Atmospheric Chemistry of C_3−C_6 Cycloalkanecarbaldehydes

Barbara D'Anna,*,[†,⊥] Armin Wisthaler,*,[‡,⊥] Øyvind Andreasen,[†] Armin Hansel,[‡] Jens Hjorth,[§] Niels R. Jensen,[§] Claus J. Nielsen,[†] Yngve Stenstrøm,[||] and Jyrki Viidanoja[§]

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway, Institut für Ionenphysik, Universität Innsbruck, Technikerstrasse 25, A-6020 Innsbruck, Austria, European Commission, DG − Joint Research Centre, Institute for Environment and Sustainability, Climate Change Unit, TP 290, I - 21020 Ispra (VA), Italy, and Department of Chemistry, Biotechnology and Food Science, Chemistry Section, Agricultural University of Norway, P.O. Box 5003, N-1432 Aas, Norway

Received: December 3, 2004; In Final Form: April 14, 2005

The rate coefficients for the gas phase reaction of NO_3 and OH radicals with a series of cycloalkanecarbaldehydes have been measured in purified air at 298 ± 2 K and 760 ± 10 Torr by the relative rate method using a static reactor equipped with long-path Fourier transform infrared (FT-IR) detection. The values obtained for the OH radical reactions (in units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}) were the following: cyclopropanecarbaldehyde, 2.13 ± 0.05; cyclobutanecarbaldehyde, 2.66 ± 0.06; cyclopentanecarbaldehyde, 3.27 ± 0.07; cyclohexanecarbaldehyde, 3.75 ± 0.05. The values obtained for the NO_3 radical reactions (in units of 10^{-14} cm^3 $molecule^{-1}$ s^{-1}) were the following: cyclopropanecarbaldehyde, 0.61 ± 0.04; cyclobutanecarbaldehyde, 1.99 ± 0.06; cyclopentanecarbaldehyde, 2.55 ± 0.10; cyclohexanecarbaldehyde, 3.19 ± 0.12. Furthermore, the reaction products with OH radicals have been investigated using long-path FT-IR spectroscopy and proton-transfer-reaction mass spectrometry (PTR-MS). The measured carbon balances were in the range 89−97%, and the identified products cover a wide spectrum of compounds including nitroperoxycarbonyl cycloalkanes, cycloketones, cycloalkyl nitrates, multifunctional compounds containing carbonyl, hydroxy, and nitrooxy functional groups, HCOOH, HCHO, CO, and CO_2.

1. Introduction

On a global scale, biogenic emissions of volatile organic compounds (VOCs) are estimated to dominate over those from anthropogenic sources by an order of magnitude. Monoterpenes ($C_{10}H_{16}$) represent a relevant fraction of the total biogenic nonmethane hydrocarbon emissions.[1] Due to their high reactivity, monoterpenes play a dominant role in the chemistry of the lower troposphere and the planetary boundary layer, in particular with respect to the formation of tropospheric ozone and secondary organic aerosol.[2−11]

The oxidation of monoterpene species such as α-pinene, β-pinene, Δ^3-carene, and sabinene forms multifunctional products with an aldehyde group in the β-position to the ring. Substituted cyclobutyl aldehydes (norpinonaldehyde and 2,2-dimethyl-cyclobutyl-1,3-dicarboxylaldehyde) have been identified both as primary[9,11] and as secondary[4] products of α-pinene and β-pinene gas phase degradation. The oxidation of primary products such as hydroxycaronaldehyde, caronaldehyde, and pinonaldehyde may result in the formation of substituted cyclopropane- and cyclobutanecarbaldehydes.

On the basis of the reactivity of aliphatic aldehydes[12−15] and on structure activity relationships (SARs),[16] the OH radical reaction with cycloalkanecarbaldehydes is expected to proceed mainly via H_{ald} abstraction (herein referred to as route A) and to a minor extent via H_{ring} abstraction (herein referred to as route B). In the presence of NO_x, aldehydic H abstraction will form [(nitroperoxy)carbonyl] cycloalkanes (NPCCAs) and cycloalkylperoxy radicals which will react to form cycloalkyl peroxynitrates, cyloalkyl nitrates, and cycloalkoxy radicals. The chemistry of cycloalkoxy radicals has previously been studied for cyclopentoxy and cyclohexoxy radicals.[17−25] The fate of cycloalkoxy radicals is either H abstraction to form the corresponding cycloketones or decomposition through ring opening.[17,18,20,25] Under atmospheric conditions, cyclopentoxy radicals undergo predominately ring opening with only a minor contribution from α-H abstraction by O_2, while for cyclohexoxy radicals both reaction pathways are important.[18,20,25] The main reaction products upon ring opening for both cyclopentoxy and cyclohexoxy radicals include a wide spectrum of mono- and multifunctional species containing carbonyl, hydroxy, and nitrooxy functional groups.[17,18,20,21,25]

Similar species are expected to be formed in the degradation of smaller cycloalkoxy radicals. Ring opening is expected to be the major reaction pathway due to the ring strain of cyclic compounds with less than five carbons.[25]

In the present study, the rate coefficients of OH and NO_3 radical reactions with cyclopropanecarbaldehyde, cyclobutanecarbaldehyde, cyclopentanecarbaldehyde, and cyclohexanecarbaldehyde have been determined. In addition, the gas phase reaction products of the cycloalkanecarbaldehydes with OH radicals in the presence of NO_x have been studied. The structure of the four investigated compounds is shown at the top of the respective Schemes 1−4.

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* To whom correspondence should be addressed. E-mail: barbara.danna@kjemi.uio.no (B.D'A.); armin.wisthaler@uibk.ac.at (A.W.).

[†] University of Oslo.

[‡] Universität Innsbruck.

[§] Institute for Environment and Sustainability.

[||] Agricultural University of Norway.

[⊥] These authors contributed equally to this work.

10.1021/jp044495g CCC: $30.25

2. Experimental Section

2.1. Kinetic Studies. The kinetic investigations were performed at the University of Oslo. The compounds were mixed in synthetic air at 298 ± 2 K and 760 ± 10 Torr in a 250 L electropolished stainless steel reactor equipped with a White-type multiple reflection mirror system of 120 m optical path length for on-line Fourier transform infrared (FT-IR) detection. Infrared spectra were recorded with a Bruker IFS 88 instrument employing a nominal resolution of 0.5 cm^{-1} and Harp−Genzel apodization and adding 100 scans; the time of registration was ~60 s.

NO_3 radicals were generated in situ by thermal decomposition of N_2O_5. OH radicals were generated by the photolysis of organic nitrites (2-propyl-nitrite (2-PN), 2-propyl-nitrite-d_6 (2-PN-d_6), and methyl nitrite) using two Philips TLD-08 fluorescence lamps ($\lambda_{max} \sim 370$ nm) mounted in a quartz tube and inserted into the reaction chamber as described previously by D'Anna et al.[26] The lamps were turned off during registration of the spectra. Typical initial volume fractions were 1−3 ppmV for cycloalkanecarbaldehydes and reference compounds and 5−20 ppmV for organic nitrites or N_2O_5.

NO_3 and OH reaction rate coefficients of cycloalkanecarbaldehydes were determined by the relative rate method. The method takes into account the simultaneous decay of a cycloalkanecarbaldehyde and a reference compound with the respective rate coefficients k_{ald} and k_{ref}, where k_{ref} is reliably known. Assuming that there are no other loss processes for the cycloalkanecarbaldehyde and the reference compound, the following relation holds:

$$\ln\left\{\frac{[\mathrm{ald}]_0}{[\mathrm{ald}]_t}\right\} = \frac{k_{ald}}{k_{ref}} \times \ln\left\{\frac{[\mathrm{ref}]_0}{[\mathrm{ref}]_t}\right\} \quad (1)$$

where $[\mathrm{ald}]_0$, $[\mathrm{ald}]_t$, $[\mathrm{ref}]_0$, and $[\mathrm{ref}]_t$ denote the concentrations of the cycloalkanecarbaldehyde and the reference at times zero and t, respectively. A plot of $\ln\{[\mathrm{ald}]_0/[\mathrm{ald}]_t\}$versus $\ln\{[\mathrm{ref}]_0/[\mathrm{ref}]_t\}$ yields the ratio k_{ald}/k_{ref} as the slope. The ratio between the concentrations of the cycloalkanecarbaldehydes and the reference compounds was found by spectral subtraction using reference spectra of the pure starting compounds, spectra of other compounds identified in the reaction mixture, and a linearly sloping background.

The chemical and photochemical stability of references and cycloalkanecarbaldehyde was investigated separately; the compounds showed lifetimes in the order of days and wall loss or direct photolysis could thus be neglected in the data analyses.

2.2. Product Studies. The OH−cycloalkanecarbaldehyde product studies were performed at the Institute for Environment and Sustainability (IES) in Ispra. Reactants were mixed in synthetic air at 299 ± 3 K and 740 ± 5 Torr total pressure in a 480 L cylindrical Teflon-coated evacuable glass reaction chamber. UV radiation was provided by 18 UV−vis lamps ($\lambda = 300-500$ nm with $\lambda_{max} \sim 370$ nm) surrounding the chamber.

OH radicals were generated by the photolysis of 2-PN-d_6.[26] Irradiations were carried out for about 30 min. Typical initial volume fractions for cycloalkanecarbaldehydes and 2-PN-d_6 were 1 ppmV and 2−3 ppmV, respectively. An additional 6−8 ppmV of NO was added to the reactant mixtures.

