J. Phys. Chem. A **2009,** *113,* 7011–7020

Atmospheric Chemistry of *n*-Butanol: Kinetics, Mechanisms, and Products of Cl Atom and OH Radical Initiated Oxidation in the Presence and Absence of NO_x.

M. D. Hurley,[†,‡] T. J. Wallington,*,[†] L. Laursen,[§] M. S. Javadi,[§] O. J. Nielsen,[§] T. Yamanaka,[⊥] and M. Kawasaki[⊥]

Systems Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, Michigan 48121-2053, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark, and Department of Molecular Engineering, Kyoto University, Kyoto 615-8510, Japan

Received: December 2, 2008; Revised Manuscript Received: April 24, 2009

Smog chamber/FTIR techniques were used to determine rate constants of *k*(Cl+*n*-butanol) = (2.21 ± 0.38) × 10^{-10} and *k*(OH+*n*-butanol) = (8.86 ± 0.85) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} in 700 Torr of N_2/O_2 diluent at 296 ± 2K. The sole primary product identified from the Cl atom initiated oxidation of *n*-butanol in the absence of NO was butyraldehyde (38 ± 2%, molar yield). The primary products of the Cl atom initiated oxidation of *n*-butanol in the presence of NO were (molar yield) butyraldehyde (38 ± 2%), propionaldehyde (23 ± 3%), acetaldehyde (12 ± 4%), and formaldehyde (33 ± 3%). The substantially lower yields of propionaldehyde, acetaldehyde, and formaldehyde as primary products in experiments conducted in the absence of NO suggests that chemical activation is important in the atmospheric chemistry of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ alkoxy radicals. The primary products of the OH radical initiated oxidation of *n*-butanol in the presence of NO were (molar yields) butyraldehyde (44 ± 4%), propionaldehyde (19 ± 2%), and acetaldehyde (12 ± 3%). In all cases, the product yields were independent of oxygen concentration over the partial pressure range of 10−600 Torr. The yields of propionaldehyde, acetaldehyde, and formaldehyde quoted above were not corrected for secondary formation via oxidation of higher aldehydes and should be treated as upper limits. The reactions of Cl atoms and OH radicals with *n*-butanol proceed 38 ± 2 and 44 ± 4%, respectively, via attack on the α-position to give an α-hydroxy alkyl radical which reacts with O_2 to give butyraldehyde. The results are discussed with respect to the atmospheric chemistry of *n*-butanol.

1. Introduction

Concerns regarding energy independence and climate change have resulted in increased interest in biofuels as an alternative energy source for transportation.[1] There are two types of liquid biofuels in the transportation sector. Methyl esters of long chain fatty acids are blended with diesel fuel. Biomass derived alcohols are blended with gasoline. Currently, corn-based ethanol is the dominant biofuel in the U.S., and sugar cane ethanol is dominant in Brazil. To increase the production scale and avoid the use of food crop corn-based ethanol, there is a substantial research effort aimed at developing the technology to process cellulosic materials (wood, grasses, agricultural wastes, etc.) into biofuels. There is interest in the conversion of cellulose into higher alcohols such as *n*-butanol as this would reduce the complications associated with water-induced phase separation of alcohol/gasoline blends.[2]

The widespread use of alcohols in liquid fuel will result in their release into the atmosphere. In the atmosphere, alcohols will undergo photochemical oxidation initiated by the OH radical. Prior to the large-scale use of alcohols, an assessment of their atmospheric chemistry and environmental impact is needed. There is a substantial kinetic and mechanistic database for smaller alcohols such as methanol, ethanol, and propanol, and the atmospheric chemistry of these compounds is generally well understood.[3,4] The kinetic and mechanistic database for larger alcohols is sparse, and the details of their atmospheric oxidation are not well understood. There have been seven studies of the kinetics of the reaction of OH radicals with *n*-butanol but only one study of the products. Similarly, there have been three studies of the kinetics of the reaction of chlorine atoms with *n*-butanol but no studies of the mechanism of this reaction. To improve our understanding of the atmospheric chemistry of alcohols, the kinetics and mechanism of the simulated atmospheric oxidation of *n*-butanol was studied using the smog chamber at Ford Motor Company.

2. Experimental Section

Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer.[5] The reactor was surrounded by 22 fluorescent black lamps (GE F40T12BLB) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (1)$$

OH radicals were produced by photolysis of CH_3ONO in the presence of NO in air

---

* To whom correspondence should be addressed. E-mail: twalling@ford.com.

[†] Ford Motor Company.

[§] University of Copenhagen.

[⊥] Kyoto University.

[‡] Retired.

10.1021/jp810585c CCC: $40.75 © 2009 American Chemical Society
Published on Web 05/22/2009

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (2)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \quad (3)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (4)$$

Relative rate techniques were used to measure the rate constant of interest relative to a reference reaction whose rate constant has been established previously. The relative rate method is a well-established technique for measuring the reactivity of Cl atoms and OH radicals with organic compounds.[6] Kinetic data were derived by monitoring the loss of *n*-butanol relative to one or more reference compounds. The decays of *n*-butanol and the reference are then plotted using the expression

$$\ln\left(\frac{[\text{Reactant}]_0}{[\text{Reactant}]_t}\right) = \frac{k_{\text{Reactant}}}{k_{\text{Reference}}} \ln\left(\frac{[\text{Reference}]_0}{[\text{Reference}]_t}\right) \quad (I)$$

where $[\text{Reactant}]_0$, $[\text{Reactant}]_t$, $[\text{Reference}]_0$, and $[\text{Reference}]_t$ are the concentrations of *n*-butanol and the reference compound at times 0 and t and k_{Reactant} and $k_{\text{Reference}}$ are the rate constants for reactions of Cl atoms or OH radicals with the *n*-butanol and the reference compound. Plots of $\ln([\text{Reactant}]_0/[\text{Reactant}]_t)$ versus $\ln([\text{Reference}]_0/[\text{Reference}]_t)$ should be linear, pass through the origin, and have a slope of $k_{\text{Reactant}}/k_{\text{Reference}}$. Unless stated otherwise, quoted uncertainties represent the precision of the measurements and include two standard deviations from regression analyses and uncertainties in the IR analysis (typically ±1−2% of the initial reactant concentrations).

CH_3ONO was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. *n*-Butanol was obtained from Sigma-Aldrich at a purity of 98%. Experiments were conducted in 700 Torr of total pressure of high-purity O_2/N_2 diluent at 296 ± 2 K. The concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. To check for unwanted loss of reactants and reference compounds via heterogeneous reactions, reaction mixtures were left to stand in the chamber for 60 min. With the exception of $CH_3CH_2CH_2CHClOH$, there was no observable (<2%) loss of any of the reactants or products in the present work.$CH_3CH_2CH_2CHClOH$ decomposes into butyraldehyde on a time scale of a few minutes. Unless stated otherwise, quoted uncertainties are 2 standard deviations from least-squares regressions.

