J. Phys. Chem. A **2007,** *111,* 12099−12105

Atmospheric Reaction of OH Radicals with 1,3-Butadiene and 4-Hydroxy-2-butenal

Torsten Berndt* and Olaf Böge

Leibniz-Institut für Troposphärenforschung e.V., Permoserstr. 15, 04318 Leipzig, Germany

Received: July 9, 2007; In Final Form: September 26, 2007

The gas-phase reaction of OH radicals with 1,3-butadiene and 4-hydroxy-2-butenal in the presence of NO has been studied in a flow tube operated at 295 ± 2 K and pressures of 950 mbar of synthetic air or 100 mbar of an O_2/He mixture. OH radicals were generated using three different experimental approaches, namely, ozonolysis of tetramethylethylene (dark reaction), photolysis of methyl nitrite, or via the reaction of HO_2 with NO (HO_2 from the reaction of H-atoms with O_2). Products of the reaction of OH radicals with 1,3-butadiene were HCHO (0.64 ± 0.08), acrolein (0.59 ± 0.06), 4-hydroxy-2-butenal (0.23 ± 0.10), furan (0.046 ± 0.014), and organic nitrates (0.06 ± 0.02) accounting for more than 90% of the reacted carbon. There was no significant dependence of product yields on experimental conditions which were varied in a wide range. The formation of the 1,4-addition product 4-hydroxy-2-butenal was confirmed unambiguously for the first time. The rate coefficient $k(\mathrm{OH} + \text{4-hydroxy-2-butenal}) = (5.1 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was determined using a relative rate technique ($p = 100$ mbar, $T = 295 \pm 2$ K). Products of the reaction of OH radicals with 4-hydroxy-2-butenal were glycolaldehyde (0.40 ± 0.06), glyoxal (0.17 ± 0.04), *trans*-butenedial (0.093 ± 0.033), and organic nitrates (0.043 ± 0.015) as well as further carbonylic substances remaining unidentified so far. Corresponding reaction mechanisms describing the formation of the detected products are proposed, and the relevance of these data for atmospheric conditions is discussed.

1. Introduction

1,3-Butadiene represents one of the most produced bulk chemicals with a worldwide, annual formation rate of 6 million tons. This substance is produced through the processing of petroleum and is mainly used in the production of synthetic elastomers (rubber and latex). An exposure to 1,3-butadiene mainly occurs in the workplace of petroleum refining including the subsequent industries. Furthermore, exposure can also occur from automobile exhaust, cigarette smoke, or polluted air especially in areas close to plastic or rubber facilities. Atmospheric mixing ratios of up to 10 ppbv have been monitored in urban areas. On the basis of human and animal studies, the EPA has classified 1,3-butadiene as a known human carcinogen.[1,2]

In the atmosphere, 1,3-butadiene degradation can be initiated by the attack of OH or NO_3 radicals, Cl-atoms, or O_3. Taking into account averaged concentrations for these reacting species and the corresponding rate coefficients, the degradation process of 1,3-butadiene is governed by the attack of OH radicals during the daytime and a tropospheric lifetime of 4 h follows for an average OH radical concentration of 10^6 molecule cm^{-3}. At night, the NO_3 radical reaction can contribute to the degradation of 1,3-butadiene, but this process works less efficiently.[3]

The knowledge concerning the first products from the reaction of OH radicals with 1,3-butadiene is relatively sparse. Computational results suggest that addition as well as H-atom abstraction are exothermic steps in which the addition of OH radicals to a terminal carbon atom of 1,3-butadiene is the most favored reaction step. The same authors did not find experimental evidence for an H-atom abstraction step as a result of MS analysis of the reaction products.[4] A LP/LIF study supported by RRKM calculations shows isomerization of initially produced β-hydroxy radicals (from photolysis of 1-iodo-3-butene-2-ol) to the thermodynamically favored α-hydroxy radicals.[5] After an equilibration time of about 10 ns, (70 ± 20)% α-hydroxy radicals and (30 ± 10)% β-hydroxy radicals were present.[5] In another experimental study investigating the kinetics of resulting peroxy radicals from the OH radical reaction with 1,3-butadiene in the presence of O_2, a good agreement between measurement and modeling was achieved assuming a ratio for 1,2-/1,4-/2,1-addition = 65/22/13.[6] (1,2-Addition denotes OH radical addition in the 1-position with subsequent O_2 addition in the 2-position.).

A few experimental studies exist in the literature describing the formation of "first-generation" stabile products from the reaction of OH radicals with 1,3-butadiene in the presence of O_2 and NO.[7−11] Consistently, the formation of HCHO, acrolein, furan, and organic nitrates is reported. Formation yields for these species show differences of up to a factor of 2 from one study to another. The formation pathways for furan are controversially discussed.[8−10] Possible precursor molecules for the furan formation considered are *cis*-4-hydroxy-2-butenal, $\cdot OCH_2CH(OH)CH{=}CH_2$ or $\cdot OCH{=}CHCH{=}CH_2$ (or isomeric $O{=}CHCH{=}CHCH_2\cdot$) radicals.[8−10] Pressure-dependent yields for HCHO and acrolein were found as a result of a flow-tube study performed at 445 and 750 Torr.[10] Up to now, the formation of 4-hydroxy-2-butenal was merely derived from mass spectrometric information including experiments with 1,3-butadiene-d_6 and the given formation yield is based on a derivatization method using response factors of structurally similar compounds.[9,11]

The subject of this investigation is product studies performed in a wide range of experimental conditions such as different approaches for OH radical generation (ozonolysis of tetramethylethylene, photolysis of methyl nitrite, or via the reaction of HO_2 with NO), variation of 1,3-butadiene consumption ($10^{11}-10^{13}$ molecule cm^{-3}), and different total pressures (100 or 950 mbar). Existing discrepancies of formation yields need

---

* Author to whom correspondence should be addressed. Fax: ++49 341 235 2325. E-mail: berndt@tropos.de.

