FTIR Kinetic, Product, and Modeling Study of the OH-Initiated Oxidation of 1-Butanol in Air

FABRIZIA CAVALLI, HARALD GEIGER,* IAN BARNES, AND KARL HEINZ BECKER Bergische Universität-GH Wuppertal, Physikalische Chemie/ FB 9, D-42097 Wuppertal, Germany

A kinetic and product study was performed on the reaction of OH radicals with 1-butanol in a 480 L indoor photoreactor and also in the EUPHORE outdoor smog chamber in Valencia, Spain. Long path in situ FTIR spectroscopy and gas chromatography with photoionization detection were used to analyze reactants and products. Using a kinetic relative rate technique, a rate coefficient of k(OH +1-butanol) = (8.28 \pm 0.85) \times 10⁻¹² cm³ s⁻¹ was measured in 740 Torr synthetic air at 298 \pm 2 K. The reaction products observed and their fractional molar yields were (in percent) butanal (51.8 \pm 7.1), propanal (23.4 \pm 3.5), ethanal (12.7 ± 2.2) , and formaldehyde (43.4 ± 2.4) . In addition, the results support the probable formation of 4-hydroxy-2butanone. Propanal, ethanal, and formaldehyde could also be formed in secondary reactions of some of the primary aldehydic products. However, under the conditions employed in the experiments, the contribution from secondary reactions is very minor. On the basis of the product studies, a detailed atmospheric degradation mechanism was constructed and tested against experimental data by chemical box model calculations. Measured and simulated concentration-time profiles for selected reactants were in excellent agreement.

1. Introduction

Oxygenated organic compounds are currently under consideration as potentially attractive replacements for traditional chlorinated and aromatic solvents. The drive behind the search for replacements is the need for more environmentally acceptable solvents with respect to ambient air quality (i.e., compounds which will help to reduce the tropospheric O_3 and photo-oxidant burden). However, the use of oxygenated replacements will also result in the release of these compounds into the atmosphere, where they will undergo photo-oxidative degradation processes, the most important and often dominant being reaction with the OH radical (1, 2). The photo-oxidation of oxygenates might contribute to some extend to the formation of photochemical air pollution in urban and regional areas (3). Therefore, before large-scale usage of these compounds, a quantification of their potential environmental impacts is desirable and, in many countries, mandatory. Accurate kinetic data and mechanistic information on the atmospheric fate of alternative oxygenated solvents are essential components in any attempts to reliably assess the ozone forming potential of these substances.

Alcohols are a class of highly volatile oxygenates, which are currently finding increasing use as solvents because they typically combine satisfactory technical performances in chemical industry applications with low costs and low health risks.

The compound investigated here, 1-butanol (propyl carbinol, *n*-butyl alcohol), currently finds a variety of applications in chemical industry (4). It is principally used in the field of surface coating either directly as a solvent or converted into derivatives, which then serve as solvents or monomer components. 1-Butanol is an excellent thinner and useful for regulating the viscosity and improving the flow properties of varnishes; it is also applied in plastic and fiber industries as well as in the production of butylamines. Besides its anthropogenic sources, the compound is directly emitted by plants (5).

While rate coefficients for the reactions of OH radicals with many alcohols are well-established, the atmospheric oxidation pathways of alcohols have received relatively little attention, and their representation in atmospheric models is, therefore, associated with substantial uncertainties.

To improve the knowledge of the atmospheric chemistry of alcohols and to facilitate their accurate description in atmospheric models, a kinetic and product investigation of the room-temperature gas-phase reaction of OH radicals with 1-butanol has been conducted. The kinetic studies were performed in a large-volume indoor photoreactor, while the product investigations were carried out in the outdoor EUPHORE (6-8) smog chamber facility in Valencia, Spain. To our knowledge, a detailed reaction mechanism for 1-butanol based on experimental measurements, such as those developed in this paper, has not yet been reported in the literature. Such a mechanism may now be applied in chemistry transport models on local or regional scales using scenarios suitable for estimating the influence of 1-butanol on tropospheric photosmog formation if the industrial emissions of this compound are significantly increased.

2. Experimental Section

The two experimental systems used for the present study have been described in detail elsewhere (6-9) and are only briefly outlined here.

2.1. Kinetic Study of the Reaction of OH Radicals with 1-Butanol. Kinetic experiments on the reaction of OH radicals with 1-butanol were carried out at 298 \pm 2 K and 740 Torr total pressure of synthetic air in a 480 L cylindrical Duran glass chamber. The chamber is surrounded by 24 fluorescent lamps (Philips T 40W/05, 320 nm < λ < 450 nm) (*9*) and is equipped with a built-in White mirror system for long path (51.6 m) in situ monitoring of reactants.

The rate coefficient for the gas-phase reaction of OH radicals with 1-butanol was determined using a relative rate method, in which the decays of the reactant (1-butanol) and of a suitable reference compound, whose rate coefficient with OH is reliably known (*10*), are monitored in parallel in the presence of OH radicals.

$$OH + 1-butanol \xrightarrow{k_1} products$$
 (R1)

$$OH + reference \xrightarrow{k_2} products \qquad (R2)$$

Provided that 1-butanol and the reference are removed solely by reaction with OH radicals, then

^{*} Corresponding author phone: +49-202-439-3832; fax:+49-202-439-2757; e-mail: geiger@uni-wuppertal.de.

$$\ln\left\{\frac{[1-\text{butanol}]_0}{[1-\text{butanol}]_t}\right\} = \frac{k_1}{k_2}\ln\left\{\frac{[\text{reference}]_0}{[\text{reference}]_t}\right\}$$
(1)

where $[1-butanol]_0$ and [reference]_0 are the concentrations of 1-butanol and the reference compound, respectively, at time 0; $[1-butanol]_t$ and [reference]_t are the corresponding concentrations at time *t*; k_1 and k_2 are the rate coefficients for reactions 1 and 2, respectively.