3. Results and Discussion

3.1. Kinetics of the Cl+*n*-Butanol Reaction in 700 Torr of Air. The rate of reaction 5 was measured relative to reactions 6−8

$$Cl + CH_3(CH_2)_3OH \rightarrow \text{products} \quad (5)$$

$$Cl + C_2H_2 \rightarrow \text{products} \quad (6)$$

$$Cl + C_2H_4 \rightarrow \text{products} \quad (7)$$

$$Cl + C_3H_6 \rightarrow \text{products} \quad (8)$$

Reaction mixtures consisted of 25−37 mTorr of *n*-butanol, 51−129 mTorr of Cl_2 and either 1.5−2.4 mTorr of C_2H_2, 3.2−7.6 mTorr of C_2H_4, or 8.5−9.9 mTorr of C_3H_6 in 700 Torr of air diluent. The observed loss of *n*-butanol versus the loss of the reference compounds is plotted in Figure 1. Linear least-squares analysis of the data in Figure 1 gives $k_5/k_6 = 4.11 \pm 0.41$, $k_5/k_7 = 2.36 \pm 0.34$, and $k_5/k_8 = 0.89 \pm 0.09$. Using reference rate constants (at 700 Torr of total pressure) of $k_6 = 5.07 \times 10^{-11}$,[7] $k_7 = 9.29 \times 10^{-11}$,[7] and $k_8 = 2.64 \times 10^{-10}$ [8] gives $k_5 = (2.08 \pm 0.21) \times 10^{-10}$, $(2.19 \pm 0.32) \times 10^{-10}$, and $(2.35 \pm 0.24) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. We cite a final value which is the average of the individual determinations together with error limits which encompass the extremes of the determinations, $k_5 = (2.21 \pm 0.38) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Results from the current work are compared with previous measurements in Table 1. As seen from Table 1, there is excellent agreement between the results from the three relative rate studies of this reaction. The result from the absolute rate

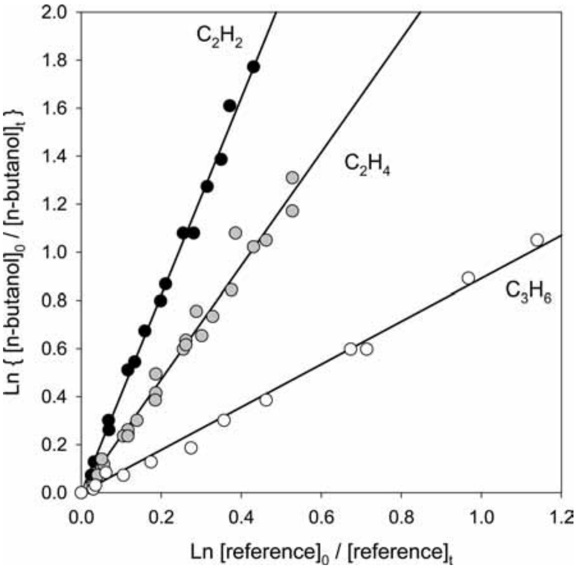

Figure 1. Loss of *n*-butanol versus acetylene (black symbols), ethene (shaded symbols), and propene (open symbols) in the presence of Cl atoms in 700 Torr of air at 296 ± 2 K.

TABLE 1: Literature Data for *k*(Cl+*n*-butanol) (10^{-10} cm^3 $molecule^{-1}$ s^{-1}) near Ambient Temperature

T	k (Cl+*n*-butanol)	technique[a]	reference	reference rate	citation
296	2.08 ± 0.21	RR	acetylene	0.507	this work
296	2.19 ± 0.22	RR	ethene	0.929	this work
296	2.35 ± 0.23	RR	propene	2.64	this work
298	1.96 ± 0.19	PLP-RF			Garzon et al.[27]
295	2.11 ± 0.11	RR	propane	1.31	Wu et al.[28]
295	2.23 ± 0.10	RR	*c*-hexane	3.07	Wu et al.[28]
298	2.04 ± 0.14	RR	*c*-hexane	3.11	Nelson et al.[29]

[a] RR, relative rate; PLP-RF, pulsed laser photolysis resonance fluorescence.

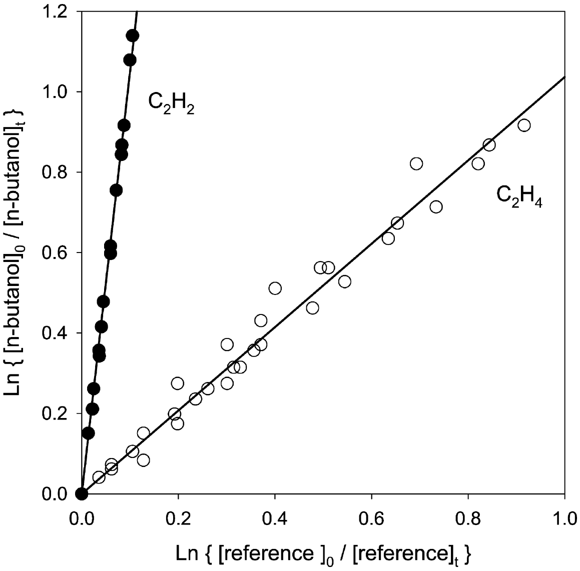

Figure 2. Loss of *n*-butanol versus acetylene (filled symbols) and ethene (open symbols) in the presence of OH radicals in 700 Torr of air at 296 ± 2 K.

study by Garzón et al.[27] is slightly below, but is consistent within the experimental uncertainties with, the results from the relative rate studies.

3.2. Kinetics of the OH+*n*-Butanol Reaction in 700 Torr of Air. The rate of reaction 9 was measured relative to reactions 10 and 11

$$OH + CH_3(CH_2)_3OH \rightarrow \text{products} \quad (9)$$

$$OH + C_2H_2 \rightarrow \text{products} \quad (10)$$

$$OH + C_2H_4 \rightarrow \text{products} \quad (11)$$

Reaction mixtures consisted of 17.9−36.6 mTorr of *n*-butanol, 50−104 mTorr of CH_3ONO, and either 1.5−2.8 mTorr of C_2H_2 or 2.8−6.8 mTorr of C_2H_4 in 700 Torr of total pressure of air diluent. Figure 2 shows the loss of *n*-butanol plotted versus the loss of the reference compounds. Linear least-squares analysis gives $k_9/k_{10} = 10.5 \pm 1.0$ and $k_9/k_{11} = 1.04 \pm 0.10$. Using reference rate constants (at 700 Torr of total pressure) $k_{10} = 8.45 \times 10^{-13}$ [9] and $k_{11} = 8.52 \times 10^{-12}$ [10] gives $k_9 = (8.87 \pm 0.85) \times 10^{-12}$ and $(8.86 \pm 0.85) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Indistinguishable values of k_9 are obtained using the two different references. We cite a final value which is the average of the individual determinations together with error limits which encompass the extremes of the determinations, $k_9 = (8.86 \pm 0.85) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. As seen from Table 2, the result from the present work is in excellent agreement with previous relative and absolute rate determinations.

The structure activity relationship (SAR) method of Kwok and Atkinson[11] is useful for estimating the rate constants for the gas-phase reactions of the OH radical with organic compounds. Bethel et al.[12] have proposed new substituent factors for use with alcohols and diols. The updated SAR method predicts k(OH+*n*-butanol) = 7.8×10^{-12} cm^3 molecule^{-1} s^{-1}, which is consistent with the literature data given in Table 2.

3.3. Mechanism of the Cl+*n*-Butanol Reaction in 700 Torr of N_2. The products and mechanism of the reaction of Cl atoms with *n*-butanol was investigated by UV irradiation of mixtures of 55−61 mTorr of *n*-butanol and 101−112 mTorr of Cl_2 in 700 Torr of N_2 diluent. Hydrogen abstraction from the −OH group by chlorine atoms is endothermic and of negligible importance. The reaction of Cl atoms with *n*-butanol proceeds via four channels

TABLE 2: Literature Data for k(OH+*n*-butanol) (10^{-12} cm^3 molecule^{-1} s^{-1}) near Ambient Temperature

T	k	technique[a]	reference	reference rate	citation
296	8.87 ± 0.85	RR	acetylene	0.845	this work
296	8.86 ± 0.85	RR	ethene	8.52	this work
296	8.31 ± 0.63	FP-RF			Wallington and Kurylo[30]
298	8.24 ± 0.84	RR	cyclohexane	7.49	Cavalli et al.[25]
295	8.66 ± 0.66	RR	propane	1.08	Wu et al.[28]
298	7.80 ± 0.20	PR-KS			Nelson et al.[29]
298	8.56 ± 0.70	RR	cyclohexane	7.49	Nelson et al.[29]
298	8.47 ± 0.34	PLP-LIF			Yujing and Mellouki[31]

[a] RR, relative rate; FP-RF, flash photolysis resonance fluorescence; PR-KS, pulsed radiolysis kinetic spectroscopy; PLP-RF, pulsed laser photolysis resonance fluorescence.