10.1021/jp075349o CCC: \$37.00

to be clarified and an unambiguous assignment for 4-hydroxy-2-butenal is needed. The results should give a deeper insight into the mechanism of the atmospheric OH radical reaction with 1,3-butadiene, allowing an extrapolation of laboratory data to the atmosphere. These findings are also of value for the very important reaction of OH radicals with isoprene (2-methyl-1,3-butadiene).

2. Experimental Section

The experiments were carried out at a temperature of 295 ± 2 K using two flow tubes with different approaches for OH radical generation.

Flow Tube A. Flow Tube A was made of duran glass and had an i.d. of 15.0 cm and a length of 310 cm. At a pressure of 950 mbar synthetic air (20 vol % O_2 in N_2), the total flow rate was set at 5000 standard $cm^3\ min^{-1}$ resulting in a bulk residence time of 10.4 min. OH radicals were generated either via photolysis of methyl nitrite or from the reaction of O_3 with tetramethylethylene (2,3-dimethyl-2-butene). For photolysis, the tube was surrounded with four Silvania BLB lamps (nominal power 36 W, lighted section: 125 cm) emitting in the range 310−410 nm. Here, initial reactant concentrations were (unit: molecule cm^{-3}) the following: 1,3-butadiene, 1.22×10^{13}; methyl nitrite, $(4.8-9.6) \times 10^{11}$; and NO, $(1.28-10.2) \times 10^{11}$. The disappearance of 1,3-butadiene was monitored by means of long-path UV spectroscopy, and the products (acrolein and furan) were followed by on-line GC-MS measurements using daily calibrations for these substances. For fixed inlets, changing of the 1,3-butadiene conversion was achieved using different initial concentrations of methyl nitrite and NO influencing the OH concentration level in the flow tube.

In the case of ozonolysis of tetramethylethylene for initial OH radical formation (dark reaction), initial concentrations were (unit: molecule cm^{-3}) the following: O_3, $(2.1-5.5) \times 10^{11}$; tetramethylethylene, 4.8×10^{11}; 1,3-butadiene, 1.1×10^{13}; and NO, $(1.4-2.1) \times 10^{12}$. Here, changing of initial concentrations of O_3 and NO concentrations yielded the different 1,3-butadiene conversions. 1,3-Butadiene conversion initiated by O_3 caused by the low reactivity of O_3 toward 1,3-butadiene, $k(O_3 + \text{1,3-butadiene}) = 5.8 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} at 295 K, can be neglected.[12] The chosen reactant concentrations ensured that OH radicals were predominantly consumed by OH + 1,3-butadiene and formed RO_2 radicals reacted with NO. It is to be noted that a large fraction of O_3 reacted with NO. Nevertheless, ozonolysis of tetramethylethylene was rapid enough to initiate the HO_x system (OH and HO_2), and a substantial fraction of OH radicals was subsequently generated via HO_2 + NO. For O_3 formation, 100 standard $cm^3\ min^{-1}$ O_2 were flushed through an ozone generator (UVP OG-2), and the resulting O_3 concentration was monitored by UV measurements at 255 nm (Perkin-Elmer, Lambda 2) using a 10 cm gas cell. The addition of this O_3/O_2 mixture to the main gas stream including the other reactants proceeded directly at the entrance to the flow tube. Analysis of reacted 1,3-butadiene and the products was performed in the same way as for the photolysis experiments.

Flow Tube B. Flow Tube B was made of quartz glass and had a 4.0 cm i.d. and a length of 100 cm. In these experiments, the carrier gas in the reaction zone consisted of a He/O_2 mixture with 8.9−19.9 vol % He (total flow rate: 5000 standard cm^3 min^{-1}, bulk residence time: 0.7 s) and the total pressure was 100 mbar. OH radicals were produced via the following reaction sequence:

$$H + O_2 + M \rightarrow HO_2 + M \tag{1}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{2}$$

Fifty centimeters downstream of the point for the entrance of 1,3-butadiene and NO diluted in O_2, in a sidearm the needed H-atoms were generated in a microwave discharge (SAIREM GMP 03 K/SM) using a mixture of 0.01−0.02 vol % H_2 in He. Initial concentrations in the reaction zone were (unit: molecule cm^{-3}) the following: 1,3-butadiene, $(9.2-18.4) \times 10^{13}$ and NO, 2.44×10^{14}; for investigations of the product's reaction (in the absence of 1,3-butadiene) concentrations were the following: 4-hydroxy-2-butenal, $(1.6-7.6) \times 10^{13}$ and mesitylene, $(1.2-6.1) \times 10^{13}$. Either moving the microwave cavity on the sidearm (change of the initial H-atom concentration in the flow tube) or changing the reactant concentration (1,3-butadiene or 4-hydroxy-2-butenal) for constant OH radical formation yielded the variety of reactant's conversion. Here, long-path FT-IR spectroscopy and on-line GC-MS analysis served as the analytical techniques.

For gas-phase analysis, almost the whole gas stream was pumped either through a gas cell with a mirror system for UV spectroscopy (cell volume: 2.6 liter; path length: 5.28 m) or for FT-IR spectroscopy (cell volume: 2.05 liter; path length: 10.0 m). The gas cells were directly flanged on the outlet of the flow tubes in each case. UV measurements (Lambda 800, Perkin-Elmer) have been performed in the range of 190−280 nm (data spacing: 0.25 nm) with an integration time of 2 s for each data point. In the FT-IR analysis (Magna 750 with MCT detector, Nicolet), 1000−3000 spectra were recorded for averaging in the range of 4000−800 cm^{-1} (resolution: 1 or 8 cm^{-1}). Simultaneously to a spectroscopic method, on-line GC-MS runs were performed for all experiments. For it, a smaller part of the total flow was pumped continuously through a heated GC-loop coupled with a prefocusing device allowing GC-MS measurements (m/z = 45−100 amu) of organic substances for tube concentrations of $\sim 10^9$ molecule cm^{-3} (HP 6890 with separation column: HP 5MS and HP MSD 5973).

The flows were set by calibrated mass flow controllers (MKS 1259 or MKS 1179), and the pressure was measured by a capacitive manometer (Baratron).

