2OH$ + NO = NITRATE	8
P30)	3.8×10^{-11}	$\cdot O{-}CH_2CH_2CH_2OH$ + NO_2 = NITRATE	8
P31)	8.24×10^{-15}	$\cdot O{-}CH_2CH_2CH_2OH$ + O_2 = 3-HYDROXYPROPIONALDEHYDE + $HO_2\cdot$	32,9
P32)	2.02×10^{2}	$\cdot O{-}CH_2CH_2CH_2OH$ = FORMALDEHYDE + $\cdot CH_2CH_2OH$	32,9
P33)	3×10^{-12}	$\cdot CH_2CH_2OH$ + O_2 = $\cdot OO{-}CH_2CH_2OH$	8
P34)	8.82×10^{-12}	$\cdot OO{-}CH_2CH_2OH$ + NO = $\cdot O{-}CH_2CH_2OH$ + NO_2	8
P35)	8×10^{-14}	$\cdot OO{-}CH_2CH_2OH$ + NO = NITRATE	8
P36)	3.8×10^{-11}	$\cdot O{-}CH_2CH_2OH$ + NO = NITRITE	8
P37)	3.8×10^{-11}	$\cdot O{-}CH_2CH_2OH$ + NO_2 = NITRATE	8
P38)	7.58×10^{-15}	$\cdot O{-}CH_2CH_2OH$ + O_2 = HYDROXYACETALDEHYDE + $HO_2\cdot$	32,9
P39)	3.97×10^{3}	$\cdot O{-}CH_2CH_2OH$ = FORMALDEHYDE + $\cdot CH_2OH$	32,9

[a] Estimated using the rate constant in [8] for the 1-propyl radical + O_2 reaction.

CONCLUSIONS

Experiments were performed to investigate the $\dot{\mathrm{O}}\mathrm{H}$ initiated photooxidation of 1-propanol. The observed products were propionaldehyde and acetaldehyde, which accounted for 85 ± 8% of the reacted carbon. The OH radical abstracts a hydrogen atom principally from the secondary carbon containing the hydroxyl group, thus forming an α-hydroxy propyl radical which reacts with oxygen to lead to propionaldehyde. Experimental data were compared to mechanism predictions, and yielded excellent agreement. The results obtained in the current study are consistent with previously published data on alcohols.

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