Hydroxyl radicals were generated by the photolysis of methyl nitrite (CH₃ONO) in synthetic air using the fluorescent lamps. NO was included in the reactant mixtures to suppress the formation of O₃ and, hence, of NO₃ radicals. The kinetic measurements were performed relative to cyclohexane. The approximate initial reactant concentrations (molecule cm⁻³) were as follows: CH₃ONO, 4.1 × 10¹⁴; NO, 4.1 × 10¹⁴; 1-butanol, 3.4×10^{14} ; and cyclohexane, 9.3×10^{13} . The concentration–time behavior of 1-butanol and cyclohexane were monitored over a 10-20 min irradiation period by in situ FTIR long path spectroscopy. The FTIR spectrometer (Nicolet Magna 520) was operated with a resolution of 1 cm⁻¹.

A few experiments using 1-butanol/cyclohexane/air mixtures (i.e., without OH precursor) were also carried out (i) in the dark and (ii) at maximum light intensity over a period of 60 min to check for complications associated with adsorption on the wall or photolysis of these compounds; no such complications were observed.

All chemicals used (1-butanol, cyclohexane, and NO) had a stated manufacturer purity of >99%. Methyl nitrite was prepared and stored as described in the literature (11).

2.2. Products of the Reaction of OH Radicals with 1-Butanol. All product investigations were performed in the European Photoreactor (EUPHORE), a large-volume outdoor smog chamber which is part of the Centro de Estudios Ambientales del Mediterraneo (CEAM) in Valencia, Spain.

The facility consists of two identical half-spherical fluorine-ethene-propene (FEP) foil chambers mounted on aluminum floor panels covered with FEP foil. The FEP foil transmits 85–90% of the light with wavelengths from >500 to 320 nm, dropping to 75% transmission at the atmospheric threshold of 290 nm. To avoid unwanted heating of the chambers, the floor panels are connected to a cooling system allowing for realistic atmospheric temperature conditions to be maintained, even during extended irradiation periods.

The chamber used for the experiments described here had a volume of about 195 m³ and two mixing fans to ensure homogeneity of the reaction mixtures. An air-drying and purification system supplied the chamber with oil vapor, hydrocarbon and NO_y -free dry air. The solar light intensity was measured in the chamber with a spectral radiantmeter (scanning double monochromator Bentham TM300). Filterband radiometers (Meteorologie Consult, Glashütten) were used to measure the photolysis frequencies of $J(O^1D)$ and $J(NO_2)$ during the days of the experiments.

1-Butanol was added to the chamber by gently heating the required amount of the substance in a stream of air entering the chamber. OH radicals were produced by the photolysis of nitrous acid (HONO), also introduced into the chamber in an air stream. HONO was prepared by dropwise addition of 15 mL of an aqueous 1% NaNO2 solution to 30 mL of a 30% sulfuric acid solution at room temperature. After allowing for the mixing of the reactants, photo-oxidation was initiated by opening the light-tight protective housing of the chamber and exposing the photoreactor contents to sunlight. The initial concentrations of 1-butanol and HONO were approximately 1.5×10^{13} and 1.8×10^{12} molecule cm⁻³, respectively. The initial concentrations of NO and NO2 were both approximately $1.8{-}2.3\times10^{12}\,\text{molecule cm}^{-3}$ and their final concentrations were 2.6 \times 10 11 and 3.5 \times 10 12 molecule cm⁻³, respectively.

An FTIR spectrometer (NICOLET Magna 550, MCT detector; 1 cm⁻¹ resolution) coupled to a White mirror system (base length, 8.17 m; total optical path length, 554.5 m) was used to monitor HCHO, HONO, and SF₆. The absorption cross-sections for the compounds used for the evaluation of the FTIR spectra were determined in separate calibration studies.

Because the FTIR technique was found to be unsuitable for the quantitative detection of 1-butanol, butanal, propanal, and ethanal, these compounds were analyzed by gas chromatography combined with photoionization detection (GC– PID). Gas samples were automatically collected from the chamber every 10 min and introduced via a heated sampling loop of 2 mL capacity onto a DB624 column at 80 °C (J & W Scientific; 30 m) mounted in a Fisons GC 8000 instrument. The GC–PID response factors for the alcohol and the products were determined by introducing known concentrations of these compounds into the chamber. This technique allowed for the determination of the higher aldehydes, with an error of $\pm 15-20\%$.

In addition, carbonyl compounds were sampled from the chamber using solid-phase 2,4-dinitrophenyl hydrazone (DNPH)-silica cartridges. Hydrazones, formed by derivatization, were separated and quantitatively measured by HPLC (Hewlett-Packard model 1050; UV detector).

NO and NO₂ were measured by two NO_x analyzers equipped with a molybdenum converter (Monitor Labs. Inc., ML 9841 A) and a photolytical converter (Eco Physics, CLD 770 AL with PLC 760), respectively.

To determine the dilution rate of the chamber, due to small leaks in the FEP foil, 3.7×10^{11} molecule cm⁻³ of SF₆ were added, as an inert tracer, to the reaction mixture. In the experiments presented here, the chamber leak rate was about 3% h⁻¹.

2.3. Computer Simulation System. All computer simulations were carried out using the box model SBOX by Stockwell et al. (*12*). This FORTRAN program incorporating the Gear algorithm (*13*) was operated on an SGI Octane running under IRIX 6.5. The program used the public domain library VODE (*14*) to integrate the ordinary differential equations.

3. Results and Discussion

3.1. Rate Coefficient for the Reaction of OH with 1-Butanol. Test experiments on 1-butanol/cyclohexane/air mixtures in the 480 L indoor reactor showed that losses of the compounds to the wall or via photolysis were <3% for both processes over a 60 min period. Compared to the measured decays for the compounds during the kinetic experiments, contributions from wall loss and photolysis were negligible.