For the determination of the rate coefficient for the reaction of OH radicals with 4-hydroxy-2-butenal, the relative rate technique was employed and mesitylene served as the reference substance. These experiments have been conducted using Flow Tube B.

$$OH + \text{4-hydroxy-2-butenal} \rightarrow \text{products} \tag{3}$$

$$OH + \text{mesitylene} \rightarrow \text{products} \tag{4}$$

From the measured signals without conversion, index “0”, and in the presence of OH radicals, no index, eq I follows:

$$\frac{k_3}{k_4} = \frac{\ln([\text{4-hydroxy-2-butenal}]_0/[\text{4-hydroxy-2-butenal}])}{\ln([\text{mesitylene}]_0/[\text{mesitylene}])} \tag{I}$$

From the ratio k_3/k_4, the desired rate coefficient k_3 follows using the literature value for k_4.[13] The concentrations of both substances were measured by means of FT-IR spectroscopy. A variation of the relative consumption of the organic substances was achieved by changing the initial concentrations of the organics and by changing the OH radical concentration according to pathways (1) and (2) (different H-atom concentration using variable H_2 contents in the gas stream for the microwave discharge).

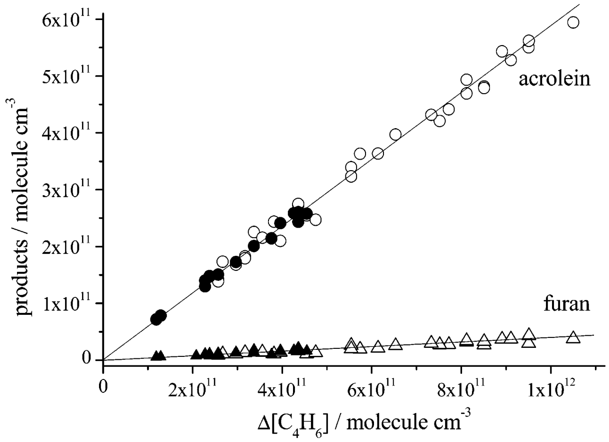


Figure 1. Concentrations of formed acrolein and furan as a function of reacted 1,3-butadiene, 950 mbar synthetic air (open symbols: photolysis of methyl nitrite for OH radicals generation, full symbols: ozonolysis of tetramethylethylene).

The gases used had stated purities as follows: He (99.999%), O_2 (99.999%), N_2 (99.999%) (Air Products), and NO (0.5 vol % mixture in N_2) (Messer Griesheim). Butadiene (>99.5%), furan (>99%), 2,3-dimethyl-2-butene (>99%), mesitylene (>99%), and acrolein (>95%) (Fluka) were used as purchased. 4-Hydroxy-2-butenal was made by hydrolysis of its diethyl acetal.[14] For this, a solution of the acetal in water/acetone was stirred at 0 °C in the presence of a sulfonic acid-based cation-exchange resin (Amberlyst 15). After filtration and concentration, the residue was extracted with methylene chloride. The organic layer was thoroughly dried over sodium sulfate and concentrated to yield 4-hydroxy-2-butenal as a colorless liquid. The needed 4-hydroxy-2-butenal diethyl acetal was synthesized via propargylaldehyde diethyl acetal,[15] which was converted to 4-hydroxy-propargylaldehyde diethyl acetal by reacting propargylaldehyde diethyl acetal with ethylmagnesium bromide followed by the addition of paraformaldehyde.[16] Reduction of 4-hydroxy-propargylaldehyde diethyl acetal with $LiAlH_4$ following the procedure of Esterbauer and Weger[16] and vacuum distillation yielded 4-hydroxy-crotonaldehyde diethyl acetal. Monomeric formaldehyde was obtained following essentially the procedure of Walker[17] except that a gentle vacuum (roughly 10 mbar) was applied in the distillation of paraformaldehyde which was dried over P_4O_{10} for at least 2 days before use. Monomeric glyoxal and monomeric glycolaldehyde were prepared according to a procedure described by Tuazon and Atkinson.[18] Methyl nitrite was synthesized as depicted by Taylor et al.[19] *trans*-Butenedial was made by hydrolysis of its bis dimethylacetal. For this, a solution of the bis dimethylacetal in water/acetone was stirred at room temperature in the presence of a sulfonic acid-based cation-exchange resin (Amberlyst-15). After filtration and concentration, the residue was extracted with methylene chloride. The organic layer was dried over sodium sulfate and concentrated afterward yielding *trans*-butenedial as yellow crystals. The bis dimethylacetal of *trans*-butenedial was synthesized by reacting furan with bromine in methanol as described by Gree et al.[20]

3. Results and Discussion

A. Products from OH + 1,3-Butadiene. First of all, the experiments were conducted at 950 mbar of synthetic air using Flow Tube A with OH radical generation either via photolysis of methyl nitrite or via the reaction of O_3 with tetramethylethylene (dark reaction). The experimental findings for the formation yields of acrolein and furan are depicted in Figure 1 (open symbols: photolysis; full symbols: ozonolysis). There were no differences in the formation yields observable applying the two different approaches for OH radical generation. That indicates that neither the irradiation in the photolysis experiments nor intermediates and products from the ozonolysis reaction influence the pathways of product formation for the desired reaction of OH radicals with 1,3-butadiene. The 1,3-butadiene conversion was held down <10%, making consecutive reactions of OH radicals with products negligible. So the functions "product concentration" versus "reacted 1,3-butadiene" show straight lines through the origin, refer to Figure 1, allowing a reliable determination of the formation yields to be 0.59 ± 0.06 for acrolein and 0.039 ± 0.011 for furan. The error limit represent two standard deviations. The O_2 content in the carrier gas was changed in a few runs of the photolysis experiments (O_2: 2 or 50 vol %, balance N_2). Under these conditions, 1,3-butadiene conversion and measured formation yields for acrolein and furan were fully in line with those obtained using synthetic air as the carrier gas.