The analytical techniques used to detect the reaction products were FT-IR spectroscopy and proton-transfer-reaction mass spectrometry (PTR-MS). On-line FT-IR spectroscopy was performed using a White-type multiple reflection mirror system of a total optical path length of 81.24 m coupled to a Bruker IFS 113 V FT-IR spectrometer. FT-IR spectra were obtained by coadding 20−40 scans recorded at a 1 cm^{-1} instrumental resolution in the range from 600 to 4000 cm^{-1}. This resulted in a FT-IR time resolution of approximately 4 min. More details can be found in Ballesteros et al.[27] FT-IR spectroscopy was used to quantify CO, CO_2, and HCHO through comparison with reference spectra of pure compounds whose concentrations were determined using a nonlinear least-squares fitting procedure (NML4)[28] based on absorption coefficients from the HITRAN database.[29] Other products (e.g., individual nitrate compounds) could not be unambiguously identified by FT-IR or were below the detection limit of the instrument. CO and CO_2 yields were corrected for artifact formation observed in a "blank" experiment where only the OH precursor (2-PN-d_6) and NO were irradiated. The accuracy of CO, CO_2, and HCHO measurements is estimated to be ±30%. HCHO was above the FT-IR detection limit only in the cyclopropanecarbaldehyde study; for the higher cycloalkanecarbaldehydes, HCHO was quantified only by PTR-MS.

PTR-MS is a chemical ionization (CI) technique for on-line detection of VOCs.[30,31] A commercial PTR-MS instrument (Ionicon GmbH, Innsbruck, Austria) was interfaced to the reaction chamber through a Silcosteel capillary (inner diameter 1.02 mm, length 30 cm, temperature 70 °C, flow rate 200 mL/min). PTR-MS standard operation (E/N = 120−140 Td; E electric field strength, N buffer gas number density, 1 Td = 10^{-17} cm^2 V $molecule^{-1}$) results in extensive fragmentation of cycloalkanecarbaldehydes and their oxidation products.[32] The PTR-MS instrument was thus operated at $E/N \sim 80$ Td, shifting the maximum in the $H_3O^+(H_2O)_{n=0,1,2}$ CI reagent ion distribution from $n = 0$ to $n = 1$. The various implications of nonstandard PTR-MS operation are described in detail by De Gouw et al.[33] and Hewitt et al.[31]

CI pathways of a series of target compounds including acyclic and cyclic aldehydes, acyclic and cyclic ketones, one dialdehyde and one hydroxyaldehyde species, alkyl nitrates, and NPCCAs were investigated as part of the calibration experiments described below. With the exception of nitrooxy and nitroperoxy compounds, CI mass spectra of compounds M were dominated by MH^+ ions. Dehydration to form $[MH - H_2O]^+$ ions was observed for larger cycloalkanecarbaldehydes and for hydroxyacetaldehyde. Dehydration is expected to be a dominant CI pathway for larger hydroxy compounds.[34] $[MH + H_2O]^+$ ions were typically observed with relative abundances of <20%. Fragmentation of the carbon skeleton, which complicates the interpretation of the CI spectra, was observed as a minor route (<25%) for cyclopropanecarbaldehyde, n-butyl nitrate, and pentane-1,5-dial. Alkyl nitrates and NPCCAs gave only weak (<1%) MH^+ signals. CI mass spectra of n-propyl nitrate[35] and n-butyl nitrate were dominated by $[MH - HNO_3]^+$ ions; minor CI pathways (<30%, in total) included $[MH + H_2O - HNO_3]^+$ ion formation, nitrous acid loss to give $[MH - HNO_2]^+$ ions, fragmentation into NO_2^+ ions, and fragmentation of the carbon skeleton. Kames et al.[36] observed a similar product ion pattern for C_1-C_8 alkyl nitrates using methane CI. CI mass spectra of NPCCAs were dominated by $[MH + H_2O - HNO_3]^+$ ions; for details, see Hansel and Wisthaler.[37] Fragmentation into the respective cycloalkyl ions and cycloalkylcarboxy ions was also observed. Due to the lack of authentic standards, CI pathways of multifunctional nitrates could not be investigated. Kames et al.[36] found abundant MH^+, $[MH - HNO_2]^+$, NO_2^+, and $[MH - HNO_3]^+$ ions from methane CI of 2-nitrooxy-ethanol.

The PTR-MS instrument was calibrated for a series of target compounds by sampling known quantities of these species from the reaction chamber. C_3-C_6 cycloalkanecarbaldehydes, C_4-

C_6 cycloketones, HCHO, and butyl nitrate were quantitatively added to the reaction chamber using a standard manometric method. Pentane-1,5-dial and hydroxyacetaldehyde, both in aqueous solution, were first quantified using the FT-IR technique by comparison with calibrated spectra of aldehydes and then fed to the PTR-MS instrument for calibration. The IR absorption coefficient of pentane-1,5-dial was assumed to be twice as large as that of pentanal.[38] Known quantities of NPCCAs were generated in the reaction chamber from cycloalkanecarbaldehyde + NO_3 in excess of NO_2. NPCCA was the only product ($\geq$99%) of this reaction detected by both FT-IR and PTR-MS. NPCCA calibration was thus performed on the basis of a 1:1 conversion of known quantities of C_3-C_6 cycloalkanecarbaldehydes into the respective NPCAAs. In addition, the PTR-MS instrument was calibrated using an oxygenate standard (Apel-Riemer Environmental Inc., Denver, CO) containing 1 ppmV of methanol, ethanol, acetaldehyde, acetone, and 2-butanone, respectively.

The sensitivity (or calibration factor) of PTR-MS with respect to a certain compound is defined as the number of mass discrimination corrected product ions produced at a trace gas mixing ratio of 1 ppbV and at a total $H_3O^+(H_2O)_{n=0,1,2}$ ion signal of 1 million normalized counts per second (ncps). For all investigated alcohols, ketones, and aldehydes with the exception of HCHO, the observed sensitivity was in the range 33 ± 5 ncps/ppbV. This calibration factor was assigned to all oxygenates for which no authentic standards were available; the associated uncertainty of ±15% corresponds to the accuracy of oxygenate measurements. The individual PTR-MS sensitivity values are given as Supporting Information (Table 7S). The reduced HCHO sensitivity of 1.6 ncps/ppbV is explained by the loss of protonated HCHO ions through reaction with H_2O, as discussed in detail by Hansel et al.[39] For butyl nitrate and NPCCAs, sensitivities in the range 25 ± 6 ncps/ppbV were found. This value was generally used for nitrate species for which no authentic standards were available; the associated uncertainty of ±25% corresponds to the accuracy of nitrate measurements. An additional uncertainty arises from the fact that ion signals may not be unambiguously attributable to simple oxygenates or to nitrate species. For such signals, the associated error is on the order of ±30%. This is in agreement with the previously described method-inherent feature of PTR-MS which constrains the variability of calibration factors for oxygenated hydrocarbons to ±30%.[30,31]

Product study data were taken from the first 18−22 min of reaction, during which about 50% of the initially present cycloalkanecarbaldehyde had reacted and a linear increase of products versus reactant loss was observed. Mass scans in the range from m/z 20 to 200 were performed with a dwell time of 1 s per m/z, resulting in a sample time resolution of 3 min. The length of the reaction time was determined by the 3−4 min time resolution of the two analytical instruments and the necessity to collect sufficient data points for an accurate linear regression analysis. PTR-MS ion signals were corrected for mass discrimination, instrumental background, and artifact formation observed in blank runs of air containing the OH precursor (2-PN-d_6) and NO. The m/z 31 signal (HCHO) was corrected for signal loss as discussed above. Only products with a signal-based yield >1% were further investigated. The number of carbon atoms was derived from the ^{13}C-signal abundance or, in the case of interferences, estimated. An error due to fragmentation of the carbon skeleton during CI is expected to be minor but cannot be excluded completely. Compound assignment was based on molecular weight information (taking into consideration the fragmentation routes described above), ^{13}C abundance, and thermal behavior of the observed signals which was studied at the end of each experiment when photolysis lamps were switched off. Sampling was then performed through a heated stainless steel inlet ($T = 150$ °C). Peroxyacyl nitrates are known to decompose at 150 °C, and ion signals associated with peroxyacyl nitrates can thus be selectively identified and quantified.[37] After tentative identification, ion count rates were converted into volume mixing ratios using the calibration factors reported above. Carbon yields of individual compounds were determined from least-squares regressions; no corrections for secondary reactions were applied except where explicitly stated.

2.3. Chemicals. For the kinetic study, N_2O_5 was synthesized by mixing gas streams of O_3 and NO_2 and trapping the products at −78 °C. N_2O_5 was purified by vacuum distillation prior to its use.

2PN and 2PN-d_6 were prepared from the corresponding alcohols following the procedure reported for butyl nitrite.[40] 2-Propanol-1,1,1,3,3,3-d_6 was prepared from acetone-d_6 by reduction with $LiAlH_4$ in dry ether. CH_3ONO was synthesized according to Taylor et al.[41]

Cyclobutanecarbaldehyde and cyclopentanecarbaldehyde were synthesized according to a standard procedure[42] adding rapidly 4.05 g (47.1 mmol) of cyclobutyl- or cyclopentyl-methanol in 50 mL of methylene chloride to a stirred suspension of 10.15 g (47.1 mmol) of pyridinium chlorochromate in 100 mL of methylene chloride. The mixture was stirred at room temperature for 3 h, diluted with 700 mL of anhydrous ether, filtered through Celite, and carefully evaporated at atmospheric pressure using a Vigreux column. The residue was dissolved in 50 mL of ether and dried with $CaCl_2$ to eliminate unreacted starting alcohol. Evaporation followed by distillation yielded 2.98 g (75%) of cycloalkanecarbaldehyde. To get an analytical sample, the distillation was repeated three times.[43] The purity of cyclobutanecarbaldehyde and cyclopentanecarbaldehyde was determined by PTR-MS analysis to be >85% and >92%, respectively.