$$Cl + CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CHOH + HCl \quad (5a)$$

$$Cl + CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CHCH_2OH + HCl \quad (5b)$$

$$Cl + CH_3CH_2CH_2CH_2OH \rightarrow CH_3CHCH_2CH_2OH + HCl \quad (5c)$$

$$Cl + CH_3CH_2CH_2CH_2OH \rightarrow CH_2CH_2CH_2CH_2OH + HCl \quad (5d)$$

followed by reaction with Cl_2 to form chlorobutanols

$$Cl_2 + CH_3CH_2CH_2CHOH \rightarrow CH_3CH_2CH_2CHClOH + Cl \quad (12)$$

$$Cl_2 + CH_3CH_2CHCH_2OH \rightarrow CH_3CH_2CHClCH_2OH + Cl \quad (13)$$

$$Cl_2 + CH_3CHCH_2CH_2OH \rightarrow CH_3CHClCH_2CH_2OH + Cl \quad (14)$$

$$Cl_2 + CH_2CH_2CH_2CH_2OH \rightarrow CH_2ClCH_2CH_2CH_2OH + Cl \quad (15)$$

By analogy to the behavior of other alkyl radicals, it is expected that the rate constants for reactions 12−15 will be on the order of 10^{-12}−10^{-11} cm^3 molecule^{-1} s^{-1}. In the present experiments with 101−112 mTorr of Cl_2 in 700 Torr of nitrogen, it is expected that reactions 12−15 will be the dominant fate of the radicals produced by reaction of chlorine atoms with *n*-butanol. α-Chloro-alcohols such as CH_2ClOH, $CHCl_2OH$, CCl_3OH, $CH_3CHClOH$, and $CH_3CClOHCH_3$ decompose heterogeneously in the chamber via elimination of HCl[13−15] to give the corresponding carbonyl compounds on a time scale typically of a few minutes. The decomposition of $CH_3CH_2CH_2CHClOH$ was complete within a few minutes and gave butyraldehyde, which provides a marker for reaction 5a.

$$CH_3CH_2CH_2CHClOH \rightarrow CH_3CH_2CH_2CHO + HCl \quad (16)$$

Of the remaining chlorobutanols, only $CH_2ClCH_2CH_2CH_2OH$ is commercially available (Fluka, >90%). A sample of $CH_2ClCH_2CH_2CH_2OH$ was used to obtain a calibrated reference spectrum. Figure 3 shows the formation of butyraldehyde and $CH_2ClCH_2CH_2CH_2OH$ versus the loss of *n*-butanol for Cl_2 initiated experiments in 700 Torr of N_2. The butyraldehyde data have been corrected for secondary reactions using the value $k(Cl+CH_3CH_2CH_2CHO) = (1.38 \pm 0.18) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} determined by Cuevas et al.[16] and the procedure described elsewhere.[17] Linear least-squares analysis of the butyraldehyde data set gives a molar yield of 33 ± 3%. The $CH_2ClCH_2CH_2CH_2OH$ data in Figure 3 have not been corrected for loss via secondary reaction with chlorine atoms since the rate constant $k(Cl+CH_2ClCH_2CH_2CH_2OH)$ has not been measured. The linearity of the data in Figure 3 suggests that loss of $CH_2ClCH_2CH_2CH_2OH$ is not of major importance. Linear least-squares analysis of the $CH_2ClCH_2CH_2CH_2OH$ data set for *n*-butanol consumptions < 30 mTorr (to avoid complications associated with loss of $CH_2ClCH_2CH_2CH_2OH$ at large consumptions) gives a molar yield of 13 ± 3%, and we conclude that $k_{5d}/k_5 = 0.13 \pm 0.03$.

3.4. Products of Cl Atom Initiated Oxidation of *n*-Butanol in the Absence of NO in 700 Torr of N_2/O_2. The mechanism of Cl atom initiated oxidation of *n*-butanol was investigated by irradiating mixtures of 30−68 mTorr of *n*-butanol and 100−210 mTorr of Cl_2 in 10−600 Torr of oxygen. Nitrogen was added as needed to provide 700 Torr of total pressure. Figure 4 shows spectra acquired before (A) and after (B) a 30 s irradiation of a mixture of 68 mTorr of *n*-butanol and 100 mTorr of Cl_2 in 700 Torr of air. The consumption of *n*-butanol in this experiment was 24%. Panel (C) shows the product spectrum derived by subtracting the IR features of *n*-butanol from the spectrum in panel (B). Comparison of the IR features in panel (C) with the references shown in panels (D) and (E) shows the formation of butyraldehyde and propionaldehyde. The residual spectrum remaining after the removal of identified compounds is ascribed to unidentified product(s).

The circles in Figure 5 show the formation of butyraldehyde, propionaldehyde, acetaldehyde, and formaldehyde versus *n*-butanol loss for experiments with 10, 140, and 600 Torr of O_2 in 700 Torr of total pressure made up of N_2 in the absence of NO. The butyraldehyde data have been corrected for loss via reaction with Cl atoms using $k(Cl+CH_3CH_2CH_2CHO) = (1.38 \pm 0.18) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [16] and the procedure described elsewhere.[17] Inspection of the data in Figure 5 reveals that there was no discernible impact of [O_2] on the product yields. Linear least-squares analysis of the composite butyraldehyde data set gives a molar yield of 38 ± 2%. The yield plots of propionaldehyde, acetaldehyde, and formaldehyde in the absence of NO are curved (see circles in Figure 5), suggesting that there are both primary and secondary sources of these compounds. The initial yields of propionaldehyde, acetaldehyde, and formaldehyde are 3 ± 2, 1 ± 1, and 4 ± 3%, respectively, and represent primary product yields. Given the small initial yields of these compounds and curved yield plots in Figure 5, we conclude that in the absence of NO, most of the observed formaldehyde, acetaldehyde, and propionaldehyde products come from secondary reactions.

The reaction of Cl atoms with *n*-butanol proceeds via four channels (reactions 5a−5d). By analogy to the behavior of other hydroxyalkyl radicals,[3] the α-hydroxyalkyl radical formed via attack at the 1 position is expected to react exclusively with oxygen to form butyraldehyde and HO_2

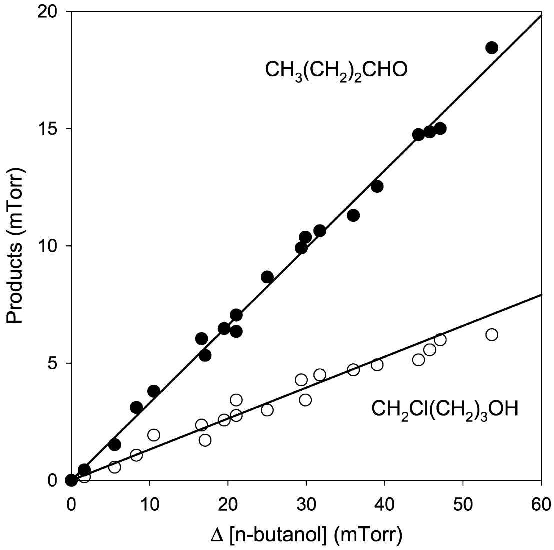

Figure 3. Formation of butyraldehyde (filled) and 4-chloro-*n*-butanol versus the loss of *n*-butanol following UV irradiation of *n*-butanol/Cl_2 in 700 Torr of total pressure of nitrogen diluent.