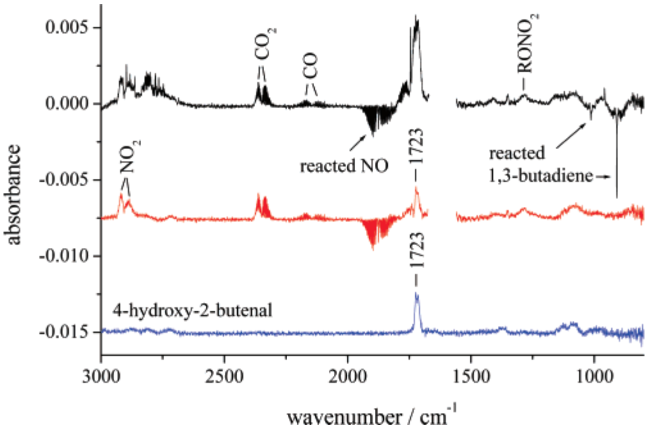


Figure 2. FT-IR analysis (resolution: 1 cm^{-1}) of a typical run at 100 mbar for the reaction OH + 1,3-butadiene. Upper part: Measured raw difference spectrum (microwave discharge: on/off). NO_2 absorptions around 1600 cm^{-1} have been omitted for more clarity. Middle part: Spectrum after addition of 1,3-butadiene reacted and subtraction of the spectra from HCHO and acrolein. Lower part: Spectrum of the reference substance 4-hydroxy-2-butenal.

As a result of online GC-MS analysis ($m/z = 45-100$ amu), there were no indications for an occurrence of further products. In UV spectra, a structureless product absorption was detected in the range 190−210 nm being attributed to acrolein, at least partly. The relatively small signal intensity did not permit a detailed product determination in this way. The sensitivity of FT-IR measurements for product determination was too low for reacted 1,3-butadiene amounts of 10^{12} molecule cm^{-3} and below.

In the next set of experiments with enhanced 1,3-butadiene conversion, Flow Tube B was chosen and operated at a pressure of 100 mbar. OH radicals have been produced via pathways (1) and (2) with H-atom formation from a microwave discharge. Product determination was performed by means of long-path FT-IR spectroscopy as well as GC-MS measurements. Figure 2 shows results from FT-IR analysis of a typical run (results from step-by-step subtraction and reference spectra are given in Supporting Information). In the upper part the difference spectrum (microwave discharge: on/off) is shown. Reacted substances appear as negative absorptions. The NO_2 absorptions around 1600 cm^{-1} have been omitted for more clarity. Formation of CO and CO_2 is due to processes occurring in the microwave discharge tube. It is difficult to decide whether CO

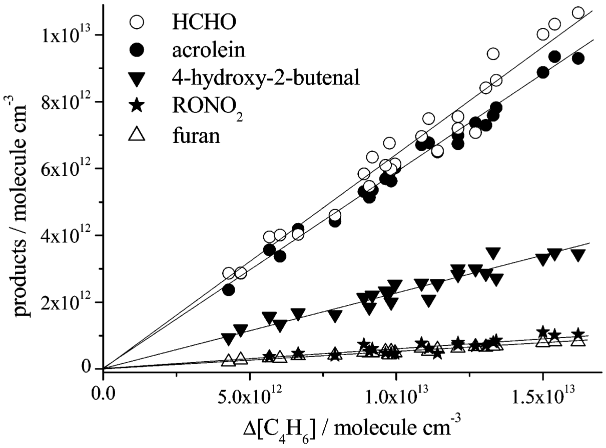


Figure 3. Concentrations of formed HCHO, acrolein, 4-hydroxy-2-butenal, organic nitrates, and furan as a function of reacted 1,3-butadiene, 100 mbar He/O_2 mixture.

and CO_2 arose partly also from the 1,3-butadiene reaction. After addition of the spectrum of 1,3-butadiene and subtraction of the spectra from HCHO and acrolein a strong absorption in the carbonyl range remained being centered at 1723 cm^{-1}, refer to the middle part in Figure 2. The position and shape of this signal are in excellent agreement with the carbonyl absorption of the reference substance 4-hydroxy-2-butenal, refer to the lower part in Figure 2. The assignment of this carbonylic species to 4-hydroxy-2-butenal is in line with the mass spectrometric information given by the Atkinson group.[9,11] The small product absorption near 1285 cm^{-1} was assigned to organic nitrates ($RONO_2$) with no further specification, and isopropyl nitrate was taken as the reference substance for quantitative determination.[10] Figure 3 shows the experimental findings from the 100 mbar runs using Flow Tube B. As for the 950 mbar experiments, the functions "product concentration" versus "reacted 1,3-butadiene" give straight lines through the origin. Resulting formation yields are (errors represent two standard deviations): HCHO, 0.64 ± 0.08; acrolein, 0.59 ± 0.05; 4-hydroxy-2-butenal, 0.23 ± 0.04; organic nitrates, 0.06 ± 0.02; furan, 0.053 ± 0.007. The 950 mbar and 100 mbar data for acrolein are in excellent agreement indicating the absence of a pressure effect in the pressure range considered. This finding is in contrast to the results of Sprengnether et al.[10] For furan, the yield at 100 mbar is somewhat higher than at 950 mbar, but the difference is within the error limits.

Furthermore, the very good agreement of furan's and acrolein's formation yield measured in Flow Tube A (residence time: ~10 min, i.d.: 15 cm) and Flow Tube B (residence time: 0.7 s, i.d.: 4 cm) points at negligible wall losses for these substances in both flow tubes. In the case of the more polar substance 4-hydroxy-2-butenal measured in Flow Tube B, a rough estimate yields an upper limit for the wall loss of ~30%. (Assuming for the diffusion-controlled wall loss: $k^{\mathrm{first}}_{\mathrm{wall}} = 4D/r^2$ and $D = 0.5$ cm^2 s^{-1}, $k^{\mathrm{first}}_{\mathrm{wall}} = 0.5$ s^{-1} follows.) Taking into account also this uncertainty caused by possible wall losses, the formation yield of 4-hydroxy-2-butenal should be given by 0.23 ± 0.10. For HCHO, negligible wall losses can be assumed in the same way as for acrolein and furan.