The kinetic investigations were performed by irradiation of CH₃ONO/NO/1-butanol/cyclohexane/air mixtures. Figure 1 illustrates the kinetic data obtained from three experiments plotted according to eq 1. An excellent straight line plot is obtained. Least-squares analysis of these data led to the rate coefficient ratio $k_1/k_2 = 1.10 \pm 0.02 (\pm 2\sigma)$, which was then put on an absolute basis using a value of k_2 (OH + cyclohexane) = 7.49×10^{-12} cm³ s⁻¹ at 298 K (*2*). This resulted in a rate coefficient for the reaction of OH with 1-butanol of $k_1 = (8.24 \pm 0.84) \times 10^{-12}$ cm³ s⁻¹. The indicated error contains an additional 10% uncertainty due to the potential systematic errors associated with the value of the reference rate coefficient.

The value of the rate coefficient measured in the present study can be compared with previous room temperature determinations reported in the literature (*15*–*17*). Using an absolute technique, Wallington and Kurylo (*15*) obtained k(OH + 1-butanol) = (8.31 ± 0.63) × 10⁻¹² cm³ s⁻¹. Nelson et al. (*16*) have reported values of k(OH + 1-butanol) = (7.80 ± 0.20) × 10⁻¹² and (8.56 ± 0.70) × 10⁻¹² cm³ s⁻¹, using absolute and relative techniques, respectively. A unit-



FIGURE 1. Plot of eq 1 for the gas-phase reaction of OH radicals with 1-butanol, using cyclohexane as reference compound.

weighted least-squares average of these three rate coefficients leads to the recommendation of k(OH + 1-butanol) =8.57 × 10⁻¹² cm³ s⁻¹ given by Atkinson (*2*). Very recently, Yujing and Mellouki (*17*) determined a value of (8.47 ± 0.34) × 10⁻¹² cm³ s⁻¹ from an absolute rate technique experiment. The value obtained here is in excellent agreement with all previous determinations.

The Structure-Activity Relationship (SAR) method of Kwok and Atkinson (18) predicts k(OH + 1-butanol) = $6.9 imes 10^{-12} \, \mathrm{cm^3 \, s^{-1}}$ at 298 K, which is in fair agreement with the experimental findings. The discrepancy between calculated and measured rate coefficient presumably indicates that the OH substituent group has a more significant effect on the -CH₂- groups than that assumed in the estimation method. This has been confirmed in a very recent SAR study by Bethel et al. (19), who calculated new substitution factors for hydroxy compounds such as 1-butanol. The updated approach yields $\hat{k}(OH + 1\text{-butanol}) = 7.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, which is fairly close to the experimental value. The rate coefficient k_1 can be combined with the estimated ambient tropospheric OH concentration (20) of 1.0×10^6 molecule cm⁻³ (24 h average) to obtain a tropospheric lifetime of 1.4 days for 1-butanol due to gas-phase reaction with OH radicals.

3.2. Products of the OH Radical Reaction with 1-Butanol. GC–PID and HPLC analysis of the products formed in the irradiation of HONO/1-butanol/air mixtures in the EUPHORE photoreactor facility showed the formation of butanal, propanal, ethanal, and formaldehyde among the products. These products have been quantified by GC–PID and HPLC response factors (except formaldehyde, which was measured by FTIR) determined from calibrations with authentic standards.

In addition, a product eluted at or very close to the retention time of 4-hydroxy-2-butanone. Because the HPLC retention time of this product closely matches that of an authentic standard of 4-hydroxy-2-butanone, it is believed that this product is 4-hydroxy-2-butanone. The HPLC response factor, HPLC peak area/concentration, used to quantify this product was obtained using an authentic standard.

Propanal, ethanal, and HCHO might also be formed in secondary reactions of some of the primary aldehydic products. However, under the conditions employed in the experiments, the contribution from secondary reactions is very minor. The initial NO_x concentration is fairly high, with



FIGURE 2. Plot of the aldehyde yields (\bigcirc) uncorrected and (O) corrected for the photolysis and reaction with OH radicals (see text) versus the amount of 1-butanol consumed for (a) butanal, (b) propanal, and (c) ethanal.

an NO/NO_2 ratio of about 1. Because the NO concentration is rapidly decreasing after opening the chamber, the main fate of the alkyl peroxy radicals, formed in the degradation reactions of the higher aldehydes, will be formation of the corresponding stable acyl peroxynitrate and not a lower aldehyde.

To derive the formation yields of the aldehydic products, their measured concentrations had to be corrected for further reaction with OH radicals, photolysis, and dilution losses. Corrections have been performed using the mathematical procedure described by Tuazon et al. (*21*) and described in a previous study from this laboratory (*22*).

The OH radical concentration was calculated from the decay of the alcohol using the rate coefficient for k_1 (OH + 1-butanol) determined in this study, and the dilution rate coefficients were determined for each experiment as previously described. Rate coefficients for reaction of OH radicals with the aldehydic products were taken from the literature (*23, 24*). The following values of k_{OH} (in units of 10^{-11} cm³ s⁻¹) were used: butanal, 2.47 ± 0.15 (*23*); propanal, 2.02 ± 0.14 (*23*); and ethanal, 1.22 ± 0.27 (*24*).

Photolysis frequencies for the photolysis of the aldehydes $k_{h\nu}$ were taken from the literature (*25*). The mean of $J(NO_2)$, measured during the experiments, was used as an indicator of the light intensity in order to select the frequencies. The following values of $k_{h\nu}$ (in units of 10^{-5} s⁻¹) were calculated relative to $J(NO_2)$ and employed in the present study: butanal, 1.26; propanal, 1.12; and ethanal, 0.23.