Other chemicals used for the kinetic studies were as follows: cyclopropanecarbaldehyde (Aldrich, 98%), cyclohexanecarbaldehyde (Fluka, ~90−95%), but-1-ene (Fluka, 99%), propene (Fluka, 99%), and synthetic air (AGA plus; CO and NO_x < 100 ppb, C_nH_m < 1 ppm). The same batches of cycloalkanecarbaldehydes and 2-PN-d_6 were used for the product studies. Other chemicals used in the product studies were the following: 1-butyl-nitrate (synthesized by nitration of 1-butanol), pentane-1,5-dial (Fluka, solution, 70% in H_2O), HCHO (Fluka, 90% CH_2O with 10% CH_3OH for stabilization), cyclobutanone (Fluka, >99%), cyclopentanone (Fluka, >99%), cyclohexanone (Fluka, >99%), hydroxyacetaldehyde (Sigma-Aldrich, dimer, >98%), cyclohexane (Carlo Erba, 99.5%), NO (Alpha Gaz, >99%), NO_2 (Messer, >98%), O_2 (SIO >99.95), and synthetic air (SIO, >99.95%).

3. Results and Discussion

3.1. Kinetics. For each compound, data of the independent experiments were analyzed according to eq 1 using a weighted least-squares procedure including uncertainties in both reactant concentrations and allowing a zero-point offset.[44] The spectral ranges and the compounds included in the data analysis are specified in Table 1. But-1-ene was used in all the experiments as a reference compound. In addition, propene was used as a reference in the OH−cyclopentanecarbaldehyde studies. Plots of $\ln\{[\text{ald}]_0/[\text{ald}]_t\}$ versus $\ln\{[\text{ref}]_0/[\text{ref}]_t\}$ are shown in Figures 1 and 2 for the NO_3 and OH experiments, respectively. Table

TABLE 1: Spectral Regions and Compounds Included in the Spectral Subtraction Procedures

		compounds included in the spectral analysis	
compound	spectral range (cm^{-1})	OH	NO_3
cyclopropanecarbaldehyde	2775−2670	HCHO, propanal, 2-PN, acetone	HCHO, propanal
cyclobutanecarbaldehyde	2760−2670	HCHO, propanal	HCHO, propanal
cyclopentanecarbaldehyde	2750−2670	HCHO, acetaldehyde, propanal	HCHO, propanal
cyclohexanecarbaldehyde	2740−2670	HCHO, propanal,	HCHO, propanal
but-1-ene	3140−3050	propanal	N_2O_5, cyclopropanecarbaldehyde[a]
propene[b]	3150−3050	acetaldehyde	

[a] Used only in the study of cyclopropanecarbaldehyde. [b] Used only in the study of cyclopentanecarbaldehyde with 2-PN.

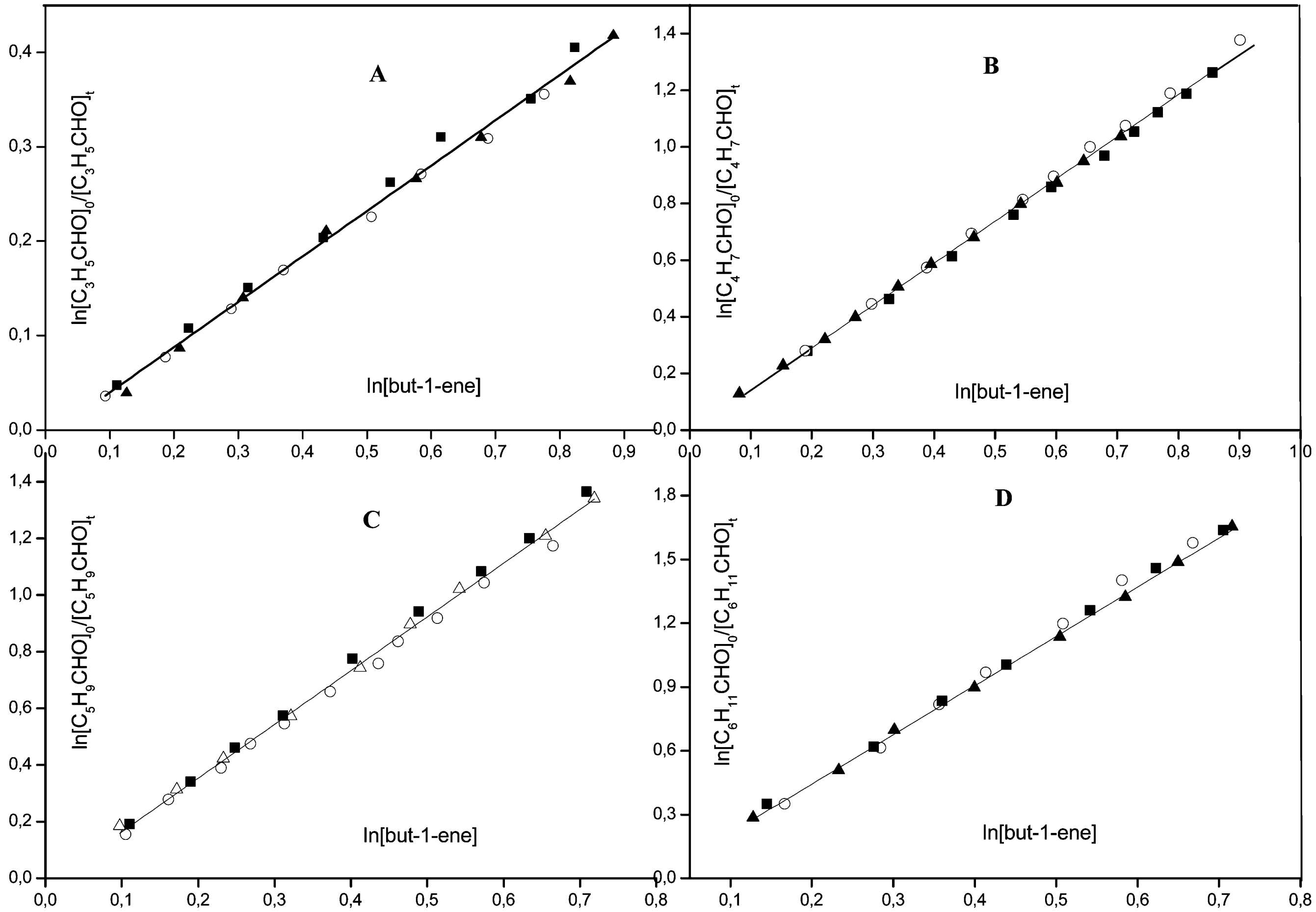


Figure 1. Plots of ln{[ald]$_0$/[ald]$_t$} versus ln{[ref]$_0$/[ref]$_t$} for the decays of cycloalkanecarbaldehydes and reference compounds during reaction with NO_3 radicals. Different symbols indicate independent experiments. The errors quoted are the 3σ statistical errors: (A, cyclopropanecarbaldehyde) 24 data points, three experiments, $k_{rel} = 0.452 \pm 0.027$; (B, cyclobutanecarbaldehyde) 31 data points, three experiments, $k_{rel} = 1.477 \pm 0.042$; (C, cyclopentanecarbaldehyde) 29 data points, three experiments, $k_{rel} = 1.891 \pm 0.072$; (D, cyclohexanecarbaldehyde) 24 data points, two experiments, $k_{rel} = 2.363 \pm 0.084$.

2 summarizes the measured reaction rate coefficients. The error limits correspond to 3σ from the statistical analyses, and neither include uncertainties in the reaction rate coefficients of the reference compounds nor possible systematic errors in the experiments. Random "experimental" errors arise from temperature fluctuations and from the quantitative determination of relative reactant concentrations by spectral subtraction. These errors are reflected in the statistical error from the least-squares analysis and amount to less than ±10% (3σ) in all cases. In addition, systematic errors may arise from competing reactions in the smog chamber. In the NO_3 studies, OH radicals may be produced from HO_2 ($HO_2 + NO_3 \rightarrow OH + NO_2 + O_2$).[45] The influence of such systematic errors in the derived rate coefficients has been shown to be negligible for the NO_3/acetaldehyde system.[26] This should also be valid for the present study performed under similar experimental conditions. In the OH studies, O_3 and NO_3 radicals are formed during the photolysis of organonitrites. Both O_3 and NO_3 react relatively fast with the reference compound 1-butene. However, a kinetic model of the reaction system indicates that the concentrations of these oxidants were too low ($[NO_3] \ll 1$ ppt, $[O_3] < 5$ ppb) to be relevant. The derived relative rate coefficients are believed to be accurate within ±10%.

3.2. Tropospheric Lifetimes. The estimated ambient concentrations of OH and NO_3 radicals combined with the measured rate coefficients may be used to derive the tropospheric lifetimes of cycloalkanecarbaldehydes. Using a globally averaged diurnal OH radical concentration of 9.4×10^5 radicals cm^{-3},[46] the calculated lifetimes range from 14 h for cyclopropanecarbaldehyde to 9 h for cyclohexanecarbaldehyde. Using a 12 h average nighttime tropospheric NO_3 radical concentration of $\sim 5.0 \times 10^8$ molecule cm^{-3},[47,48] the calculated lifetimes range from 8 days for cyclopropanecarbaldehyde to 1.5 days for cyclohexanecarbaldehyde.