In Table 1, the results of this study are compiled with those available in the literature. Caused by the fact that no pressure effect was observable, average formation yields from the 100 and 950 mbar run can be given applicable to atmospheric conditions: HCHO (0.64 ± 0.08), acrolein (0.59 ± 0.06), 4-hydroxy-2-butenal (0.23 ± 0.10), organic nitrates (0.06 ± 0.02), and furan (0.046 ± 0.014). These products account for 94% of reacted carbon assuming that the organic nitrates consist of C_4 compounds. Generally, the findings of this flow-tube study are in good agreement with those of the chamber experiments from the Atkinson group.[9,11] A definite explanation for the discrepancies regarding the results from the Harvard high-pressure flow system by Sprengnether et al. cannot be given.[10]

Schemes 1−4 show proposed pathways for product formation starting from the 1,2-adduct, the 2,1-adduct, and the 1,4-adduct (*trans*- and *cis*-isomer), respectively. According to Schemes1 and 2, the 1,2- and 2,1-adducts are responsible for the formation of HCHO and acrolein being expected in equal-molar ratio. The measurements yielded a slightly higher (but not statistically significant) HCHO yield regarding acrolein pointing probably at an additional pathway for HCHO formation, see also the results of the chamber experiments of the Atkinson group.[9] Consecutive reactions of OH radicals with products under conditions of the present study are too small to explain significant HCHO formation, and it would be highly speculative to postulate an additional HCHO source. Formation of 1,2- and 2,1-adducts accounts for 60−70% of reacted 1,3-butadiene inclusive the pro-rata organic nitrates. Jenkin et al. estimated a value of 78% for the sum of both adduct yields.[6] Generation of 4-hydroxy-2-butenal is considered to proceed via the *trans*-1,4-adduct, at least mainly, see Scheme 3. The synthesis route of the reference substance was sensitive to the *trans*-isomer. The good agreement of spectral features between reaction product and reference substance points clearly at the formation of 4-hydroxy-2-butenal, and it can be assumed that the *trans*-isomer is dominant. Nevertheless, also the *cis*-1,4-adduct can yield 4-hydroxy-2-butenal in competition with furan formation, see Scheme 4. Here, the δ-hydroxy-alkoxy radical can undergo an internal H-transfer step before H-abstraction by O_2 takes place.[21] For the pathways leading to furan, no detailed information can be given. Furan yields measured in this study were not sensitive regarding experimental conditions such as total pressure, residence time, irradiation/dark reaction. From chamber experiments, a nonlinear increase of furan concentration with the extent of irradiation was reported.[9] Sprengnether et al. observed relatively low furan yields using the "wall-less" Harvard flow-system and favored cyclization of *cis*-4-hydroxy-2-butenal for furan formation.[10] All these observations together do not offer a clear insight as to how furan formation proceeds and, therefore, this question remains unresolved.

B. Kinetics of the Reaction OH + 4-Hydroxy-2-butenal. The rate coefficient of the reaction of OH radicals with 4-hydroxy-2-butenal was measured at 295 ± 2 K and a pressure of 100 mbar using Flow Tube B. The relative rate technique was chosen with mesitylene as the reference substance. Experimental findings are plotted in Figure 4 according to eq I. The slope is $k_3/k_4 = 0.89 \pm 0.12$ and the intercept 0.008 ± 0.022. Error limits given represent 2σ values. Using $k_4 = (5.73 \pm 0.53) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} ($T = 296 \pm 2$ K) from the literature,[13] $k_3 = (5.1 \pm 0.8) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} follows.

Baker et al. investigated in a chamber study of the system OH/1,3-butadiene the consecutive reaction of 4-hydroxy-2-butenal with OH radicals and derived a rate coefficient for this reaction $k_3 = (5.7 \pm 1.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 ± 2 K.[11] This value is in in excellent agreement with the data obtained in this study applying a more direct way.

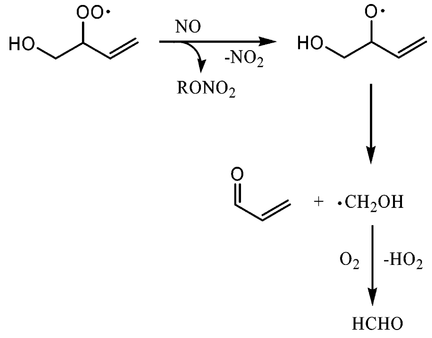
C. Products from OH + 4-Hydroxy-2-butenal. The experiments have been performed at 100 mbar using Flow Tube B with OH radical generation via pathways (1) and (2). Initial concentrations of 4-hydroxy-2-butenal were in the range $(3.0-7.6) \times 10^{13}$ molecule cm^{-3} and the reactant conversion was

TABLE 1: Formation Yields of “First-Generation” Stable Products

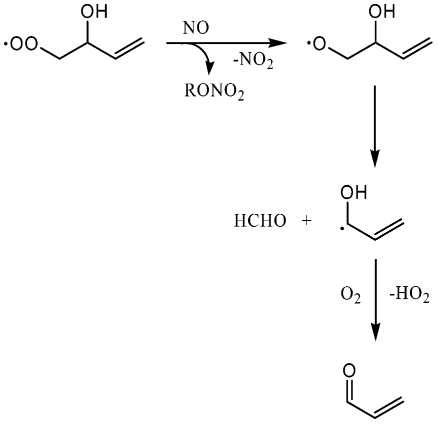
initial NO; 1,3-butadiene [molecule cm^{-3}]	T [K]	pressure [mbar]	HCHO	acrolein	4-hydroxy-2-butenal	organic nitrates	furan	ref
$(0.27-5.9) \times 10^{13}$; $(1.2-4.9) \times 10^{13}$	298 ± 2	ambient		0.98 ± 0.12				7
0; $(8.6-15) \times 10^{15}$	n.s.[a]	1013		$0.33-0.54$[b]			$0.04-0.065$[b]	8
$(1.9-2.5) \times 10^{14}$; $(5.7-25) \times 10^{13}$	298 ± 2	987	0.62 ± 0.05	0.58 ± 0.04		0.07 ± 0.03	$0.03-0.04$	9
5.0×10^{14}; 2.94×10^{15}	297 ± 3	593	0.69 ± 0.10	0.69 ± 0.07		0.11 ± 0.06	0.019 ± 0.002	10
7.8×10^{14}; 1.42×10^{15}	297 ± 3	1000	0.58	0.54		0.11	0.016	10
$(1.2-2.4) \times 10^{13}$; $(1.2-1.9) \times 10^{13}$	298 ± 2	987		0.58 ± 0.10	$0.25 + 15/-10$[c]			11
2.44×10^{14}; $(9.2-18.4) \times 10^{13}$	295 ± 2	100	0.64 ± 0.08	0.59 ± 0.05	0.23 ± 0.10	0.06 ± 0.02	0.053 ± 0.007	this study
$(1.3-21) \times 10^{11}$; $(1.1-1.2) \times 10^{13}$	295 ± 2	950		0.59 ± 0.06			0.039 ± 0.011	this study

[a] n.s.: not stated. [b] Experiments with methyl nitrite photolysis. [c] Determined indirectly, because no standard was available.