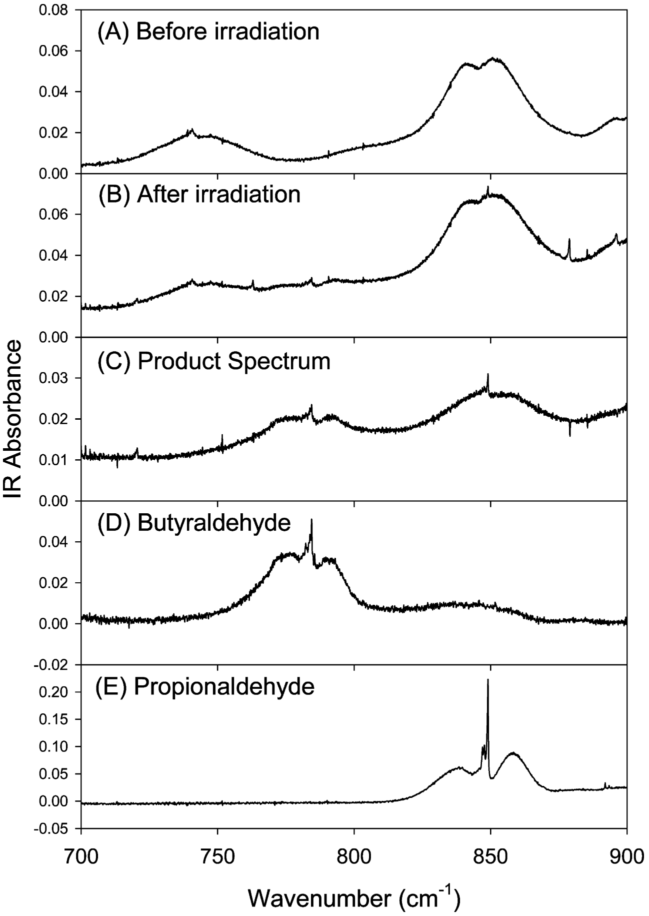

Figure 4. IR spectra obtained before (A) and after (B) a 30 s irradiation of 68 mTorr of *n*-butanol and 100 mTorr of Cl_2 in 700 Torr of air. Panel (C) shows the product spectrum obtained by subtracting 76% of panel (A) from panel (B). Panels (D) and (E) show the reference spectra for $CH_3CH_2CH_2CHO$ and CH_3CH_2CHO.

$$CH_3CH_2CH_2CHOH + O_2 \rightarrow CH_3CH_2CH_2C(O)H + HO_2 \quad (17)$$

The β, γ, and δ hydroxyalkyl radicals formed from the abstraction of a hydrogen atom at the 2, 3, and 4 positions, respectively, will add oxygen to give hydroxyalkylperoxy radicals. In the absence of NO, the hydroxyalkylperoxy radicals will react with peroxy radicals to give hydroxyalkoxy radicals. As illustrated in Figures 6−8, the fate of the hydroxyalkoxy radicals is expected to be reaction with O_2, decomposition, or isomerization via a hydrogen shift through a six-member transition state. Peroxy radical self-reactions proceed via two channels, a channel giving two RO radicals and a molecular channel giving ROH and R′CHO.[3] The formation of HO_2 radicals (e.g., via reaction 17) raises the possibility that reaction of RO_2 radicals with HO_2 radicals to form hydroperoxides,[3] ROOH, is important. These possibilities are included in Figures 6−8. Averaging the yields of butyraldehyde in the presence and absence of oxygen with error bars to include the extremes of both measurements, we conclude that $k_{5a}/k_5 = 0.38 \pm 0.02$.

Combining $k_{5a}/k_5 = 0.38 \pm 0.02$ with $k_5 = (2.21 \pm 0.38) \times 10^{-10}$ gives $k_{5a} = (8.4 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This can be compared to values of $k(-CH_2OH)$ site-specific rate constants (with reaction occurring at the $-CH_2-$ portion) of $(8.8 \pm 1.8) \times 10^{-11}$ in C_2H_5OH[14] and $(10.4 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} in n-C_3H_7OH.[18] The reactivities of the $-CH_2OH$ groups in ethanol, *n*-propanol, and *n*-butanol toward chlorine atoms are indistinguishable. Comparing k_{5a} with the reactivity of Cl atoms toward $-CH_2-$ groups in C_3H_6 (7.74×10^{-11}) and n-C_4H_{10} (7.29×10^{-11}), it is evident that the −OH group activates the 1 position. The reactivity of the n-C_3H_7- group in *n*-butanol, $k_5 - k_{5a}/k_5 = (1.4 \pm 0.3) \times 10^{-10}$, is similar to that in alkanes $[=k(Cl+n\text{-hexane})/2 = (1.65 \pm 0.25) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}].[19]

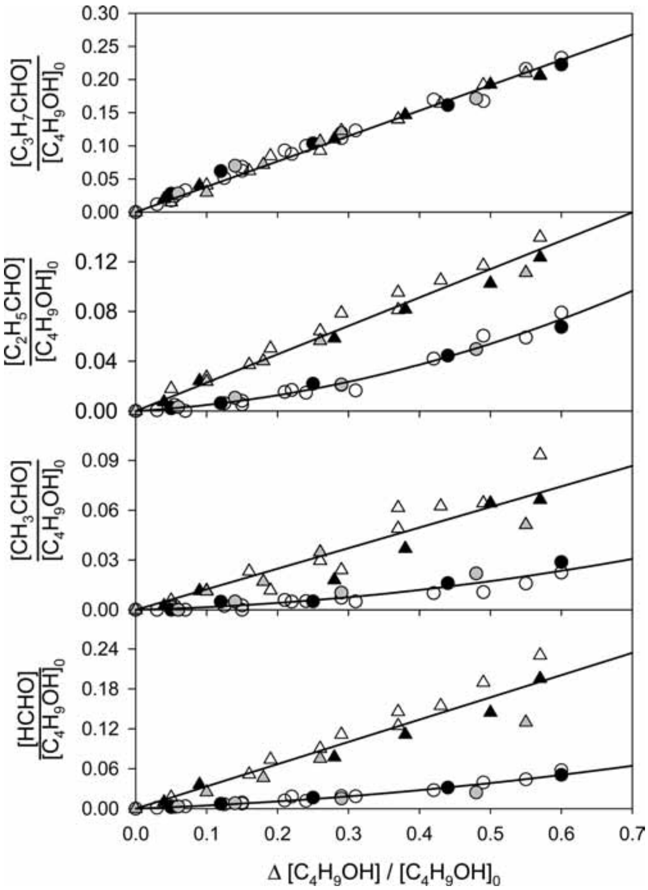

Figure 5. Formation of butyraldehyde, propionaldehyde, acetaldehyde, and formaldehyde versus the loss of *n*-butanol following UV irradiation of *n*-butanol/Cl_2 with 10 (filled symbols), 140 (open symbols), or 700 Torr of O_2 (shaded symbols) in 700 Torr of total pressure of nitrogen diluent in the presence (triangles), or absence (circles), of NO_x.

3.5. Products of Cl Atom Initiated Oxidation of *n*-Butanol in the Presence of NO in 700 Torr of N_2/O_2. The mechanism of Cl atom initiated oxidation of *n*-butanol in the presence of NO was investigated by irradiating mixtures of 30−60 mTorr of *n*-butanol, 100−204 mTorr of Cl_2, and 50−100 mTorr of NO in 10−600 Torr of oxygen diluent. Nitrogen was added as needed to provide 700 Torr of total pressure.

The triangles in Figure 5 show the formation of butyraldehyde, propionaldehyde, acetaldehyde, and formaldehyde versus the loss of *n*-butanol for experiments in 700 Torr of diluent in the presence of NO. The data have been corrected for loss of the products via secondary reactions with Cl atoms using the procedure described elsewhere.[17] In light of the complexity of the chemical system, we did not include an estimation of the formation of C_2H_5CHO, CH_3CHO, and HCHO from oxidation of the higher aldehydes. The yields of C_2H_5CHO, CH_3CHO, and HCHO should be regarded as upper limits. Data for different O_2 concentrations are indistinguishable. Linear least-squares analyses of the data in Figure 5 give molar yields of butyraldehyde (38 ± 2%), propionaldehyde (23 ± 3%), acetaldehyde (12 ± 4%), and formaldehyde (33 ± 3%). Quoted uncertainties are 2 standard deviations from the regression analyses. The presence of NO ensures rapid removal of RO_2 (converted into RO radicals and, to a small degree, organic nitrates, $RONO_2$) and HO_2 radicals

$$RO_2 + NO \rightarrow RO + NO_2 \quad (18a)$$

$$RO_2 + NO + M \rightarrow RONO_2 + M \quad (18b)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (4)$$

The presence of NO simplifies the mechanistic interpretation of the product yields because it provides a more direct conversion of peroxy into alkoxy radicals via reaction 18a and removes the need to consider $RO_2 + RO_2$ and $RO_2 + HO_2$ reactions.