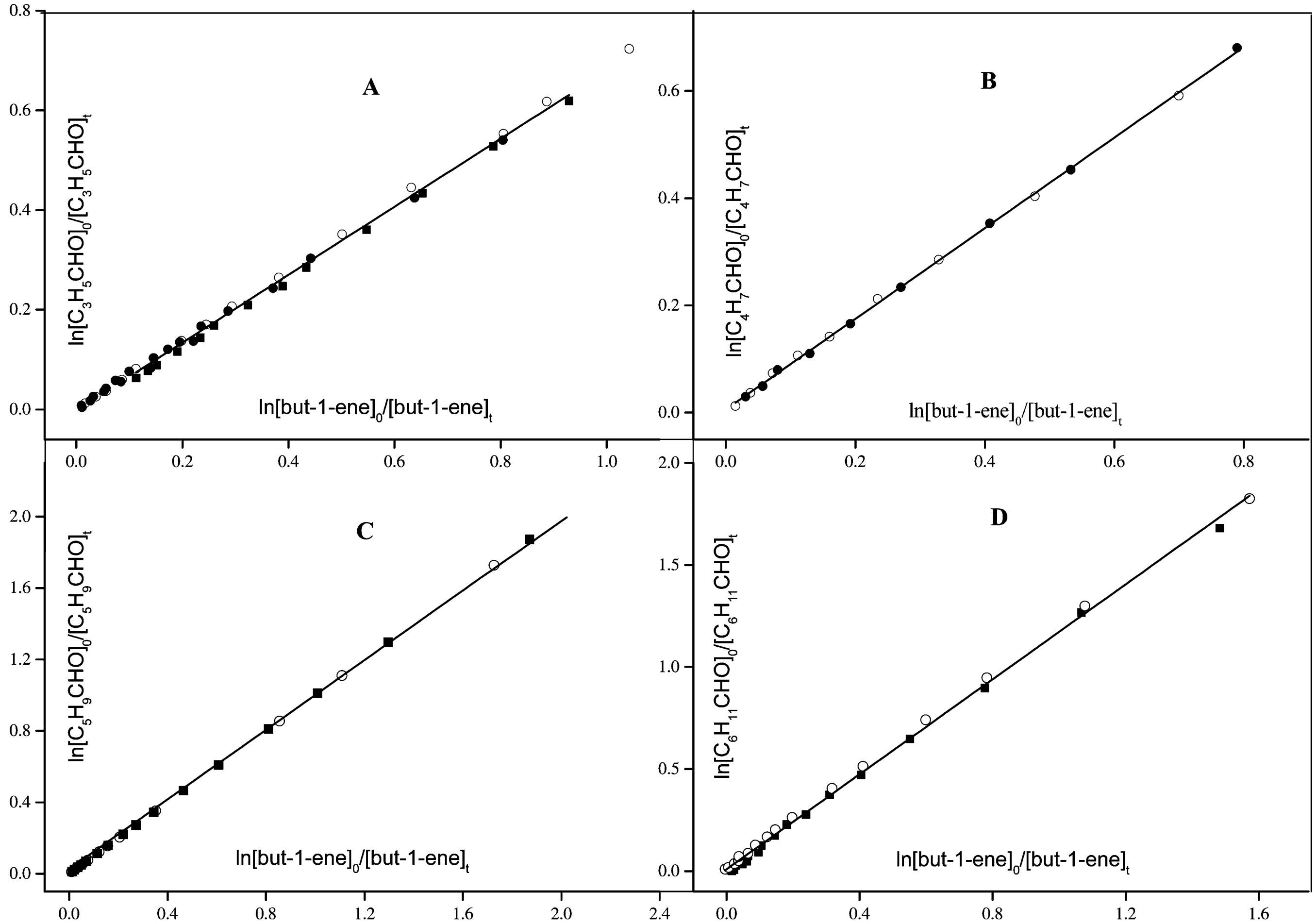


Figure 2. Plots of ln{[ald]$_0$/[ald]$_t$} versus ln{[ref]$_0$/[ref]$_t$} for the decays of cycloalkanecarbaldehydes and reference compounds during reaction with OH radicals. Different symbols indicate independent experiments. The errors quoted are the 3σ statistical errors: (A, cyclopropanecarbaldehyde) 48 data points, three experiments, k_{rel} = 0.678 ± 0.006; (B, cyclobutanecarbaldehyde) 18 data points, two experiments, k_{rel} = 0.847 ± 0.007; (C, cyclopentanecarbaldehyde) 27 data points, two experiments, k_{rel} = 1.043 ± 0.007; (D, cyclohexanecarbaldehyde) 33 data points, two experiments, k_{rel} = 1.195 ± 0.017.

TABLE 2: Rate Coefficients (in Units of cm^3 molecule^{-1} s^{-1}) for the Reaction of Cycloalkanecarbaldehydes with NO$_3$ and OH Radicals at 298 K

compound	k_{NO_3} ($\times 10^{-14}$)	k_{OH} ($\times 10^{-11}$)	
cyclopropanecarbaldehyde	0.61 ± 0.04[a]	2.13 ± 0.05[b]	
cyclobutancarbaldehyde	1.99 ± 0.06[a]	2.66 ± 0.06[b]	
cyclopentanecarbaldehyde	2.55 ± 0.10[a]	3.27 ± 0.07[b]	2.74 ± 0.05[c]
cyclohexanecarbaldehyde	3.19 ± 0.12[a]	3.75 ± 0.05[b]	

[a] Reference but-1-ene, $k_{NO_3} = 1.35 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[78] [b] Reference but-1-ene, $k_{OH} = 3.14 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[78] [c] Reference propene, $k_{OH} = 2.63 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[78]

3.3. Product Study. Due to the complexity of the reaction mechanism, the degradation schemes (Schemes 1−4) are simplified. Reactants such as NO, NO$_2$, and O$_2$ are omitted. The identified or tentatively identified products generated by the OH−cycloalkanecarbaldehyde radical reaction are presented in the degradation schemes with an asterisk and in bold.

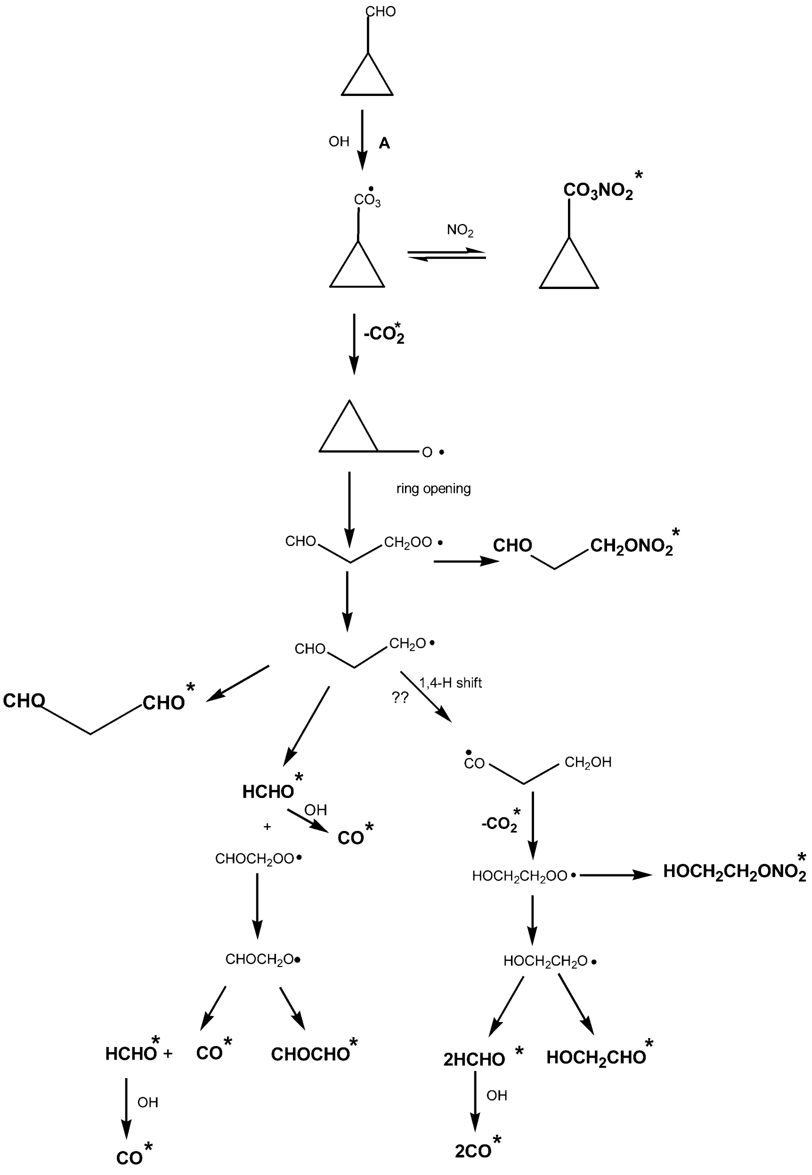
3.3.1. Cyclopropanecarbaldehyde. Table 3 summarizes the products and the respective molar and carbon yields of the OH−cyclopropanecarbaldehyde reaction. Scheme 1 shows the proposed degradation paths. [(Nitroperoxy)carbonyl]cyclopropane (NPCCPr) is the major reaction product with a carbon yield of 35.9%. The ion signal at *m*/*z* 103 ([MH + H$_2$O − HNO$_3$]$^+$) and cyclopropyl and cyclopropylcarbonyl fragment ions at *m*/*z* 41 and *m*/*z* 69, respectively, have been fully assigned to NPCCPr. NPCCPr identification and quantification is based on results from the thermal decomposition study and the NPCCPr fragmentation pattern obtained in the NO$_3$−cyclopropanecarbaldehyde experiment.