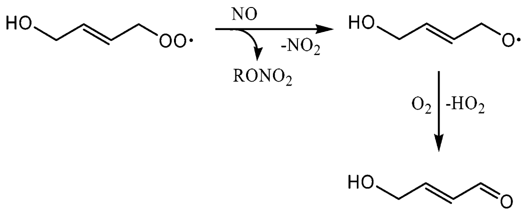
SCHEME 1: Product Formation Starting from the 1,2-Addition on 1,3-Butadiene



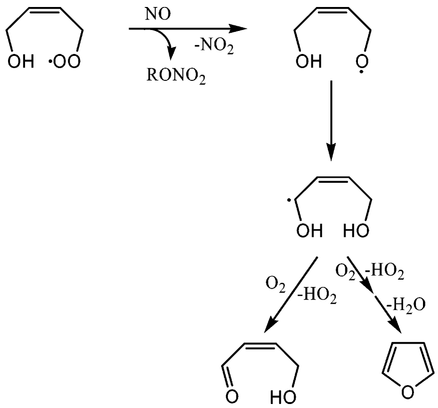
SCHEME 2: Product Formation Starting from the 2,1-Addition on 1.3-Butadiene



SCHEME 3: Product Formation Starting from the 1,4-Addition on 1,3-Butadiene (*trans*-Isomer)



SCHEME 4: Product Formation Starting from the 1,4-Addition on 1,3-Butadiene (*cis*-Isomer)



18−27%. On-line GC-MS analysis showed glycolaldehyde, glyoxal, and *trans*-butenedial as the reaction products. From FT-IR measurements, beside strong absorptions in the carbonyl range of 1700−1800 cm^{-1}, an intense signal from CO$_2$ as well as spectral features of organic nitrates were observed, see Figure 5. Reference spectra are given in Supporting Information. Reliable determination of CO$_2$ concentrations as a reaction product of 4-hydroxy-2-butenal conversion was impossible caused by the interference of CO$_2$ arising from the microwave discharge. Product yields of the reaction of OH radicals with 4-hydroxy-2-butenal measured by FT-IR were as follows (errors represent two standard deviations): glycolaldehyde, 0.40 ± 0.06; glyoxal, 0.17 ± 0.04; *trans*-butenedial, 0.093 ± 0.033; and organic nitrates, 0.043 ± 0.015. Possible uncertainties arising from wall losses have not been considered. It is to be noted that the similarity of spectral features of 4-hydroxy-2-butenal and the products glycolaldehyde, glyoxal, and *trans*-butenedial (for the applied resolution of 8 cm^{-1}) can result in systematic errors from the procedure of spectra subtraction. Furthermore, after subtraction of known products, residual bands remained in the carbonyl range, see Figure 5. That points at the formation of further carbonylic substances not identified so far. The identified substances excluding CO$_2$ account for roughly 42% of reacted carbon only.

For comparison, as a result of a very indirect approach for the determination of the glycolaldehyde yield resulting from OH + 4-hydroxy-2-butenal (starting from OH + 1,3-butadiene), a value of ∼100% is discussed.[11] This result is clearly in contradiction to the finding of the present study. Despite the mentioned uncertainties arising probably from the subtraction procedure, a glycolaldehyde yield close to 100% as a result of

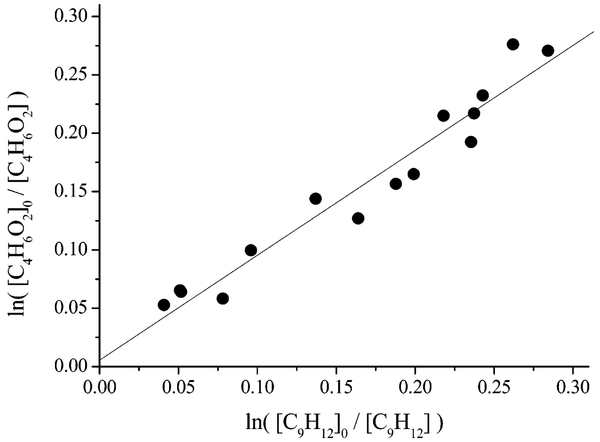


Figure 4. Plot according to eq I for the reaction of OH radicals with 4-hydroxy-2-butenal using mesitylene as the reference substance, 100 mbar He/O_2 mixture.