As discussed previously, reaction 17 is the sole fate of the $CH_3CH_2CH_2CHOH$ radical. The only source of propionaldehyde as a primary product is decomposition of the $CH_3CH_2CH(O)CH_2OH$ radical formed from abstraction of a hydrogen atom in the 2 position, which should lead to equal amounts of propionaldehyde and formaldehyde. The only source of acetaldehyde as a primary product is decomposition of the $CH_3CH(O)CH_2CH_2OH$ radical formed from abstraction of a hydrogen atom in the 3 position, which should lead to acetaldehyde and HCHO. The fact that the data plots are, within the experimental uncertainties, linear suggests that the bulk of the observed propionaldehyde, acetaldehyde, and formaldehyde are primary products in the system. Using butyraldehyde as a marker for channel 5a gives $k_{5a}/k_5 = 0.38$. The observation of substantial yields of propionaldehyde and acetaldehyde shows that decomposition is a significant fate of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals.

The conclusion that decomposition is an important fate of $CH_3CH_2CH(O)CH_2OH$ radicals is consistent with the observation by Atkinson et al.[20] of the formation of propionaldehyde

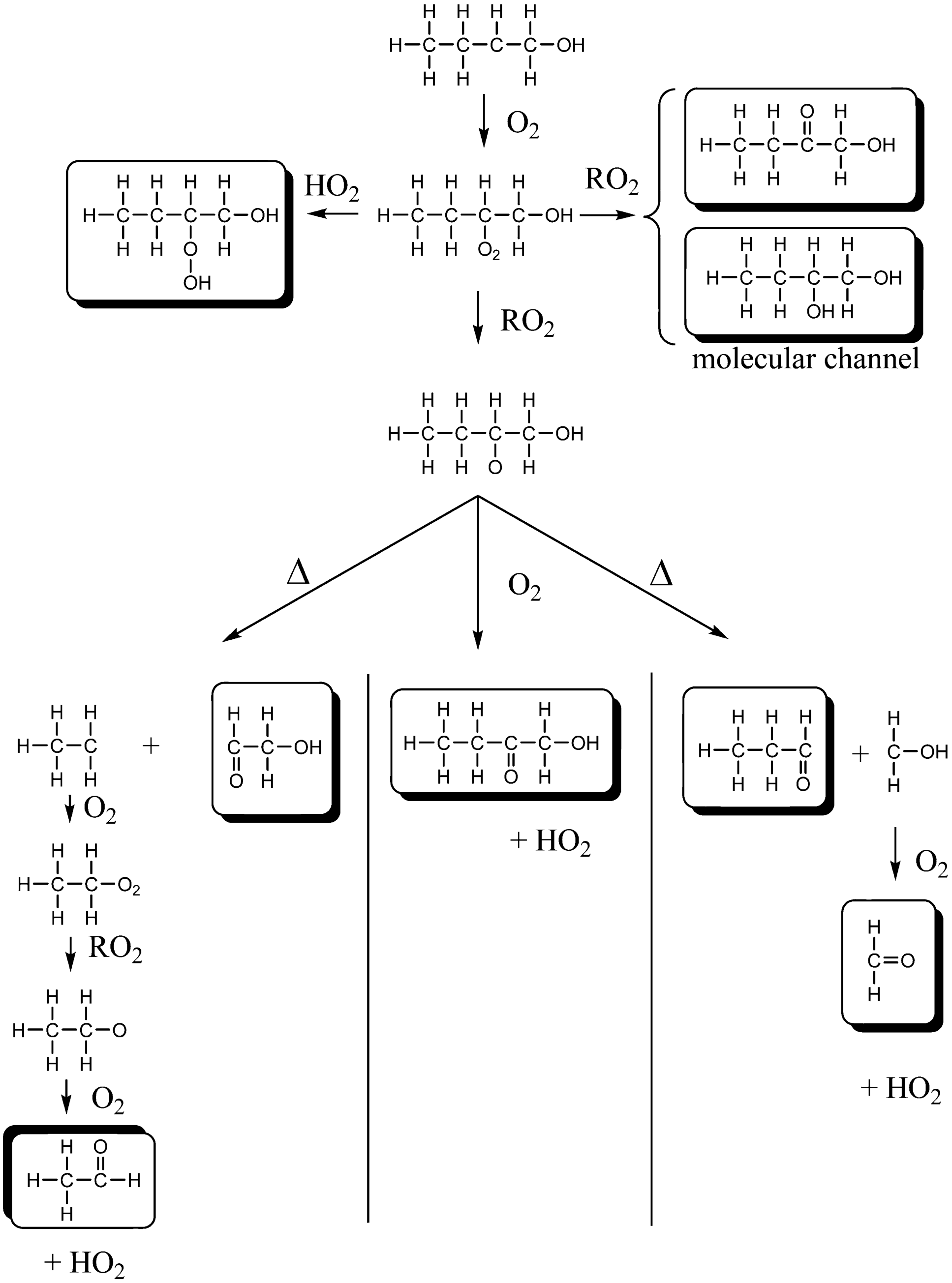

Figure 6. Fate of the β-hydroxyalkyl radical in the Cl atom/OH radical initiated oxidation of *n*-butanol.

in a 94 ± 12% yield following the OH radical initiated oxidation of 1-butene in the presence of NO. The conclusion that decomposition is an important fate of $CH_3CH(O)CH_2CH_2OH$ radicals is consistent with the approximately 40:60 ratio for decomposition and reaction with O_2 as the fates of the 2-butoxy radical in 1 atm of air.[19] It seems likely that reaction with O_2 is a competing loss of $CH_3CH(O)CH_2CH_2OH$ radicals, and given the data scatter in the CH_3CHO yield plot in Figure 5, we are not able to exclude an effect of $[O_2]$ consistent with such a competition.

The decomposition of $CH_3CH_2CH(O)CH_2OH$ radicals gives propionaldehyde and HCHO, while the decomposition of $CH_3CH(O)CH_2CH_2OH$ radicals gives acetaldehyde and CH_2CH_2OH radicals, which (from the reported products of the OH initiated oxidation of ethene) gives approximately 1.6 molecules of HCHO and 0.2 molecules of glycolaldehyde.[10] Hence, we would expect the HCHO yield to be equal to the sum of propionaldehyde plus 1.6 times the acetaldehyde yield. The sum of the observed propionaldehyde plus 1.6 times the acetaldehyde yield from Figure 5 is 35 ± 5% and is somewhat below, but consistent within the experimental uncertainties with, the expected value (42 ± 7%). This may reflect secondary formation of propionaldehyde and/or acetaldehyde in the system.