TABLE 1. Product Formation Yields from the Gas-Phase Reaction of the OH Radical with 1-Butanol in the Presence of NO_x

product	formation yield ^a
butanal	0.518 ± 0.071
propanal	0.234 ± 0.035
ethanal	0.127 ± 0.022
formaldehyde ^b	0.434 ± 0.024
4-hydroxy-2-butanone ^b	0.05 ± 0.01
organic nitrates	≤0.04
carbon yield	\leq 0.92 \pm 0.16

^a Corrected for photolysis and reaction with OH radicals as described in the text. Indicated errors are two least-squares standard deviations of the data shown in Figure 2 combined with overall uncertainties in the alcohol and carbonyl GC–PID calibration factors of $\pm 10\%$ and $\pm 5\%$, respectively. Additional uncertainties in the formation yields due to uncertainties in the multiplicative correction factor *F* (see text) are $\pm 2\%$ for the formation of butanal, ± 10 for the formation of propanal, and $\pm 13\%$ for the formation of ethanal. ^b Uncorrected formation yields, derived in the early stage of the reaction; indicated error limits are two standard deviations.

The correction factors, $[RHO]_t^{corr}/[RHO]_t$ were ≤ 1.5 for butanal, ≤ 1.3 for propanal, and ≤ 1.1 for ethanal. The estimated overall uncertainties in the OH reaction rate coefficient of 1-butanol and in the rate coefficients for reaction with OH and photolysis of the products lead to maximum uncertainties in the correction factors of $\pm 8\%$ for the formation of butanal, $\pm 10\%$ for the formation of propanal, and $\pm 13\%$ for the formation of ethanal.

The corrected aldehydes concentrations are plotted against the amount of 1-butanol consumed in Figure 2.

The corrected values for the formation yields are given in Table 1. The molar formation yield of 0.434 ± 0.024 given for HCHO was derived from the uncorrected concentrations plotted against the consumption of 1-butanol in the early stage of the reaction, when secondary processes can largely be neglected. Similarly, the value of 0.05 ± 0.01 indicated for 4-hydroxy-2-butanone represents its semiquantitative molar formation yield obtained by plotting the uncorrected HPLC concentrations of 4-hydroxy-2-butanone against the amounts of 1-butanol consumed in the early stages of the reaction.

In summary, the carbonyl and the hydroxycarbonyl products observed and quantified in this work account for $92 \pm 16\%$ C of the overall OH radical reaction with 1-butanol.

3.3. Mechanistic Considerations Based on SAR and the Product Yield Data. The reaction of OH with 1-butanol proceeds by H-atom abstraction from the various -CH₃, CH_2 , and -OH groups. Using the SAR technique (18), it can be estimated that the relative importance of OH attack at the various -CH₃, -CH₂-, and -OH groups of 1-butanol is the following: from the -OH group, 2.4%; from the -CH₂group at the β position, 58.3%; from the $-CH_2$ - group at the β position, 20.4%; from the $-CH_2-$ group at the γ position, 16.5%; and from the -CH₃ group, 2.4%. Very recently, Bethel et al. (19) updated the SAR parameters. The new substitution factors reported by these authors lead to probabilities for the OH attack at the OH group and the α , β , γ , and δ positions of 2.2%, 42.7%, 38.3%, 14.7%, and 2.2%, respectively. In particular, the values for the β and γ attack are significantly different to those predicted by the former set of parameters developed by Kwok and Atkinson (18).

The α -hydroxy alkyl radical, formed by H-atom abstraction from the $-CH_2-$ group at the 1-position, reacts with O_2 to form butanal in unit yield (2)

$$CH_3CH_2CH_2C(*)HOH + O_2 \rightarrow CH_3CH_2CH_2CHO + HO_2$$
(R3)

The hydroxy alkyl radicals formed after H-atom abstraction from the $-CH_2-$ group at the β and γ positions will add O₂ to form hydroxy alkyl peroxy radicals, which can react with NO or NO₂. Addition of NO₂ will form thermally labile hydroxy alkyl peroxy nitrates. In the presence of NO, the hydroxy alkyl peroxy radicals form hydroxy alkyl nitrate and hydroxy alkoxy radicals plus NO₂.

The contribution of the channel forming organic nitrates in these RO₂·+NO reactions is considered to be small (\leq 4%). This value was derived from the yield of butyl nitrates, 0.077 ± 0.009 (*26*), obtained in the irradiation of CH₃ONO/ NO/*n*-butane/air mixtures. The results of previous studies (*27–29*) suggest that hydroxy butyl nitrate formation yields from the reaction of hydroxy butyl peroxy radicals with NO is a factor of ~2 lower than the butyl nitrate formation yields from the OH reaction with *n*-butane in the presence of NO.

The further expected reactions of the alkoxy radicals are outlined in Scheme 1. In this reaction scheme, the alkyl and alkyl peroxy radicals have been omitted for clarity, and only the reactions of the alkoxy and acyl radicals involved are shown (the given branching ratios refer to the box model calculations described in the following paragraphs).

The β -hydroxy alkoxy radical (I) formed after the H-atom abstraction from the $-CH_2-$ group at the β position can react with O₂ to form 4-hydroxy-3-butanone (II) or decompose to propanal and HCHO (via reaction of CH₂OH (III) with O₂). Isomerization by a 1,5-H shift via a six-membered transition state cannot occur for this β -hydroxy alkoxy radical. Furthermore, isomerizations by a 1,4-H shift via a five-membered transition state are expected to be 3–4 orders of magnitude slower at 296 K than 1,5-H shift isomerizations (*30*) because of the higher ring strain involved and are, therefore, considered to be of negligible importance.