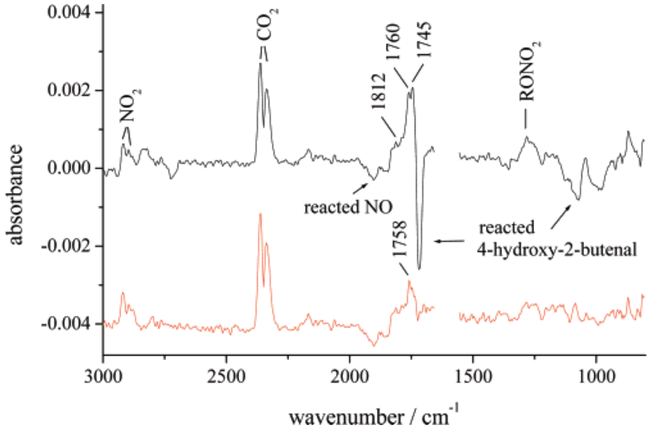
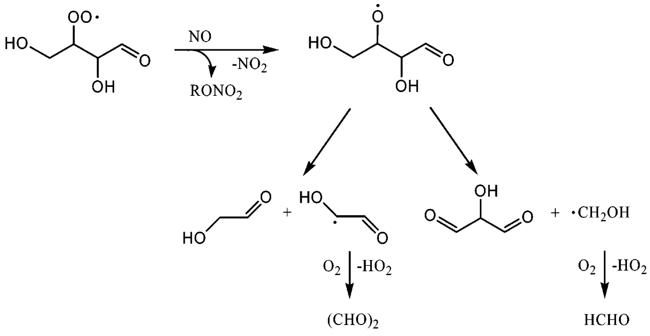
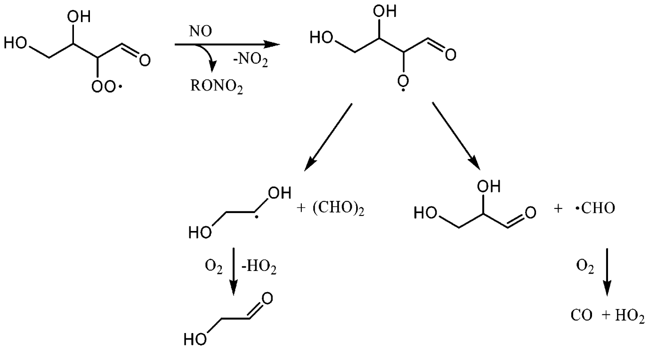


Figure 5. FT-IR analysis (resolution: 8 cm^{-1}) of a typical run for the reaction OH + 4-hydroxy-2-butenal. Upper part: Measured raw difference spectrum (microwave discharge: on/off). NO_2 absorptions around 1600 cm^{-1} have been omitted for more clarity. Lower part: Spectrum after addition of 4-hydroxy-2-butenal reacted and subtraction of the spectra from glycolaldehyde, glyoxal, and *trans*-butenedial.

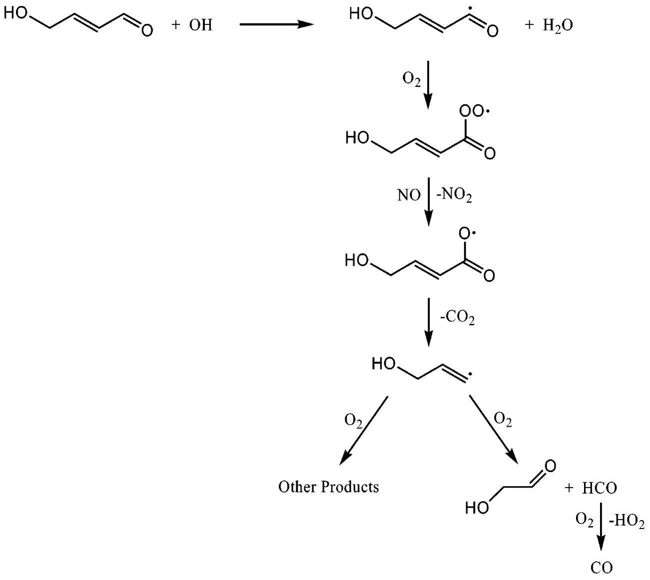
SCHEME 5: Product Formation Starting from the 2,3-Addition on 4-Hydroxy-2-butenal



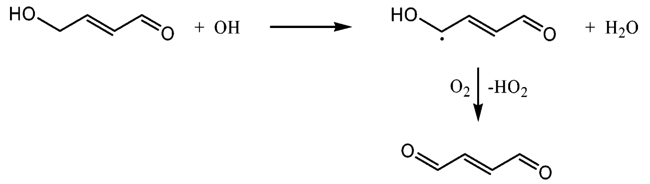
SCHEME 6: Product Formation Starting from the 3,2-Addition on 4-Hydroxy-2-butenal



SCHEME 7: Product Formation Starting from H-Abstraction from the Aldehyde Group on 4-Hydroxy-2-butenal



SCHEME 8: Formation of *trans*-Butenedial Starting from H-Abstraction from the OH-Carbon Atom on 4-Hydroxy-2-butenal



the present study seems to be impossible. Glycolaldehyde shows a strong and broad absorption around 2850 cm^{-1}, see the reference spectrum in Supporting Information. Assuming in the subtraction procedure a significant higher glycolaldehyde yield (e.g., 0.5−0.6), in the resulting spectrum negative absorptions appear in the 2850 cm^{-1} range.

Possible pathways leading to the reaction products obtained and to other potential products are depicted in Schemes 5 and 6 for addition steps as well as for the two H-abstraction steps in Schemes 7 and 8. From a structure−reactivity relationship, addition to the double bond is favored accounting for 66%, H-abstraction from the aldehyde group 29%, and H-abstraction from the OH-carbon atom 5%.[11] According to Schemes 5 and 6, β-scission of the former double bond results finally in the formation of glycolaldehyde and glyoxal in an equal-molar ratio. The observed glyoxal yield was 17 ± 4%, indicating that either the other way of β-scission forming hydroxy-malonaldehyde (Scheme 5) and glyceraldehyde (Scheme 6) is important or/and addition of OH radicals on the double bond is generally overestimated. Hydroxy-malonaldehyde and glyceraldehyde are possible candidates for explaining the carbon lack in the products detected. The stable organic product of the H-abstraction step on the aldehyde group is glycolaldehyde, see Scheme 7. In addition, also other products are possible if for the reaction of the vinyl-type radical with O_2 different channels are of importance. With a total glycolaldehyde yield of 40 ± 6% (17 ± 4% used for the addition steps), 23 ± 10% can be attributed to the H-abstraction step on the aldehyde group. This value can be taken as a lower limit for the relative importance of the OH radical attack on the aldehyde group. The only product expected from the H-abstraction step on the OH-carbon atom is *trans*-butenedial, see Scheme 8. Therefore, the *trans*-butenedial yield of 9.3 ± 3.3% stands for the relative importance of the OH radical attack on the OH-carbon atom.