Other major reaction products are CO and CO$_2$ which account for a carbon yield of 11.5 and 19.4%, respectively. The ion signal at *m*/*z* 31 is associated with HCHO (MH$^+$), which was also detected by FT-IR. The FT-IR derived HCHO carbon yield, 20.7 ± 1.4%, is in good agreement with the PTR-MS derived yield, 19.6 ± 2.0%. The formation of CO$_2$ may be explained by decomposition of cyclopropylcarboxy radicals, and the formation of CO and HCHO, by the unimolecular decomposition of CHOCH$_2$CH$_2$O$^•$ and CHOCH$_2$O$^•$ radicals (see Scheme 1). Part of the observed CO may also arise from the secondary reaction of HCHO with OH radicals. OH reaction rate coefficients of 2.13×10^{-11} cm^3 molecule^{-1} s^{-1} for cyclopropanecarbaldehyde (this work) and 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} for HCHO[49] result in a corrected HCHO carbon yield of 24.4% at 50% cyclopropanecarbaldehyde conversion. After the lights had been turned off, the formation of CO, CO$_2$, and HCHO was observed from NPCCPr decomposition, confirming that these species are primary reaction products. The observation of CHOCH$_2$CH$_2$O$^•$ unimolecular decomposition contradicts previous studies on similar systems: calculations on the carbonyl alkoxy radical, CH$_3$COCH$_2$CH$_2$O$^•$, predict that unimolecular decomposition does not occur under atmospheric conditions,[50] and studies of the 1-propoxy radical also indicate that unimolecular decomposition is quite slow (~(1−4) × 10^2 s^{-1} [51−56]).

TABLE 3: Ion Signals, Molar Yields, and Carbon Yields of the OH−Cyclopropanecarbaldehyde Reaction Products (the Indicated Errors Are Standard Errors of the Least-Squares Fits)

compound	signal (*m*/*z*)	molar yield (%)	C yield (%)	interferences (*m*/*z*)
nitroperoxy carbonyl cyclopropane (NPCCPr)	41, 69, 103	35.9	35.9 ± 1.5	
HCHO	31	78.4	19.6 ± 2.0	
	(FT-IR)	82.7	20.7 ± 1.4	
2-nitrooxy-ethanol	61	3.7	1.9 ± 0.2	2-hydroxy-ethanal
propane-1,3-dial	73	2.0	1.5 ± 0.1	3-nitrooxy-propanal
unidentified	87	0.9	0.9 ± 0.1	
total VOCs			60.8	
CO	(FT-IR)	46.1	11.5 ± 0.6	
CO_2	(FT-IR)	77.8	19.4 ± 0.7	
total			**91.8**	

SCHEME 1: Degradation Paths in the OH-Initiated Oxidation of Cyclopropanecarbaldehyde



Ethanedial, which may also arise from $CHOCH_2O^{\bullet}$ decomposition, has been observed in traces (<1%) at *m*/*z* 59 (MH^+). Studies on the acetonoxy radical, $CH_3COCH_2O^{\bullet}$,[57] and propionoxy radical, $CH_3CH_2COCH_2O^{\bullet}$,[50] show that decomposition to HCHO and the carbonyl radical is the dominant reaction pathway. Similarly, it is expected that the carbonyl alkoxy radical, $CHOCH_2O^{\bullet}$, will predominantly decompose to form HCHO and CO.

Some minor products have also been detected. The ion signal at *m*/*z* 73 with a carbon yield of 1.5% has been assigned to propane-1,3-dial (MH^+). The signal at *m*/*z* 73 may also be partly associated with 3-nitrooxy-propanal ($[MH - HNO_2]^+$). Traces of its molecular ion (MH^+) have been detected at *m*/*z* 120.

The ion signal at *m*/*z* 61 with a carbon yield of 1.9% may be associated with 2-nitrooxy-ethanol ($[MH - HNO_2]^+$). Other ion signals possibly associated with 2-nitrooxy-ethanol have been observed in traces at *m*/*z* 45 ($[MH - HNO_3]^+$) and *m*/*z* 108 (MH^+). In CI of 2-nitrooxy-ethanol, however, HNO_3 loss (*m*/*z* 45) apparently dominates over HNO_2 loss (*m*/*z* 61),[36] which is inconsistent with the signal ratio observed here. The ion signal

TABLE 4: Ion Signals, Molar Yields, and Carbon Yields of the OH−Cyclobutanecarbaldehyde Reaction Products (the Indicated Errors Are Standard Errors of the Least-Squares Fits)

compound	signal (*m*/*z*)	molar yield (%)	C yield (%)	interferences (*m*/*z*)
nitroperoxy carbonyl cyclobutane (NPCCB)	55, 83, 117	30.3	30.3 ± 1.3	
3-hydroxy-propanal	57, 75	31.3	18.8 ± 1.0	3-nitrooxy-propanol (75)
HCHO	31	52.4	10.5 ± 0.8	
4-nitrooxy-butanal	71	3.7	3.0 ± 0.3	cylobutyl nitrate cyclobutanone
2-nitrooxy-ethanol	45, 61	7.6	3.0 ± 0.2	2-hydroxy-ethanal (61)
butane-1,4-dial	87	3.7	2.9 ± 0.1	4-nitrooxy-butanal
3-nitrooxy-propanol	59, 77	2.6	1.5 ± 0.2	ethanedial (59) unidentified species (77)
propane-1,3-dial	73	2.4	1.4 ± 0.1	
unidentified	101	1.3	1.3 ± 0.2	
cyclobutyl nitrate	55	<1.3	<1.0	
unidentified	29	1.5	0.6 ± 0.2	
total VOCs			74.4	
CO	(FT-IR)	27.9	5.6 ± 0.5	
CO_2	(FT-IR)	74.1	14.8 ± 1.1	
total			**94.8**	

at *m*/*z* 61 may also partly arise from 2-hydroxy-ethanal (MH^+). Fragmentation of cyclopropanecarbaldehyde produced an intense *m*/*z* 43 ion signal, hindering the detection of the 2-hydroxy-ethanal fragment ($[MH - H_2O]^+$). In the current absence of other explanations for the *m*/*z* 61 ion signal, the formation of 2-nitrooxy-ethanol and/or 2-hydroxy-ethanal may be explained via a 1,4-H shift of the $CHOCH_2CH_2O^\bullet$ radical. Such a reaction involves a five-membered transition state with some strain energy. The activation energy for a 1,4-H shift in the 1-butoxy radical has been calculated to be in the range from 54 to 75 kJ/mol, with the rate coefficient at 1 atm being $\sim 10^2$ s^{-1}.[58] In addition, there is no experimental evidence of a 1,4-H shift in 3-hexoxy and 3-pentoxy radicals.[59,60] However, the hydrogen of an aldehydic group is weakly bound to the substrate and H_{ald} abstraction is expected to be easier. The formed β-hydroxy alkoxy radical, $HOCH_2CH_2O^\bullet$, will preferentially decompose to $HCHO + {}^\bullet CH_2OH$ with a rate coefficient of $\sim(1-2) \times 10^5$ s^{-1},[61,62] while reaction with O_2 will produce 2-hydroxy-ethanal with a rate coefficient of $\sim 4 \times 10^4$ s^{-1}.[61,63]

The ion signal at *m*/*z* 87 has been corrected for a minor contribution from NPCCPr and amounts to a carbon yield of 0.9%. This signal remains unidentified and will be discussed later.

Using the SAR[16] method, a fractional contribution of route B of ~1% was calculated. For cyclopropanecarbaldehyde, this decomposition route can thus be safely neglected.

It can thus be concluded that the OH−cyclopropanecarbaldehyde reaction essentially proceeds via H_{ald} abstraction. To a first approximation, 36% of the reacted cyclopropanecarbaldehyde produces NPCCPr with the remaining 64% forming mainly $CO_2 + 2HCHO + CO$. The observed CO_2, HCHO, and CO molar yields were 78, 98 (corrected for the secondary OH reaction), and 46%, respectively. The CO_2 yield implies a cyclopropoxy radical formation percentage higher than that expected from HCHO and CO yields. It must, however, be considered that these estimates are affected by a relatively large uncertainty due to the low measurement accuracy of ±30%.

3.3.2. Cyclobutanecarbaldehyde. Table 4 summarizes the products and the respective molar and carbon yields for the reaction of cyclobutanecarbaldehyde with OH radicals. Scheme 2 illustrates the proposed degradation pathways.