Literature estimates (31) of the enthalpy for the decomposition ($\Delta H_d = 3.3 \text{ kJ mol}^{-1}$) and reaction with O₂ ($\Delta H_{O_2} =$ 1423.7 kJ mol⁻¹) of this β -hydroxy alkoxy radical (I) can be used to predict the relative importance of the two reaction pathways using the empirical estimation method of Atkinson and Carter (32). This approach assumes that a correlation exists between the thermochemical behavior of these reactions and the rate constants for alkoxy radical decomposition and reaction with O₂; in particular, decomposition dominates whenever $\Delta(\Delta H) = (\Delta H_d - \Delta H_{O_2}) < 163$ kJ mol⁻¹, while the O_2 reaction normally dominates for $\Delta(\Delta H) > 184 \text{ kJ mol}^{-1}$. Thus, on the basis of the previously reported heats of reaction for decomposition and O_2 reaction and using the Atkinson estimation method (33), the decomposition of I is calculated to dominate over the reaction with oxygen with a decomposition rate $k_{\rm d}$ of 1.1×10^5 s⁻¹ at 298 K compared to an O₂ reaction rate $k_{O_2}[O_2]$ of 4.1 × 10⁴ s⁻¹.

The identification among the degradation products of propanal in a molar formation yield of 0.234 ± 0.035 clearly supports that the decomposition channel is the main fate of the β -hydroxy butoxy radical (**I**), which is calculated to account for ~20% of the overall reaction of 1-butanol with OH radicals. The present results are in good agreement with the experimental data of previous studies on the degradation mechanism of 1-butene (*28, 34*) (note that CH₃CH₂CH-(O')CH₂OH is also formed by OH radical addition to 1-butene), which showed that the sole fate of **I** was decomposition. The present results are also consistent with the literature estimations (*32*) of the decomposition and O₂ reaction rate constants for **I**.

The possible reaction sequences for the γ -hydroxy alkoxy radical (**IV**) formed after the H-atom abstraction from the $-CH_2-$ group at the γ position are also shown in Scheme 1.

The present GC–PID and HPLC product data show that ethanal is formed with a yield of 12.7 \pm 2.2%. Ethanal is expected to be formed from the decomposition of (IV). The 'CH₂CH₂OH radical (V), formed as "coproduct", undergoes

SCHEME 1. Reaction Scheme for the OH-Initiated Oxidation of 1-Butanol in the Presence of NO_x Developed on the Basis of the Present Smog Chamber Studies^a



^a The stated branching ratios were obtained by fitting the chemical model to experimental concentration-time profiles (see text).

addition of O_2 and reaction with NO to form the corresponding alkoxy radical, which subsequently decomposes (82%) to form HCHO and reacts with O_2 to form glycolaldehyde (**VI**) (18%) (35). While HCHO was identified by GC– PID, HPLC and FTIR, glycoladehyde was not observed with any of these analytical techniques, indicating that its yield must be very low, as expected.

The other decomposition channel involving $C_{\gamma}-C_{\delta}$ scission would produce 3-hydroxy propanal (VII) and a CH₃[•] radical. However, this channel is considered to be of minor importance because no clear evidence for 3-hydroxy propanal formation could be obtained from the product analysis. Furthermore, because of the greater stability of •CH₂CH₂OH (**V**) compared to CH₃• (*36*, *37*), the channel leading to ethanal and •CH₂CH₂OH is predicted to be dominant.

On the basis of the experimental ratio k_d/k_{O_2} [O₂] ≈ 2.6 as derived from the molar formation yields of the products arising from the two reaction channels, the reaction of the γ -hydroxy butoxy radical (**IV**) with O₂ to form 4-hydroxy-2-butanone would appear to be much less important than decomposition. A similar observation was made in a previous study in this laboratory (*22*) on the γ -hydroxy pentoxy radical.

The δ -hydroxy alkoxy radical, 'OCH₂CH₂CH₂CH₂OH (**VIII**), formed after the H-atom abstraction from the $-CH_3$ group, is only of marginal importance in the atmospheric OH initiated degradation mechanism of 1-butanol, accounting for only an estimated 2.2% (SAR estimation (*19*)) of the overall reaction. The possible products of the alkoxy radical reactions could not be identified in the present study, presumably because of their very low concentrations.

3.4. Chemical Modeling. To confirm the experimental findings on the OH-initiated degradation of 1-butanol, computer simulations using a simple box model were performed on the basis of the oxidation scheme described previously and illustrated in Scheme 1. The branching ratios for the OH attack to 1-butanol as well as the reactions of the alkoxy radicals I and IV given in Scheme 1 and Table 2 were obtained by fitting the model to the experimental concen-

tration-time profiles for 1-butanol, butanal, propanal, ethanal, HCHO, NO, and ozone.

The reactions describing the inorganic chemistry of the system as well as the photolysis reactions for NO₂, O₃, HONO, HNO₃, HNO₄, NO₃, H₂O₂, and formaldehyde were taken from the Regional Atmospheric Chemical mechanism (RACM) of Stockwell et al. (*12*), which is widely used to model the chemistry occurring in urban air. The NO₂ photolysis frequency was taken from the filterband radiometer measurements in EUPHORE. All other photolysis frequencies, except those for ethanal, propanal, and butanal, were evaluated relative to J_{NO_2} using the algorithm of Madronich (*38*). For the evaluation, the radiation data were used as described by Stockwell et al. (*12*) for the RACM mechanism, except those for the higher aldehydes which were taken from an EUPHORE study performed by Moortgat (*25*).

The reactions used for the description of the OH-initiated degradation of 1-butanol are summarized in Table 2. Unknown rate coefficients in the mechanism were set to values for similar reactions taken from established literature data (e.g., the evaluations of DeMore et al. (39) and Atkinson et al. (40). The rate coefficients for the reactions of the four different alkyl radicals with O_2 were set to $1\times 10^{-11}\,\text{cm}^3\,\text{s}^{-1},$ while for the alkylperoxy + NO reactions forming the corresponding alkoxy radicals I, IV, and VIII, a k value of $7.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ was used. Here, an additional nitrate formation fraction of 2% was considered for each reaction (see Section 3.3.). The rate coefficients for the alkoxy $+ O_2$ reactions were all set to 8×10^{-15} cm³ s⁻¹. The first-order decay constants for the other alkoxy reaction pathways were calculated with respect to this value considering the branching ratios given in Scheme 1. For the further degradation of CH₃, CH₂OH (III) and CH₂CH₂OH (V) radicals, wellestablished literature data (39, 40) were incorporated into the model. The OH-initiated oxidation of butanal, propanal, and ethanal was also explicitly treated in the simulations. Besides the rate coefficients for the OH reactions discussed previously, mechanistic and rate data recommended by