4. Summary

The gas-phase reaction of OH radicals with 1,3-butadiene and 4-hydroxy-2-butenal in the presence of NO has been investigated in a flow tube at 295 ± 2 K and pressures of 950 mbar of synthetic air or 100 mbar of an O_2/He mixture. OH radicals were generated via ozonolysis of tetramethylethylene (dark reaction), photolysis of methyl nitrite, or via the reaction of HO_2 with NO (HO_2 from the reaction of H-atoms with O_2). Analysis of gaseous products has been performed by means of long-path UV or FT-IR spectroscopy as well as by on-line GC-MS measurements carried out simultaneously.

Measured products of the reaction of OH radicals with 1,3-butadiene were HCHO (0.64 ± 0.08), acrolein (0.59 ± 0.06), 4-hydroxy-2-butenal (0.23 ± 0.10), furan (0.046 ± 0.014), and organic nitrates (0.06 ± 0.02) accounting for 94% of the reacted carbon (organic nitrates are assumed to be C_4 compounds). The formation of 4-hydroxy-2-butenal was confirmed unambiguously for the first time. There was no dependence of product yields on experimental conditions which were varied in a relatively wide range, that is, consumed 1,3-butadiene, $10^{11}-10^{13}$ molecule cm^{-3}; residence time, 0.7 s to 10.4 min; and total pressure, 100−950 mbar. The lack of any dependencies should allow application of the findings of this study to the atmospheric 1,3-butadiene conversion initiated by OH radicals.

The rate coefficient of the reaction of OH radicals with 4-hydroxy-2-butenal, $k_3 = (5.1 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, was measured at 295 ± 2 K and a pressure of 100 mbar using a relative rate technique with mesitylene as the reference substance.

Identified products of the reaction of OH radicals with 4-hydroxy-2-butenal measured at 100 mbar were glycolaldehyde (0.40 ± 0.06), glyoxal (0.17 ± 0.04), *trans*-butenedial (0.093 ± 0.033), and organic nitrates (0.043 ± 0.015) as well as further carbonylic substances remaining unidentified. Possible products in addition are hydroxy-malonaldehyde and glyceraldehyde helping to fulfill the carbon balance.

Finally, this study shows that the atmospheric degradation of 1,3-butadiene initiated by OH radicals is well understood. Identified products can almost fulfill the carbon balance, and the mechanisms proposed for product formation are in line with the current understanding of atmospheric reaction pathways.

Furthermore, 1,3-butadiene represents the simplest conjugated diene and can be considered as a model substance for isoprene (2-methyl-1,3-butadiene), the major nonmethane hydrocarbon emitted globally.[23] In the isoprene/OH system, the formation of corresponding hydroxycarbonyls (like 4-hydroxy-2-butenal from the 1,3-butadiene/OH system) are proposed using mass spectrometric information.[11,22] Here, because of the complexity of hydroxycarbonyls, an unambiguous identification seems to be difficult. The finding from the simpler 1,3-butadiene/OH system can be taken as a further argument for the formation of corresponding hydroxycarbonyls from isoprene as a conclusion by analogy.

Acknowledgment. The authors thank K. Pielok and H. Macholeth for technical assistance.

Supporting Information Available: The spectra demonstrating the step-by-step subtraction procedure for the example shown in Figure 2 including all reference spectra used in this study are given. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) U.S. Department of Labor, Occupational Safety & Health Administration, www.osha.gov/SLTC/butadiene/index.html, November 2006.

(2) Cote, I. L.; Bayard, S. P. *Environ. Health Perspect.* **1990**, *86*, 149.

(3) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.

(4) Li, Z.; Nguyen, P.; de Leon, M. F.; Wang, J. H.; Han, K.; He, G. Z. *J. Phys. Chem. A* **2006**, *110*, 2698.

(5) Greenwald, E. E.; Park, J.; Anderson, K. C.; Kim, H.; Reich, B. J. E.; Miller, S. A.; Zhang, R.; North, S. W. *J. Phys. Chem. A* **2005**, *109*, 7915.

(6) Jenkin, M. E.; Boyd, A. A.; Lesclaux, R. *J. Atmos. Chem.* **1998**, *29*, 267.

(7) Maldotti, A.; Chiorboli, C.; Bignozzi, C. A.; Bartocci, C.; Carassiti, V. *Int. J. Chem. Kinet.* **1980**, *12*, 905.

(8) Ohta, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 960.

(9) Tuazon, E. C.; Alvarado, A.; Aschmann, S. M.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **1999**, *33*, 3586.

(10) Sprengnether, M.; Demerjian, K. L.; Donahue, N. M.; Anderson, J. G. *J. Geophys. Res.* **2002**, *107* (D15), ACH 8.

(11) Baker, J.; Arey, J.; Atkinson, R. *Environ. Sci. Technol.* **2005**, *39*, 4091.

(12) Treacy, J.; El Hag, M.; O'Farrell, D.; Sidebottom, H. *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 422.

(13) Kramp, F.; Paulson, S. E. *J. Phys. Chem. A* **1998**, *102*, 2685.

(14) Nadkarni, D. V.; Sayre, L. M. *Chem. Res. Toxicol.* **1995**, *8*, 284.

(15) Sheehan, J. C.; Robinson, C. A. *J. Am. Chem. Soc.* **1967**, *71*, 1436.

(16) Esterbauer, H.; Weger, W. *Monatsh. Chem.* **1967**, *98*, 1994.

(17) Walker, F. *J. Am. Chem. Soc.* **1933**, *55*, 2821.

(18) Tuazon, E. C.; Atkinson, R. *Int. J. Chem. Kinet.* **1989**, *21*, 1141.

(19) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. *Int. J. Chem. Kinet.* **1980**, *12*, 231.

(20) Gree, R.; Tourbah, H.; Carrie, R. *Tetrahedron Lett.* **1986**, *27*, 4983.

(21) Dibble, T. S. *J. Phys. Chem. A* **2002**, *106*, 6643.

(22) Zhao, J.; Zhang, R.; Fortner, E. C.; North, S. W. *J. Am. Chem. Soc.* **2004**, *126*, 2686.

(23) Guenther, A., et al. *J. Geophys. Res.* **1995**, *100* (D5), 8873.