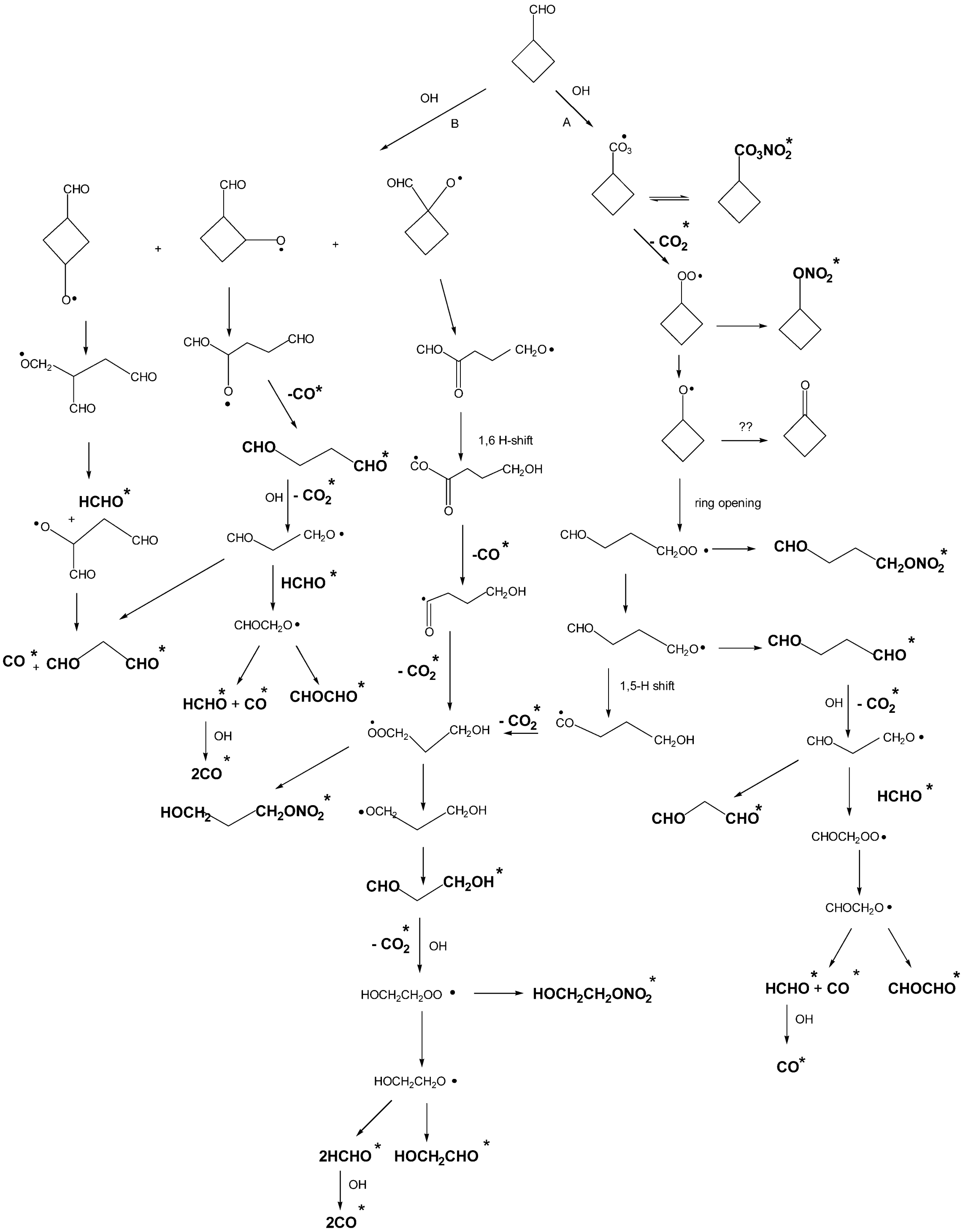
[(Nitroperoxy)carbonyl]cyclobutane (NPCCB) accounts for a carbon yield of 30.3% and forms ion signals at *m*/*z* 117 ($[MH + H_2O - HNO_3]^+$) and cyclobutyl and cyclobutylcarbonyl fragments at *m*/*z* 55 and *m*/*z* 83, respectively. NPCCB identification and quantification is based on results from the thermal decomposition study and the NPCCB fragmentation pattern obtained in the NO_3−cyclobutanecarbaldehyde experiment.

The ion signals *m*/*z* 57 and *m*/*z* 75 have been assigned to 3-hydroxy-propanal ($[MH - H_2O]^+$, MH^+), the major acyclic product accounting for 18.8% of the carbon yield. OH reaction rate coefficients of 2.66×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for cyclobutanecarbaldehyde (this work) and 1.99×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for 3-hydroxy-propanal[64] result in a corrected 3-hydroxy-propanal yield of 24.8% at 50% cyclobutanecarbaldehyde conversion. However, part of the *m*/*z* 75 signal may be attributable to 3-nitrooxy-propanol ($[MH - HNO_2]^+$) with the molecular ion (MH^+) at *m*/*z* 122 being present in traces. 3-Hydroxy-propanal may be formed via route A after ring opening, isomerization through a 1,5-H shift, and further decomposition (see Scheme 2). The rate coefficient for a 1,5-H shift from a secondary group ($-CH_2-$) has been evaluated to be $\sim 10^6$ s^{-1}.[65,66] The same compound may also be formed via route B after ring opening, isomerization through a 1,6-H shift, and decomposition of the carbonyl hydroxy alkoxy radical. This process is less favorable than the 1,5-H shift for entropic reasons.[58,67] However, isomerization via a 1,6-H shift has been observed when the hydrogen to be removed is bound to an oxygen-substituted carbon.[68] A rate coefficient of 5.6×10^3 s^{-1} was derived for a 1,6-H shift in $CH_3OCH_2OCH_2O^\bullet$ by quantum chemical calculations,[69] but no data are available for a 1,6-H shift from an aldehydic group. Abstraction via a 1,6-H shift from an aldehydic group has been proposed in a previous study as a possible decomposition pathway.[20]

CO and CO_2 are also major products accounting for carbon yields of 5.6 and 14.8%, respectively. CO_2 may arise primarily from decomposition of cyclobutylcarboxy and 4-hydroxy butyryloxy radicals and from the secondary OH reaction of 3-hydroxy-propanal. CO may arise from the decomposition of a carbonyl alkoxy radical via route B, from secondary OH reactions of C_3 and C_4 dialdehydes, and also from the reaction of HCHO with OH radicals.

HCHO has been quantified by PTR-MS only, as levels just barely exceeded the detection threshold of the FT-IR instrument. The HCHO signal at *m*/*z* 31 (MH^+) accounts for a carbon yield of 10.5%. No HCHO formation was observed from NPCCB decomposition after the lights had been turned off, indicating that HCHO is a secondary reaction product. HCHO may partly arise from the secondary reaction of 3-hydroxy-propanal with OH radicals. Secondary OH reaction of highly reactive C_3 and C_4 dialdehydes may also generate minor amounts of HCHO.

SCHEME 2: Degradation Paths in the OH-Initiated Oxidation of Cyclobutanecarbaldehyde



A possible degradation product of 3-hydroxy-propanal is 2-nitrooxy-ethanol observed at *m*/*z* 45 ($[MH - HNO_3]^+$) and *m*/*z* 61 (($[MH - HNO_2]^+$) with a total carbon yield of 3.0%. Contrarily to the cylopropanecarbaldehyde experiment, the ion signal at *m*/*z* 45 was found to dominate over the *m*/*z* 61 signal which is consistent with the expected CI pathways for 2-nitrooxy-ethanol.[36] Traces of the 2-nitrooxy-ethanol molecular ion (MH^+) have been detected at *m*/*z* 108. The ion signal at *m*/*z* 61 (0.6% C yield) may also be partly assigned to 2-hydroxy-ethanal (MH^+) formed from the decomposition of 3-hydroxypropanal. As discussed previously, the β-hydroxy alkoxy radical, $HOCH_2CH_2O^{\bullet}$, will mainly decompose to give HCHO + $^{\bullet}CH_2OH$[61,62] and only to a minor extent to form 2-hydroxy-ethanal.[62,63] 2-Hydroxy-ethanal may also be formed via route B, but the contribution from this pathway is probably negligible.

The ion signal at *m*/*z* 87 with a C yield of 2.9% has been assigned to butane-1,4-dial (MH^+). Butane-1,4-dial may be formed by H abstraction from the $CHO(CH_2)_2CH_2O^{\bullet}$ radical (route A) or by HCO elimination from the $CHOCH(O^{\bullet})CH_2CH_2CHO$ radical (route B). The signal may also be associated with 4-nitrooxy-butanal ($[MH - HNO_2]^+$). Traces of its molecular ion (MH^+) have been detected at *m*/*z* 134.

Secondary OH reactions of butane-1,4-dial may generate propane-1,3-dial (*m*/*z* 73, MH^+) observed with a carbon yield of 1.4% as well as traces of ethanedial (*m*/*z* 59, MH^+). A fraction of propane-1,3-dial may also arise via route B through decom-

TABLE 5: Ion Signals, Molar Yields, and Carbon Yields of the OH−Cyclopentanecarbaldehyde Reaction Products (the Indicated Errors Are Standard Errors of the Least-Squares Fits)

compound	signal (*m*/*z*)	molar yield (%)	C yield (%)	interferences (*m*/*z*)
nitrooxy carbonyl cyclopentane (NPCCP)	69, 97, 131	33.4	33.4 ± 1.3	
4-hydroxy-butanal	71, 89	18.4	12.2 ± 0.9	
5-nitrooxy-pentanal	85	10.5	8.7 ± 0.6	cyclopentanone 2-hydroxybutane-1,4-dial cyclopentyl nitrate
5-hydroxy-2-nitrooxy-pentanal	101	6.3	5.3 ± 0.3	pentane-1,5-dial 5-nitrooxy-pentanal
cyclopentyl nitrate	69	4.4	3.7 ± 0.3	
unidentified	115	1.8	1.8 ± 0.2	
2-hydroxy-4-nitrooxy-butanal	87	2.4	1.6 ± 0.1	butane-1,4-dial
3-hydroxy-propanal	75	2.5	1.3 ± 0.1	
HCHO	31	6.9	1.2 ± 0.4	
HCOOH	47	3.7	0.6 ± 0.1	
unidentified	43	1.1	0.4 ± 0.1	
total VOCs			70.1	
CO	(FT-IR)	40.5	6.7 ± 0.2	
CO_2	(FT-IR)	75.7	12.6 ± 0.3	
total			**89.4**	

position of the $CHOCH(O^{\bullet})CH_2CHO$ radical. As discussed previously, it is expected that the carbonyl alkoxy radical, $CHOCH_2O^{\bullet}$, will decompose to form HCHO and CO. The ion signals at *m*/*z* 59 ($[MH - HNO_3]^+$) and *m*/*z* 77 ($[MH + H_2O - HNO_3]^+$, with a total carbon yield of 1.5%, are thus primarily assigned to 3-nitrooxy-propanol. As mentioned above, traces of the to 3-nitrooxy-propanol molecular ion (MH^+) have been detected at *m*/*z* 122. An additional unidentified compound is likely to contribute to the ion signal at *m*/*z* 77.