Figure 5 shows the yields of butyraldehyde, propionaldehyde, acetaldehyde, and formaldehyde following the chlorine atom initiated oxidation of *n*-butanol in the presence (triangles) and absence (circles) of NO_x. It is striking that while the yield of butyraldehyde is not affected by the presence of NO, the yields of the smaller aldehydes are substantially higher for experiments when NO is present. As discussed above, the source of butyraldehyde is reaction of the α-hydroxyalkyl radical $CH_3CH_2CH_2CHOH$ with O_2. The rate constant for this reaction is expected to be on the order of 10^{-11} cm^3 $molecule^{-1}$ s^{-1},[3] and O_2 is a reactant which is in vast excess in the system; hence, it is not surprising that the butyraldehyde yield is unaffected by the presence of NO. As shown in Figures 6−8, the source

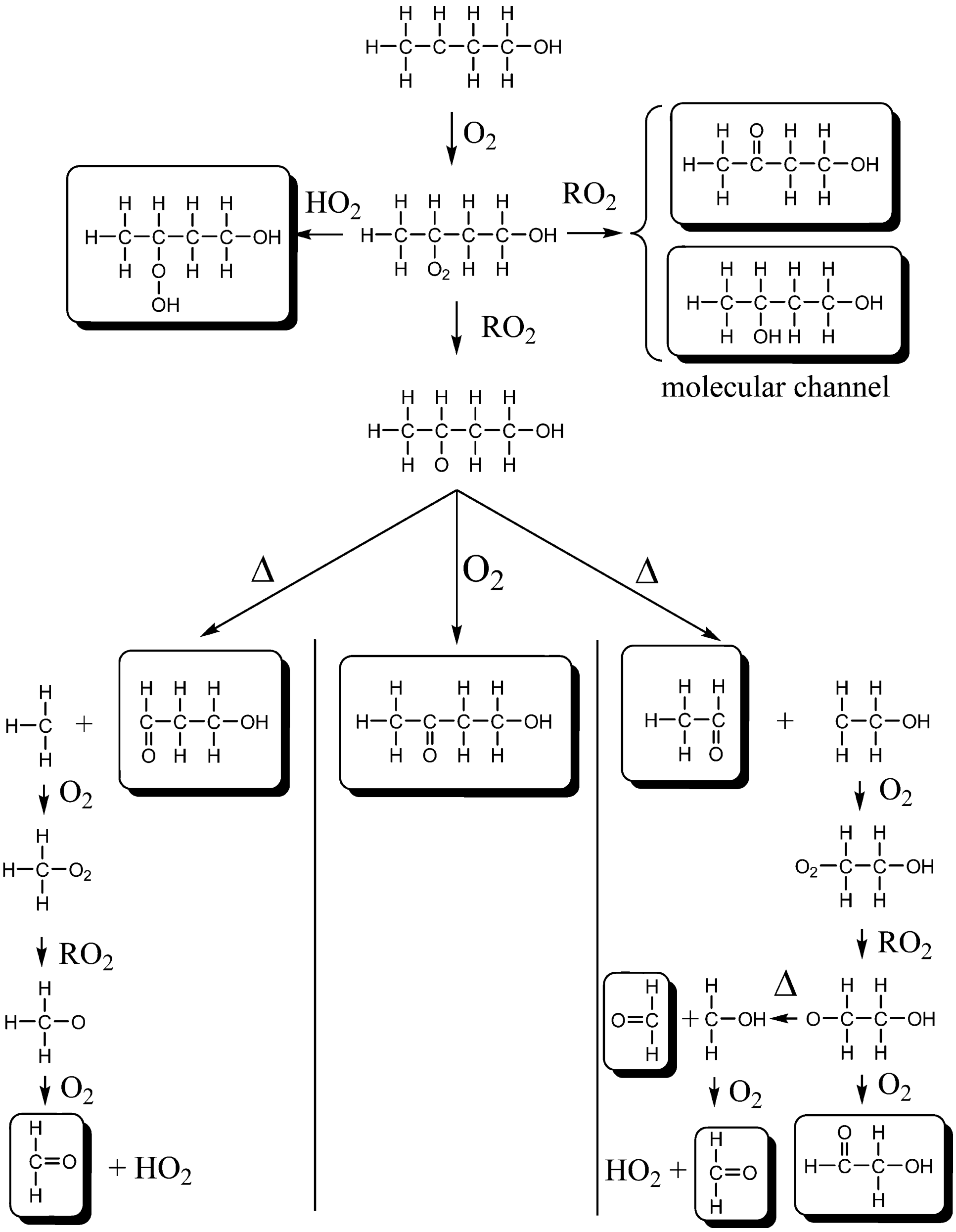

Figure 7. Fate of the γ-hydroxyalkyl radical in the Cl atom/OH radical initiated oxidation of *n*-butanol.

of propionaldehyde, acetaldehyde, and formaldehyde as primary products in the system is the decomposition of the alkoxy radicals $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$. As seen in Figure 5, the initial yields of propionaldehyde, acetaldehyde, and formaldehyde are much greater when NO is present than those when it is absent. The observed formation of propionaldehyde, acetaldehyde, and formaldehyde as substantial primary products shows that decomposition is an important fate of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals formed in the presence of NO.

There are two possible explanations for the large effect of NO on the yields of propionaldehyde, acetaldehyde, and formaldehyde as primary products. First, in the absence of NO, $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals are formed in sufficiently small yields such that propionaldehyde, acetaldehyde, and formaldehyde are not discernible as primary products. Second, in the presence of NO, a substantial fraction of the $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals formed are chemically activated and decompose promptly. Prompt decomposition of nascent $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals will increase the observed yields of propionaldehyde, acetaldehyde, and formaldehyde.

Regarding the first explanation, we note that from the available mechanistic database for the self-reactions of peroxy radicals, it seems likely that a substantial fraction (approximately 40% by analogy to the $C_2H_5O_2$ and *i*-$C_3H_7O_2$ self-reactions[21]) of the self- and cross-reactions of the peroxy radicals in the system will give molecular products. Furthermore, HO_2 radicals formed in reaction 17 will react with peroxy radicals to give hydroperoxides (see Figures 6−8) and hence will suppress the formation of alkoxy radicals. The curvature in the yields of propionaldehyde, acetaldehyde, and formaldehyde seen in Figure 5 is consistent with their formation during oxidation of the molecular products of the peroxy radical self- and cross-reactions and the hydroperoxides. It is clear that the yield of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals will be suppressed in the absence of NO. However, it is not clear that the magnitude of this effect is sufficient to entirely explain the effect of NO on the primary yields of propionaldehyde, acetaldehyde, and formaldehyde seen in Figure 5.