TABLE 2. Chemical Mechanism for the OH-Initiated Oxidation of 1-Butanol in the Presence of NO_x Used for the Computer Simulations in the Present Work^a

no.	reaction			<i>k</i> (298 К) ^b	ref
R4 R5	OH + 1-butanol α -alkyl + O_2	\rightarrow	0.55 $\alpha\text{-alkyl}$ + 0.25 $\beta\text{-alkyl}$ + 0.17 $\gamma\text{-alkyl}$ + 0.03 $\delta\text{-alkyl}$ + H2O 1-butanal + HO2	$\begin{array}{l} 8.28 \times 10^{-12} \\ 1 \times 10^{-11} \end{array}$	c d
R6 R7 R8 R9 R10	$ \begin{split} \beta\text{-alkyl} + \text{O}_2 \\ \text{CH}_3\text{CH}_2\text{C}(\text{OO}\bullet)\text{CH}_2\text{OH} + \text{NO} \\ \text{I} \\ \text{I} + \text{O}_2 \\ \text{III} + \text{O}_2 \end{split} $	$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$	β -Alkyl Chemistry CH ₃ CH ₂ C(OO•)CH ₂ OH I + NO ₂ propanal + III II + HO ₂ HCHO + HO ₂	$\begin{array}{l} 1 \times 10^{-11} \\ 7.5 \times 10^{-12} \\ 7.4 \times 10^5 \\ 8 \times 10^{-15} \\ 9.1 \times 10^{-12} \end{array}$	d d c d 39
R11 R12 R13 R14 R15 R16 R17 R18 R19 R20 R21 R22	$\begin{array}{l} \gamma \text{-alkyl} + O_2 \\ CH_3C(OO\bullet)CH_2CH_2OH + NO \\ IV + O_2 \\ IV \\ V + O_2 \\ CH_2(OO\bullet)CH_2OH + NO \\ CH_2(O\bullet)CH_2OH + O_2 \\ CH_2(O\bullet)CH_2OH \\ IV \\ \bullet CH3 + O_2 \\ CH_3 OO\bullet + NO \\ CH_3O\bullet + O_2 \end{array}$	1 1 1 1 1 1 1 1 1 1 1 1	γ -Alkyl Chemistry CH ₃ C(OO·)CH ₂ CH ₂ OH IV + NO ₂ 4-hydroxy-2-butanone + HO ₂ ethanal + V CH ₂ (OO·)CH ₂ OH CH ₂ (O·)CH ₂ OH + NO ₂ HOCH ₂ CHO + HO ₂ HCHO + III VII + •CH ₃ CH ₃ O• CH ₃ O• CH ₃ O• CH ₃ O• + NO ₂ HCHO + HO ₂	$\begin{array}{c} 1 \times 10^{-11} \\ 7.5 \times 10^{-12} \\ 8 \times 10^{-15} \\ 3.3 \times 10^5 \\ 1 \times 10^{-11} \\ 9 \times 10^{-12} \\ 8 \times 10^{-15} \\ 1.8 \times 10^5 \\ 1.9 \times 10^4 \\ 3 \times 10^{-16} \\ 7.7 \times 10^{-12} \\ 1.9 \times 10^{-15} \end{array}$	d d c d 35 c 39 39 39
R23 R24 R25	$\begin{array}{l} \delta\text{-alkyl} + O_2\\ CH_2(OO\bullet)CH_2CH_2CH_2OH + NO\\ \textbf{VIII} + O_2 \end{array}$	\rightarrow \rightarrow \rightarrow	δ -Alkyl Chemistry CH ₂ (OO•)CH ₂ CH ₂ CH ₂ OH VIII + NO ₂ HO(CH ₂) ₃ CHO + HO ₂	1×10^{-11} 7.5×10^{-12} 8×10^{-15}	d d d
R26 R27 R28 R29 R30 R31 R32 R33 R34 R35 R36 R37 R38 R39	$\begin{array}{l} OH + HCHO (+ O_2) \\ OH + ethanal (+ O_2) \\ CH_3C(OO\bullet)O + NO \\ CH_3C(OO\bullet)O + NO_2 \\ OH + propanal (+ O_2) \\ CH_3CH_2C(OO\bullet)O + NO \\ CH_3CH_2\bullet + O_2 \\ CH_3CH_2OO\bullet + NO \\ CH_3CH_2OO\bullet + NO \\ CH_3CH_2O\bullet + O_2 \\ CH_3CH_2O\bullet + O_2 \\ CH_3CH_2C(OO\bullet)O + NO_2 \\ OH + 1-butanal (+ O_2) \\ CH_3CH_2CH_2C(OO\bullet)O + NO \\ CH_3CH_2CH_2CO\bullet + O_2 \\ CH_3CH_2CH_2C(OO\bullet)O + NO \\ CH_3CH_2CH_2CO\bullet + O_2 \\ CH_3CH_2CH_2O\bullet + O_2 \\ CH_3CH_2CC(OO\bullet)O + NO_2 \end{array}$	1 1 1 1 1 1 1 1 1 1 1 1 1	$\begin{array}{l} \textbf{OH} + \textbf{Aldehyde Chemistry} \\ \textbf{CO} + \textbf{HO}_2 + \textbf{H}_2 \textbf{O} \\ \textbf{CH}_3 \textbf{C}(\textbf{OO} \bullet) \textbf{O} + \textbf{H}_2 \textbf{O} \\ \bullet \textbf{CH}_3 + \textbf{NO}_2 + \textbf{CO}_2 \\ \textbf{peroxy acetyl nitrate (PAN)} \\ \textbf{CH}_3 \textbf{CH}_2 \textbf{C}(\textbf{OO} \bullet) \textbf{O} + \textbf{H}_2 \textbf{O} \\ \textbf{CH}_3 \textbf{CH}_2 \textbf{C}(\textbf{OO} \bullet) \textbf{O} + \textbf{H}_2 \textbf{O} \\ \textbf{CH}_3 \textbf{CH}_2 \bullet + \textbf{NO}_2 + \textbf{CO}_2 \\ \textbf{CH}_3 \textbf{CH}_2 \textbf{O} \bullet \\ \textbf{HO}_2 \\ \textbf{peroxy propionyl nitrate (PPN)} \\ \textbf{CH}_3 \textbf{CH}_2 \textbf{CH}_2 \textbf{C}(\textbf{OO} \bullet) \textbf{O} + \textbf{H}_2 \textbf{O} \\ \textbf{CH}_3 \textbf{CH}_2 \textbf{CH}_2 \textbf{O} \bullet \\ \textbf{NO}_2 + \textbf{CO}_2 \\ \textbf{propanal} + \textbf{HO}_2 \\ \textbf{peroxy butyryl nitrate (PBN)} \end{array}$	$\begin{array}{c} 1.0\times10^{-11}\\ 1.21\times10^{-11}\\ 2.0\times10^{-11}\\ 1.0\times10^{-11}\\ 2.0\times10^{-11}\\ 2.0\times10^{-11}\\ 8.0\times10^{-12}\\ 8.85\times10^{-12}\\ 9.95\times10^{-15}\\ 6.4\times10^{-12}\\ 2.47\times10^{-11}\\ 2.0\times10^{-11}\\ 8\times10^{-15}\\ 6.4\times10^{-12}\\ \end{array}$	39 40 44 40 39 39 44 23 40 d