The ion signal at *m*/*z* 71 accounting for a carbon yield of 3.0% may be assigned to 4-nitrooxy-butanal ($[MH - HNO_3]^+$), cyclobutanone (MH^+), or cyclobutyl nitrate ($[MH - HNO_2]^+$). The formation of the nitrooxyaldehyde is considered to be most favorable. As stated above, traces of its molecular ion (MH^+) have been detected at *m*/*z* 134. Previous experimental results are available for the cyclopentoxy radical (lower strain energy than cyclobutoxy radical), and ring opening represents the major decomposition pathway.[25] Other studies show that the elimination of hydrogen through reaction with O_2 implies a change from sp^3 to sp^2 hybridization of the carbon in the four-membered ring, increasing the ring strain, while ring opening causes the release of ring strain in the cyclobutoxy radical, reducing the energy barrier for the reaction.[70]

An accurate analysis of the ion signal at *m*/*z* 55 associated with cyclobutyl nitrate ($[MH - HNO_3]^+$) is not possible due to the interfering $H_3O^+(H_2O)_2$ CI reagent ion signal. It is, however, possible to analyze the ^{13}C isotope on *m*/*z* 56, which does not suffer from this interference. Though affected by a large error, an upper limit for the *m*/*z* 55 carbon yield of 1% may be derived.

The fragment ion signal at *m*/*z* 29 cannot be attributed to a specific compound. The ion signal at *m*/*z* 101 remains unidentified and will be discussed later.

An ∼11% fractional contribution of route B was calculated using the SAR[16] method. There is no unambiguous experimental evidence for product formation via route B. Ion signals which are expected to be unequivocally attributable to multifunctional ring opening products from route B (e.g., 2-keto-pentane-1,5-dial and 2-keto-5-nitrooxy-pentanal, see Scheme VS in the Supporting Information) have not been observed. Other products such as 3-hydroxypropanal, dialdehydes, HCHO, and CO are primarily generated via route A, but a minor contribution from route B cannot be ruled out.

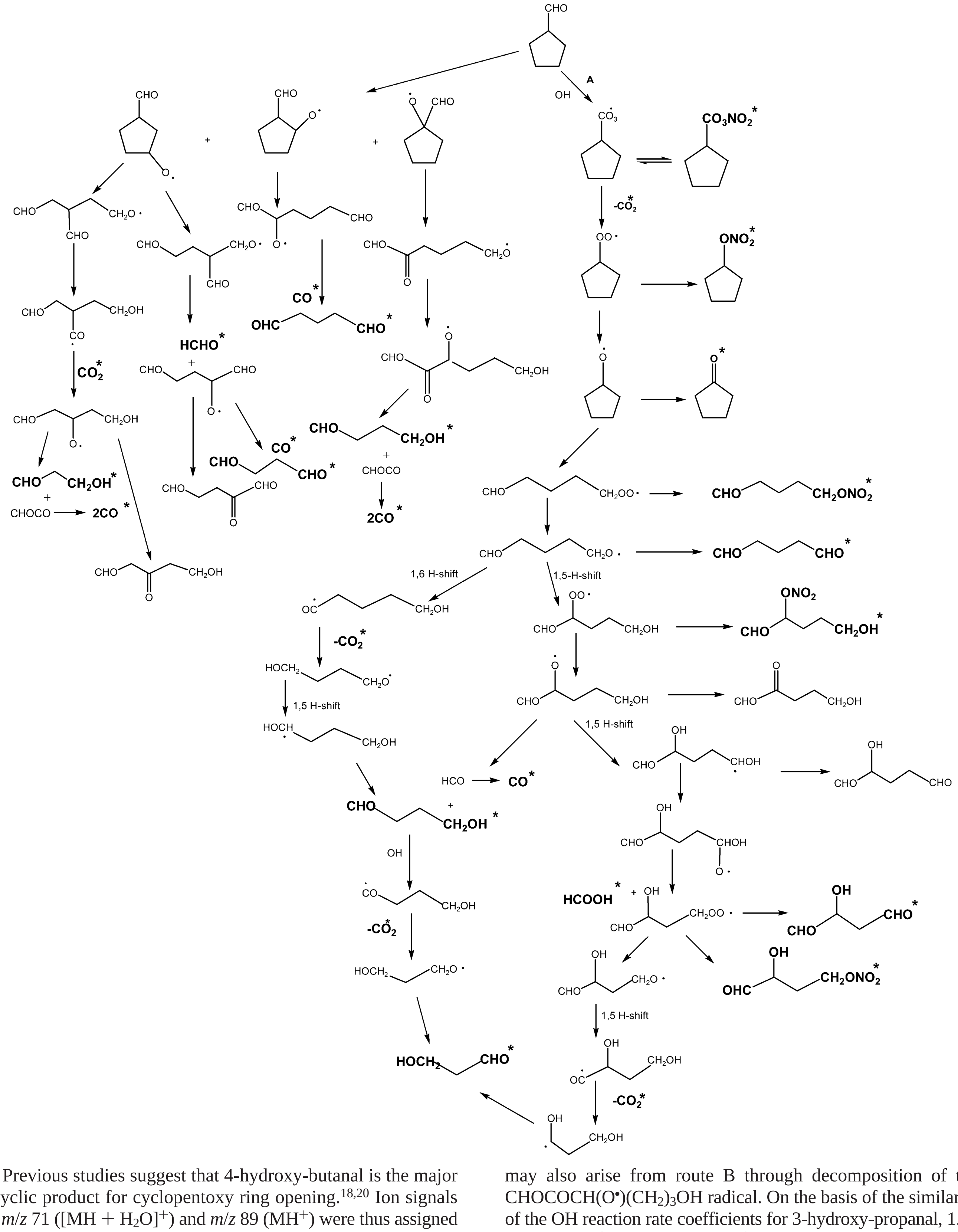
On the basis of a SAR[16] evaluation and considering the current knowledge on alkoxy radical degradation, it can, however, be assumed that the large majority of the observed products arises from degradation via route A.[55,58,67−69,71]

It can be concluded that the OH−cyclobutanecarbaldehyde reaction proceeds essentially via H_{ald} abstraction (≥90%) leading to the formation of 30% NPCCB and ∼60% cyclobutylperoxy radical + CO_2. Of the 60% cyclobutylperoxy radical fraction, ∼10% goes into minor products (cyclobutyl nitrate, cyclobutanone, 4-nitrooxy-butanal, butane-1,4-dial, and its oxidation products) and ∼50% goes into CO_2 + 3-hydroxy-propanal. After correction for secondary reaction with OH radicals, the observed molar 3-hydroxy-propanal yield is 41%; the CO_2 molar yield is 74% which is lower than that expected from decomposition of cyclobutylcarboxy radicals and 4-hydroxy butyryloxy radicals. Again, it must be pointed out that these estimates have a relatively large uncertainty due to the low measurement accuracy, that is, ±30% for CO_2 and ±25% for NPCCB.

3.3.3. Cyclopentanecarbaldehyde. Table 5 summarizes products and respective molar and carbon yields for the reaction of cyclopentanecarbaldehyde with OH radicals. Scheme 3 shows the proposed degradation paths. [(Nitroperoxy)carbonyl]cyclopentane (NPCCP) is the main reaction product with a carbon yield of 33.4%. The ion signal at *m*/*z* 131 ($[MH + H_2O - HNO_3]^+$) and the cyclopentylcarbonyl fragment ion at *m*/*z* 97 have been fully assigned to NPCCP; the cyclopentyl fragment ion at *m*/*z* 69 is partly attributed to NPCCP. Qualitative and quantitative assignments are based on results from the thermal decomposition study and the NPCCP fragmentation pattern obtained in the NO_3−cyclopentanecarbaldehyde experiment.

A fraction of the ion signal at *m*/*z* 69 accounting for a carbon yield of 3.7% has been assigned to cyclopentyl nitrate ($[MH - HNO_3]^+$). The given value may slightly underestimate the cyclopentyl nitrate yield because it does not take into account HNO_2 loss as a possible CI pathway. Using the SAR method,[16] the decomposition via route A was calculated to amount to 70% with 33.4% going into NPCCP and the remaining 36.6% going into cyclopentyl radicals (see Scheme 3). Product yields can thus be calculated relative to cyclopentyl radical decomposition and be compared with literature values reported for cyclopentane oxidation. The cyclopentyl nitrate yield relative to cyclopentyl radical decomposition is 12.0% which is considerably higher than the 4.5 ± 1.5% yield reported by Takagi et al.[25] Aside from the inaccuracy of the measurements, this discrepancy may be explained by the presence of interfering species at *m*/*z* 69 and by the fact that the SAR method[16] underestimates the fractional abundance of route A. Hanson et al.[18] did not observe cyclopentyl nitrate, but HNO_3 loss in their PTR-MS study was not considered as a possible CI pathway for cyclopentyl nitrate.

SCHEME 3: Degradation Paths in the OH-Initiated Oxidation of Cyclopentanecarbaldehyde



Previous studies suggest that 4-hydroxy-butanal is the major acyclic product for cyclopentoxy ring opening.[18,20] Ion signals at *m/z* 71 ($[MH + H_2O]^+$) and *m/z* 89 (MH^+) were thus assigned to 4-hydroxy-butanal, observed with a total carbon yield of 12.2. 4-Hydroxy-butanal may be formed via route A through a 1,6-H shift from a weakly bound H (such as the aldehydic −CHO) or through a 1,5-H shift followed by elimination of HCO. The 1,6-H shift is considered to be less favorable.[58,67] However, Orlando et al.[20] found indirect experimental evidence for the feasibility of this process. A minor fraction of 4-hydroxy-butanal may also arise from route B through decomposition of the $CHOCOCH(O^\bullet)(CH_2)_3OH$ radical. On the basis of the similarity of the OH reaction rate coefficients for 3-hydroxy-propanal, 1.99×10^{-11} cm^3 molecule^{-1} s^{-1}, [64] and propanal, 2.00×10^{-11} cm^3 molecule^{-1} s^{-1},[72] the OH 4-hydroxy-butanal rate coefficient can be approximated to that of butanal, 2.4×10^{-11} cm^3 molecule^{-1} s^{-1}.[72] Thus, assuming OH rate coefficients of 3.27×10^{-11} cm^3 molecule^{-1} s^{-1} for cyclopentanecarbaldehyde (this work) and 2.4×10^{-11} cm^3 molecule^{-1} s^{-1} for 4-hydroxy-butanal,[72] a corrected 4-hydroxy-butanal carbon yield of 16.1%

is derived at 50% cyclopentanecarbaldehyde conversion. The corrected 4-hydroxy-butanal yield relative to cyclopentyl radical decomposition is 66.1% which is significantly higher than the 54% yield estimated by Hanson et al.[18] This finding may again be explained by the fact that the SAR method[16] underestimates the fractional abundance of route A.