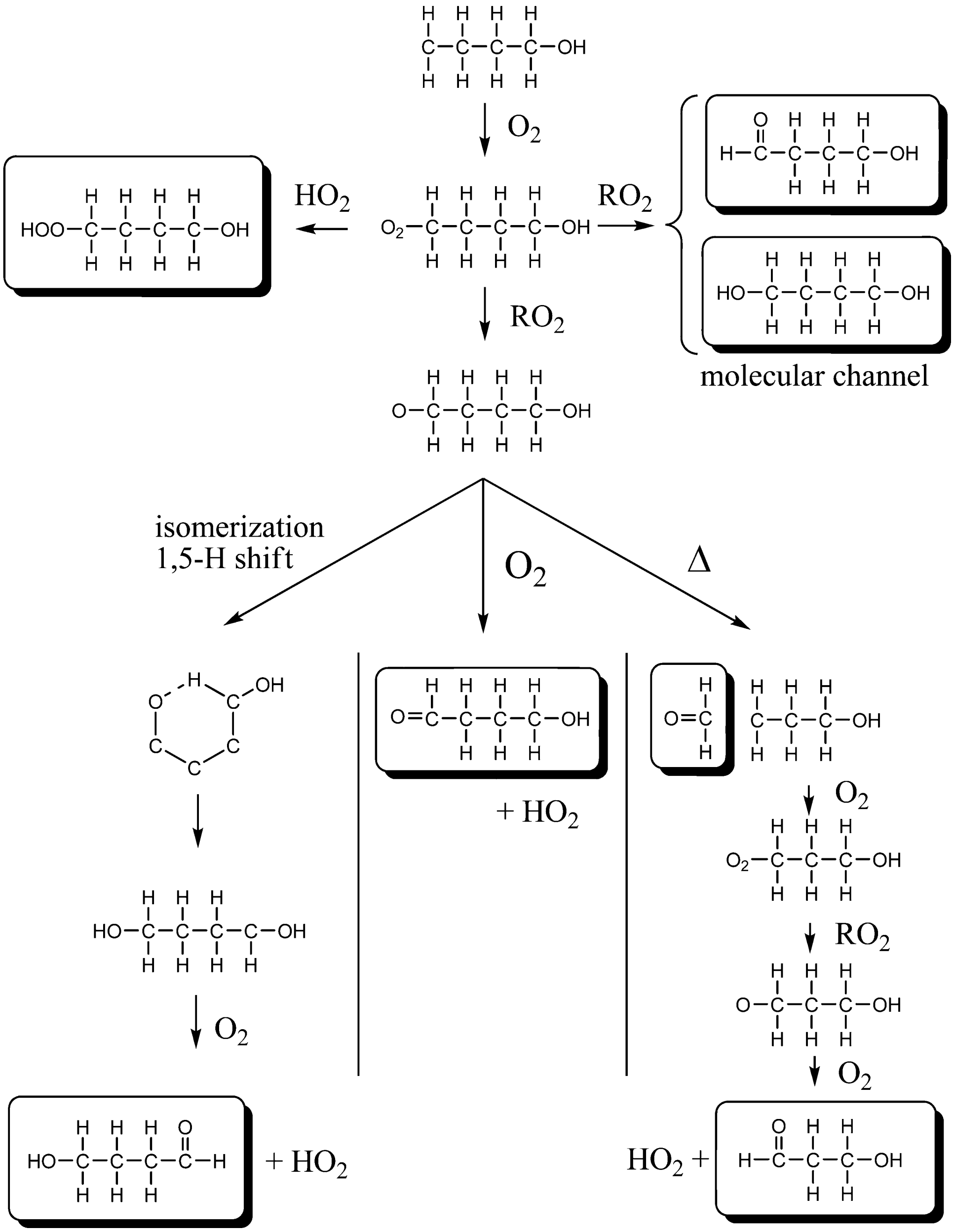

Figure 8. Fate of the δ-hydroxyalkyl radical in the Cl atom/OH radical initiated oxidation of *n*-butanol.

Regarding the second explanation, it is known that the reactions of peroxy radicals with NO deposit a significant fraction of the approximately 11−17 kcal mol^{-1} reaction exothermicity into the nascent RO radical.[22] There are no data available for the activation barriers for decomposition of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals. However, it has been established that the structurally similar oxygenated alkoxy radicals $CH_3CH(O)CH_2OH$ and $CH_3CH_2CH(OH)CH_2O$ have barriers for decomposition of approximately 7 kcal mol^{-1} and that chemical activation plays a dominant role in their atmospheric chemistry.[22−24] It seems reasonable to conclude that chemical activation of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals will be significant and will contribute to the large difference in propionaldehyde, acetaldehyde, and formaldehyde yields in experiments performed with, and without, NO shown in Figure 5.

3.6. Products of OH Radical Initiated Oxidation of *n*-Butanol in the Presence of NO_x in 700 Torr of Air. The mechanism of OH radical initiated oxidation of *n*-butanol in the presence of NO_x was investigated by irradiating mixtures of 59−121 mTorr of *n*-butanol, 50 mTorr of CH_3ONO, and 0−25 mTorr of NO in 700 Torr of air. Figure 9 shows the formation of butyraldehyde, propionaldehyde, and acetaldehyde versus the loss of *n*-butanol for experiments in 700 Torr of air in the presence of NO. The data have been corrected for losses via secondary reaction of the products with OH radicals.[17] In light of the complexity of the chemical system, we did not include an estimation of the secondary formation of C_2H_5CHO, CH_3CHO, and HCHO from oxidation of the higher aldehydes. The yields of C_2H_5CHO, CH_3CHO, and HCHO should be regarded as upper limits. Linear least-squares analyses of the data in Figure 9 give molar yields of butyraldehyde, propionaldehyde, and acetaldehyde of 44 ± 4, 19 ± 2, and 12 ± 3%, respectively. Quoted uncertainties are two standard deviations from the regression analyses.

By analogy to the reactivity of the −OH group in methanol and ethanol, it is expected that only approximately 2% of the reaction of OH radicals with *n*-butanol at ambient temperature occurs via attack on the −OH group.[3] The majority of the

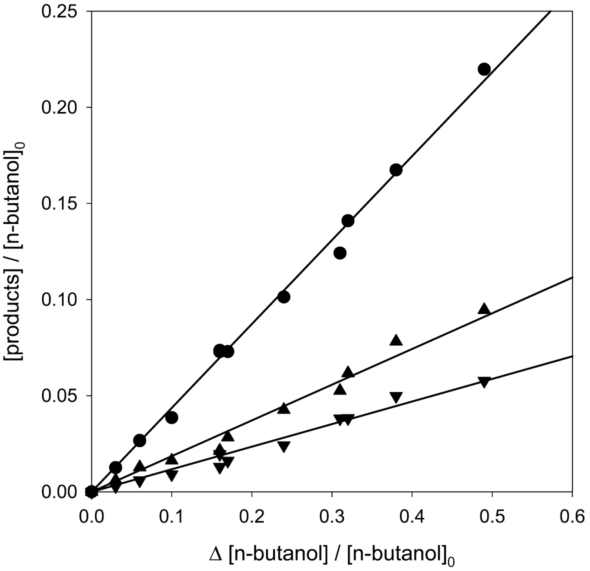

Figure 9. Formation of butyraldehyde (●), propionaldehyde (▲), and acetaldehyde (▼) versus loss of *n*-butanol following UV irradiation of *n*-butanol /CH_3ONO mixtures in 700 Torr of air diluent.

reaction of OH radicals with *n*-butanol proceeds via four channels

$$OH + CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CHOH + H_2O \quad (9a)$$

$$OH + CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CHCH_2OH + H_2O \quad (9b)$$

$$OH + CH_3CH_2CH_2CH_2OH \rightarrow CH_3CHCH_2CH_2OH + H_2O \quad (9c)$$

$$OH + CH_3CH_2CH_2CH_2OH \rightarrow CH_2CH_2CH_2CH_2OH + H_2O \quad (9d)$$

As discussed previously, reaction 17 is the sole fate of $CH_3CH_2CH_2CHOH$ radicals, and hence from the butyraldehyde yield, we conclude that $k_{9a}/k_9 = 0.44 \pm 0.04$.

Cavalli et al.[25] studied the products of the OH radical initiated oxidation of 1-butanol in the presence of NO_x in the 195 m^3 outdoor EUPHORE smog chamber. The reaction products observed (and molar yields) were butyraldehyde (51.8 ± 7.1%), propionaldehyde (23.4 ± 3.5%), acetaldehyde (12.7 ± 2.2%), and formaldehyde (43.4 ± 2.4%). The results of the present study are in agreement with these product yields within the stated uncertainties.

The SAR method is useful for estimating branching ratios for the various sites of attack of the OH radicals with an organic compound. Using the SAR method of Kwok and Atkinson[11] with the refinements of Bethel et al.[12] gives values of 0.43, 0.38, and 0.15 for k_{9a}/k_9, k_{9b}/k_9, and k_{9c}/k_9, respectively. The value for k_{9a}/k_9 determined in this work is consistent with the refined SAR value.

4. Implications for Atmospheric Chemistry

We present a large body of self-consistent data concerning the kinetics and mechanisms of the Cl atom and OH radical initiated oxidation of *n*-butanol. The atmospheric oxidation of *n*-butanol is initiated by reaction with OH radicals, which occurs with a rate constant of $k_9 = (8.86 \pm 1.0) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} in 700 Torr of air diluent at 296 K. Using an estimate for the 24 h average OH radical concentration in the atmosphere of 10^6 molecules cm^{-3} [26] provides an atmospheric lifetime of *n*-butanol of 1.3 days. We find that in the presence of NO_x, the OH radical initiated atmospheric oxidation of *n*-butanol gives butyraldehyde, propionaldehyde, and acetaldehyde as the major products in yields of 44 ± 4, 19 ± 2, and 12 ± 3%, respectively. These product yields are in good agreement with those measured by Cavalli et al.[25] in the presence of NO_x.