^a The structures of I–VIII are illustrated in Scheme 1. ^b In cm³ s⁻¹ (second-order) and s⁻¹ (first-order). ^c This work. ^d Estimated from similar reactions (*39*, *40*).

DeMore et al. (*39*) and Atkinson et al. (*40*) were used for this purpose. The photolytic degradation schemes of these compounds were also taken from the literature (*25*). In total, the reaction scheme used for the simulations consisted of 88 elementary reactions.

It was decided to start the computer simulations 5 min after opening the chamber, because the slow opening procedure (over 3 min) was difficult to model and would have led to large uncertainties of the simulated concentration-time profiles. Accordingly, the measured concentrations for 1-butanol, HCHO, ethanal, propanal, butanal, NO_x, and O_3 at t = 5 min served as initial parameters for the calculations. Figures 3 and 4 illustrate the comparison of experimental and modeled concentration-time profiles for selected reactants for a typical run. Nearly all data are in excellent agreement, except those for NO whose experimentally obtained concentrations are slightly overestimated by the model. The reason for this disparity remains unclear. At longer reaction times, the calculated formaldehyde concentration is also slightly larger than measured in the experiment. This might be due to an unknown wall loss of HCHO or uncertainties of its photolysis frequencies used in the simulations. In particular, formaldehyde is often overestimated in the modeling of smog chamber studies (41), a known



FIGURE 3. OH-Initiated oxidation of 1-butanol; comparison of experimental and simulated concentration—time profiles for 1-butanol (\bullet), NO (\bullet), O₃ (\blacksquare), and HCHO (\bigcirc). The solid lines are the results of computer simulations (initial conditions (ppbV): 1-butanol, 591.4; NO, 56.0; NO₂, 87.0; O₃, 35.2; butanal, 6.1; propanal, 2.1; ethanal, 1.6; formaldehyde, 3.4; 760 Torr air; 294 K).



FIGURE 4. OH-Initiated oxidation of 1-butanol; comparison of experimental and simulated concentration—time profiles for butanal (■), propanal (♦), and ethanal (●). The solid lines are the results of computer simulations (initial conditions: see Figure 3).

problem which could also not be solved in the present study. However, in this work the disparity between modeled and measured HCHO concentration was always less than 20%. NO_2 has not been plotted, because there was interference of the NO_2 measurements at longer reaction times by other nitrogen oxides. Accordingly, these experimental data could not be used.

In summary, the OH-initiated degradation scheme of 1-butanol in the presence of NO_x developed in the present study describes the experimental data generated in a large outdoor smog chamber well and can be used for the purposes of modeling oxidant formation in urban air masses, either in an explicit form or after suitable lumping, in chemical modules applied in chemistry transport models.

Acknowledgments

The authors thank the technical staff of CEAM for their assistance with the measurements in the EUPHORE chamber and the financial support by the "Generalitat Valenciana". F.C. gratefully acknowledges the European Commission for funding her research at the Bergische Universität Wuppertal within the framework of the Environmental and Climate Research and the Specific RTD Program. Support of the work within the 4th Framework Program (EUROSOLV) is also gratefully acknowledged.

Literature Cited

- (1) Atkinson, R. Atmos. Environ. 1990, 24, 1-41.
- (2) Atkinson, R. J. Phys. Chem. Ref. Data (Monograph No. 2) 1994, 1–216.
- (3) Lamanna, M. S.; Goldstein, J. J. Geophys. Res. 1999, 104, 21247– 21262.
- (4) Ullman's Encyclopedia of Industrial Chemistry, 5th Completely Revised edition; VCH: Weinheim, Germany, 1993; A19, pp 49– 60.
- (5) Kesselmeier, J.; Staudt, M. J. Atmos. Chem. 1991, 13, 23-88.
- (6) The European Photoreactor EUPHORE; Final report of the EC project, Contract no. EV5V-CT92-0059; Becker, K. H., Ed.; Wuppertal, Germany, 1996 (http://www.physchem. uni-wuppertal.de/PC-WWW_Site/Publications/Publications. html).
- (7) The European Photoreactor EUPHORE–Report 1997; Barnes, I., Wenger, J., Eds.; Wuppertal, Germany, 1998.