Cavalli et al.[25] developed a detailed chemical mechanism describing the atmospheric oxidation of *n*-butanol. The branching ratios for reaction of OH radicals with *n*-butanol and the rates of decomposition and reaction with O_2 of the $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ alkoxy radicals were obtained by fitting the mechanism to the experimental concentration−time profiles for *n*-butanol, butyraldehyde, propionaldehyde, acetaldehyde, formaldehyde, NO, and ozone. Chemical activation effects were not widely recognized when Cavalli et al.[25] constructed their model, and such effects were not considered.

Cavalli et al.[25] included the following reactions involving *β*- and *γ*-peroxy radicals in their model

$$CH_3CH_2CH(OO)CH_2OH + NO \rightarrow CH_3CH_2CH(O)CH_2OH + NO_2 \quad (19)$$

$$CH_3CH_2CH(O)CH_2OH + M \rightarrow CH_3CH_2CHO + CH_2OH + M \quad (20)$$

$$CH_3CH_2CH(O)CH_2OH + O_2 \rightarrow CH_3CH_2C(O)CH_2OH + HO_2 \quad (21)$$

$$CH_3CH(OO)CH_2CH_2OH + NO \rightarrow CH_3CH(O)CH_2CH_2OH + NO_2 \quad (22)$$

$$CH_3CH(O)CH_2CH_2OH + M \rightarrow CH_3CHO + CH_2CH_2OH + M \quad (23)$$

$$CH_3CH(O)CH_2CH_2OH + O_2 \rightarrow CH_3C(O)CH_2CH_2OH + HO_2 \quad (24)$$

with $k_{19} = k_{22} = 1.0 \times 10^{-11}$, $k_{21} = k_{24} = 8.0 \times 10^{-15}$, $k_{20} = 7.4 \times 10^5$ s^{-1}, and $k_{23} = 3.3 \times 10^5$ s^{-1}. The relative importance of reaction with O_2 and decomposition as fates of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals is given by $k_{21}[O_2]/k_{20}$ and $k_{24}[O_2]/k_{23}$. For experiments conducted using $[O_2] = 10$ Torr, $k_{21}[O_2]/k_{20} = 0.003$ and $k_{24}[O_2]/k_{23} = 0.008$. For experiments conducted using $[O_2] = 600$ Torr, $k_{21}[O_2]/k_{20} = 0.2$ and $k_{24}[O_2]/k_{23} = 0.5$. For $[O_2] = 10-600$ Torr, decomposition accounts for 99−83 and 99−67% of the fate of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals, respectively. The absence of any discernible effect of $[O_2]$ on the propionaldehyde and acetaldehyde yields in our experiments conducted with $[O_2] = 10-600$ Torr in the presence of NO (triangles in Figure 5) is consistent with the kinetic parameters deduced by Cavalli et al.[25]

Although our experimental results are consistent with predictions based upon the model of Cavalli et al.,[25] this does not necessarily validate the kinetic parameters used in the model. Chemical activation effects were not included in the model and are likely to be important (see section 3.5). Inclusion of chemical activation of $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals in the model could be compensated by increasing the rate constant ratios k_{21}/k_{20} and k_{24}/k_{23} to match the observed product yields. Hence, the rate constant ratios k_{21}/k_{20} and k_{24}/k_{23} reported by Cavalli et al.[25] should be treated as lower limits. The chemical model of Cavalli et al.[25] was constructed by fitting product data observed in experiments in 740 Torr of air with 10−50 ppb of NO (typical of polluted urban areas). While it is clear that the model is useful in describing the atmospheric chemistry of *n*-butanol in polluted urban areas, the utility of the model in low NO_x environments is not clear. Additional experiments to quantify the role of chemical activation in $CH_3CH_2CH(O)CH_2OH$ and $CH_3CH(O)CH_2CH_2OH$ radicals formed by reaction of the corresponding peroxy radicals with NO are needed. Such experiments should provide a more complete picture of the atmospheric chemistry of *n*-butanol for incorporation in global atmospheric models.

References and Notes

(1) *Biofuels for transport*; International Energy Agency: Paris, France, 2004.

(2) Mueller, S. A.; Anderson, J. E.; Wallington, T. J. *J. Chem. Educ.* **2009**, in press.

(3) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. *Atmos. Chem. Phys.* **2006**, *6*, 3625.

(4) Atkinson, R.; Arey, J. *Chem. Rev.* **2003**, *103*, 4605.

(5) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.

(6) Atkinson, R. *J. Phys. Chem. Ref. Data* **1989**, Monograph 1.

(7) Wallington, T. J.; Andino, J. M.; Lorkovic, I. M.; Kaiser, E. W.; Marston, G. *J. Phys. Chem.* **1990**, *94*, 3644.

(8) Ezell, M. J.; Wang, W.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2002**, *1*, 5813.

(9) Sørensen, M.; Kaiser, E. W.; Hurley, M. D.; Wallington, T. J.; Nielsen, O. J. *Int. J. Chem. Kinet.* **2003**, *35*, 191.

(10) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press: Oxford, U.K., 2000.

(11) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.

(12) Bethel, H. L.; Atkinson, R.; Arey, J. *Int. J. Chem. Kinet.* **2001**, *33*, 310.

(13) Wallington, T. J.; Schneider, W. F.; Barnes, I.; Becker, K. H.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **2000**, *322*, 97.

(14) Taatjes, C. A.; Christensen, L. K.; Hurley, M. D.; Wallington, T. J. *J. Phys. Chem. A* **1999**, *103*, 9805.

(15) Yamanaka, T.; Kawasaki, M.; Hurley, M. D.; Wallington, T. J.; Schneider, W. F. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4211.

(16) Cuevas, C. A.; Notario, A.; Martýnez, E.; Albaladejo, J. *Atmos. Environ.* **2006**, *40*, 3845.

(17) Meagher, R. J.; McIntosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet.* **1997**, *29*, 619.

(18) Yamanaka, T.; Kawasaki, M.; Hurley, M. D.; Wallington, T. J.; Xiao, L.; Schneider, W. F. *J. Phys. Chem. A* **2008**, *112*, 2773.

(19) Calvert, J. G.; Derwent, R. G.; Orlando, J. J.; Tyndall, G. S.; Wallington, T. J. *The Mechanisms of Atmospheric Oxidation of the Alkanes*; Oxford University Press: Oxford, U.K., 2008.

(20) Atkinson, R.; Tuazon, E. C.; Carter, W. P. L. *Int. J. Chem. Kinet.* **1985**, *17*, 725.

(21) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. *Chem. Rev.* **1992**, *92*, 667.

(22) Orlando, J. J.; Tyndall, G. S.; Wallington, T. J. *Chem. Rev.* **2003**, *103*, 4657.

(23) Vereecken, L.; Peeters, J.; Orlando, J. J.; Tyndall, G. S.; Ferronato, C. *J. Phys. Chem. A* **1999**, *103*, 4693.

(24) Caralp, F.; Forst, W.; Rayez, M.-T. *Phys. Chem. Chem. Phys.* **2003**, *5*, 476.

(25) Cavalli, F.; Geiger, H.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **2002**, *36*, 1263.

(26) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; John Wiley and Sons: New York, 1986.

(27) Garzón, A.; Cuevas, C. A.; Ceacero, A. A.; Notario, A.; Albaladejo, J.; Fernández-Gómez, M. *J. Chem. Phys.* **2006**, *125*, 104305.

(28) Wu, H.; Mu, Y.; Zhang, X.; Jiang, G. *Int. J. Chem. Kinet.* **2003**, *35*, 81.

(29) Nelson, L.; Rattigan, O.; Neavyn, R.; Sidebottom, H.; Treacy, J.; Nielsen, O. J. *Int. J. Chem. Kinet.* **1990**, *22*, 1111.

(30) Wallington, T. J.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1987**, *19*, 1015.

(31) Yujing, M.; Mellouki, A. *Chem. Phys. Lett.* **2001**, *333*, 63.

JP810585C