- (8) The European Photoreactor EUPHORE—2nd Report 1998–1999; Barnes, I., Brockmann, K. J., Eds.; Wuppertal, Germany, 2000 (http://www.physchem.uni-wuppertal.de/PC-WWW_Site/ Publications/Publications.html).
- (9) Barnes, I.; Becker, K. H.; Zhu, T. J. Atmos. Chem. 1993, 17, 353– 373.
- (10) Bierbach, A.; Barnes, I.; Becker, K. H.; Wiesen, E. Environ. Sci. Technol. 1994, 28, 715–729.
- (11) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fezekas, G. B.; Kozlowski, R.; Takacs, G. A. Int. J. Chem. Kinet. 1980, 12, 231– 240.
- (12) Stockwell, W. R.; Kirchner, F.; Kuhn, M.; Seefeld, S. J. Geophys. Res. 1997, 102, 25847–26879.
- (13) Gear, C. W. Numerical Initial Value Problems in Ordinary Differential Equations, Prentice Hall Series in Automatic Computation; Prentice-Hall: New York, 1971; Vol. 17.
- (14) Brown, P. N.; Byrne, G. D.; Hindmarsh, A. C. J. Sci. Stat. Comput. 1989, 10, 1038–1051.
- (15) Wallington, T. J.; Kurylo, M. J. Int. J. Chem. Kinet. 1987, 19, 1015–1023.
- (16) Nelson, L.; Rattingan, O.; Neavyn, R.; Sidebottom, H. Int. J. Chem. Kinet. 1990, 22, 1111–1126.
- (17) Yujing, M.; Mellouki, A. Chem. Phys. Lett. 2001, 333, 63-68.
- (18) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685–1695 and references therein.
- (19) Bethel, H. L.; Atkinson, R.; Arey, J. Int. J. Chem. Kinet. 2001, 33, 310–316.
- (20) Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang, J.; Alyea, F. N.; Cunnold, D. M.; Fraser, P. J.; Hartley, D. E.; Simmonds, P. G. *Science* **1995**, *269*, 187–192.
- (21) Tuazon, E. C.; MacLeod, H.; Atkinson, R.; Carter, W. P. L. Environ. Sci. Technol. 1986, 20, 383–387.
- (22) Cavalli, F.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **2000**, *34*, 4111–4116.
- (23) Papagni, C.; Arey, J.; Atkinson, R. Int. J. Chem. Kinet. 2000, 32, 79-84.
- (24) Semmes, D. H.; Ravishankara, A. R.; Gump-Perkins, C. A.; Wine, P. H. Int. J. Chem. Kinet. **1985**, *17*, 303–313.
- (25) Evaluation of Radical Sources in Atmospheric Chemistry through Chamber and Laboratory Studies (RADICAL); Final report of the EC Project, Contract no. ENV4-CT97-0419; Moortgat, G. K., Ed.; Mainz, Germany, 2000.
- (26) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. J. Phys. Chem. 1982, 86, 4563–4569.
- (27) Atkinson, R. J. Phys. Chem. Ref. Data 1997, 26, 215-290.
- (28) Atkinson, R.; Tuazon, E. C.; Carter, W. P. L. Int. J. Chem. Kinet. 1985, 17, 725–734.
- (29) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. Environ. Sci. Technol. 1995, 29, 1674–1680.
- (30) Baldwin, A. C.; Barker, J. R.; Golden, D. M.; Hendry, D. G. J. Phys. Chem. 1977, 81, 2489–2492.
- (31) Atkinson, R. Atmos. Environ. 1990, 24, 1-41.
- (32) Atkinson, R.; Carter, W. P. L. J. Atmos. Chem. 1991, 13, 195-210.
- (33) Atkinson, R. Int. J. Chem. Kinet. 1997, 29, 99-111.
- (34) Kwok, E. S. C.; Atkinson, R.; Arey, J. Environ. Sci. Technol. 1996, 30, 1048–1052.
- (35) Orlando, J. J.; Tyndall, G. S.; Blide, M.; Ferronato, C.; Wallington, T. J.; Vereecken, L.; Peeters, J. J. Phys. Chem. A 1998, 102, 8116– 8123.
- (36) McMillen, D. F.; Golden, D. M. Annu. Rev. Phys. Chem. 1982, 33, 493–532.
- (37) Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. Int. J. Chem. Kinet. 1979, 11, 147–154.
- (38) Madronich, S. J. Geophys. Res. 1987, 92, 9740-9752.
- (39) DeMore, W. B.; Sander, S.; Howard, C. J.; Ravishankara, A. R.; Golden, D. M.; Kolb, C. E.; Hanson, R. F.; Kurylo, M. J.; Molina, M. J. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation No. 12, JPL Publication 97-4, Pasadena, CA, 1997.
- (40) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. J. Phys. Chem. Ref. Data 1997, 26, 521–1011.
- (41) Sampling Device for the Measurement of Peroxy Radicals in Atmospheric Systems (SAMPLER); Final report of the EC project, Contract no. ENV4-CT97-0389; Geiger, H., Ed.; Wuppertal, Germany, 2000 (http://www.physchem.uni-wuppertal.de/PC-WWW_Site/pub/Projektberichte/SAMPLER. PDF).
- (42) Becker, K. H.; Geiger, H.; Wiesen, P. Chem. Phys. Lett. **1991**, 184, 256–261.

- (43) Taylor, P. H.; Rahman, M. S.; Arif, M.; Dellinger, B.; Marshall,
 P. Symp. (Int.) Combust., [Proc.] 1996, 26, 497–504.
- (44) Sehested, J.; Christensen, L. K.; Nielsen, O. J.; Bilde, M.; Wallington, T. J.; Schneider, W. F.; Orlando, J. J.; Tyndall, G. S. Int. J. Chem. Kinet. 1998, 30, 475–489.

Received for review September 3, 2001. Revised manuscript received December 10, 2001. Accepted December 17, 2001.

ES010220S