CO and CO_2 represent a large portion of the reaction products with respectively 6.7 and 12.6% of the total carbon yield. CO_2 arises primarily from decomposition of cyclopentylcarboxy radicals and from the secondary OH reaction of 4-hydroxy-butanal. Part of the CO_2 may also be generated through decomposition of the 5-hydroxy-1-pentanoyl radical, as suggested by Orlando et al.,[20] or via route B. CO may arise from decomposition of the $CHOC(O^\bullet)(CH_2)_3OH$ radical, as indicated by Orlando et al.[20] Minor amounts of CO may also be formed via route B (see Scheme 3).

Hanson et al.[18] observed 2-hydroxypentane-1,5-dial from the Cl-atom-initiated oxidation of cyclopentane. 2-Hydroxypentane-1,5-dial is expected to be predominantly detected at *m*/*z* 99 ($[MH - H_2O]^+$). In the present study, the reactant cyclopentanecarbaldehyde produced an intense ion signal at *m*/*z* 99 (MH^+), hindering the detection of 2-hydroxypentane-1,5-dial. However, cyclopentanecarbaldehyde also formed an ion signal at *m*/*z* 81 ($[MH - H_2O]^+$) and the *m*/*z* 99:*m*/*z* 81 signal ratio did not increase during the reaction with OH radicals. This finding suggests that 2-hydroxypentane-1,5-dial formation is only minor.

The ion signal at *m*/*z* 85 accounting for a carbon yield of 8.7% may be assigned to several compounds. The dominant contribution is most likely due to 5-nitrooxy-pentanal ($[MH - HNO_3]^+$). Traces of its molecular ion have been detected at *m*/*z* 148 (MH^+). Takagi et al.[25] report an overall yield of acyclic nitrates of 7.5% which are believed to consist mainly of 5-nitrooxy-pentanal, 5-hydroxy-2-nitrooxy-pentanal, and 2-hydroxy-4-nitrooxy-butanal (see Scheme 3). For the latter two nitrates, the carbon yields were ≤5.3% and ≤1.6%, respectively; see below. Hanson et al.[18] report a yield of 3% for 5-nitrooxy-pentanal. A minor fraction of the ion signal at *m*/*z* 85 may thus arise from cyclopentyl nitrate ($[MH - HNO_2]^+$) and cyclopentanone (MH^+). Previous studies report low cyclopentanone yields: <0.2%,[25] <0.5%,[20] and <5%.[18] 2-Hydroxybutane-1,4-dial ($[MH - H_2O]^+$) may also contribute to the ion signal at *m*/*z* 85.

The ion signal at *m*/*z* 101 accounting for a carbon yield of 5.3% has been tentatively assigned to 5-hydroxy-2-nitrooxy-pentanal ($[MH - HNO_3]^+$). 5-Nitrooxy-pentanal ($[MH - HNO_2]^+$) and pentane-1,5-dial (MH^+) may also be observed at *m*/*z* 101. A low abundance of *m*/*z* 57 (a fragment of *m*/*z* 101 observed in the pentane-1,5-dial calibration) suggests that the contribution from pentane-1,5-dial is minor.

The ion signal at *m*/*z* 75 accounting for a carbon yield of 1.3% is associated with 3-hydroxy-propanal arising from 4-hydroxy-butanal decomposition.

The ion signal at *m*/*z* 47 accounting for 0.6% carbon yield has been assigned to HCOOH. Takagi et al.[25] and Orlando et al.[20] also observed HCOOH from cyclopentyl radical decomposition.

The ion signal at *m*/*z* 31 has been assigned to HCHO (MH^+), observed with a carbon yield of 1.2%. Hanson et al.[18] and Orlando et al.[20] did not observe HCHO in the decomposition of cyclopentyl radicals, indicating that it may be formed via route B.

The ion signal at *m*/*z* 43 is a fragment ion that cannot be attributed to a specific compound.

The ion signal at *m*/*z* 87 may be assigned to 2-hydroxy-4-nitrooxy-butanal ($[MH - HNO_3]^+$). Traces of its molecular ion have been detected at *m*/*z* 150 (MH^+). Another candidate is butane-1,4-dial (MH^+) arising from route B.

As mentioned above, the decomposition via route B was calculated to amount to about 30% using the SAR method.[16] A detailed degradation scheme of route B is given in the Supporting Information (Scheme VIS). As in the case of cyclobutanecarbaldehyde, no unambiguous experimental evidence for product formation via route B was found. Ion signals which are expected to be unequivocally attributable to multifunctional ring opening products from route B (e.g., 2-keto-hexane-1,6-dial and 2-keto-6-nitrooxy-hexanal) have not been observed. Other products such as dialdehydes or 4-hydroxy-butanal are primarily generated via route A, but the contribution from route B may be significant. As discussed above, a significant fraction of the observed CO may arise from route B.

It can thus be concluded that the OH−cyclopentanecarbaldehyde reaction proceeds predominantly via H_{ald} abstraction. The SAR method[16] predicts 70% decomposition via route A, but the experimental data indicate that this value should be taken as a lower limit. With an ~33% NPCCP yield, the formation of the cyclopentylperoxy radical amounts to ≥37%. The major product of cyclopentylperoxy radical decomposition is 4-hydroxy-butanal with a corrected molar yield of 24%; minor products (cyclopentyl nitrate, cyclopentanone, 5-nitrooxy-pentanal, pentane-1,5-dial, and 5-hydroxy-2-nitrooxy-pentanal) account for a molar yield of ~21% in total. The CO and CO_2 molar yields of 40 and 76%, respectively, are somehow higher than those expected from their major production channels: 24% CO yield from $CHOC(O^\bullet)(CH_2)_3OH$ radical decomposition and ≥37% CO_2 yield from cyclopentylcarboxy radical decomposition. As pointed out before, the observed CO and CO_2 yields are affected by a large uncertainty (±30%). Furthermore, additional production channels for both species have been indicated above.

3.3.4. Cyclohexanecarbaldehyde. Table 6 shows products and the respective molar and carbon yields for the reaction of cyclohexanecarbaldehyde with OH radicals. Scheme 4 illustrates the proposed reaction scheme.

[(Nitroperoxy)carbonyl]cyclohexane (NPCCH) is the major reaction product with a carbon yield of 33.3%. The ion signal at *m*/*z* 145 $[MH + H_2O - HNO_3]^+$ and the cyclohexylcarbonyl fragment ion at *m*/*z* 111 have been fully assigned to NPCCH; the cyclohexyl fragment ion at *m*/*z* 83 is partly attributed to NPCCH. NPCCH identification and quantification is based on results from the thermal decomposition study and the NPCCH fragmentation pattern obtained in the cyclohexanecarbaldehyde + NO_3 experiment.

The second major cyclic compound is cyclohexanone observed at *m*/*z* 99 (MH^+) with a carbon yield of 22.2%. As discussed below, several species may produce an ion signal at *m*/*z* 99, and thus, the reported carbon yield for cyclohexanone should be regarded as an upper limit. Using the SAR method,[16] the decomposition via route A was calculated to amount to 57% with 33.3% going into NPCCH and the remaining 23.7% going into cyclohexyl radicals (see Scheme 4). Product yields can thus be calculated relative to cyclohexyl radical decomposition and be compared with literature values reported for cyclohexane oxidation. The cyclohexanone yield relative to cyclohexyl radical decomposition is 109.3%, which largely exceeds previously reported values: 23 ± 13,[25] 28,[18] 32 ± 4,[17] 35 ± 4,[73] 36 ± 6,[20] and 39%.[21] This large discrepancy indicates that the SAR method[16] used underestimates the fractional abundance of route

TABLE 6: Ion Signals, Molar Yields, and Carbon Yields of the OH−Cyclohexanecarbaldehyde Reaction Products (the Indicated Errors Are Standard Errors of the Least-Squares Fits)

compound	signal (*m*/*z*)	molar yield (%)	C yield (%)	interferences (*m*/*z*)
nitroperoxy carbonyl cyclohexane (NPCCH)	83, 111, 145	33.3	33.3 ± 1.1	
cyclohexanone	99	25.9	22.2 ± 0.5	6-nitrooxy-hexanal cyclohexyl nitrate 3-hydroxypentane-1,5-dial
cyclohexyl nitrate	83, 101	15.4	13.2 ± 1.0	3-hydroxy-5-nitrooxy-pentanal (101) pentane-1,5-dial (101)
3-hydroxyhexane-1,6-dial	71, 85, 113	<8.7	<7.5 ± 0.3	4-hydroxy-butanal (71) 2-hydroxybutane-1,4-dial (85)
hexane-1,6-dial	97, 115	6.9	5.9 ± 0.2	6-hydroxy-3-nitrooxy-hexanal (115) 6-nitrooxy-hexanal (115) 2,3-dihydroxypentane-1,5-dial (115)
unidentified	129	2.8	2.8 ± 0.1	
2-keto-7-nitrooxy-heptanal (route B)	127	1.4	1.4 ± 0.1	nitrooxy-cyclohexanecarbaldehyde
HCHO	31	9.1	1.3 ± 0.2	
HCOOH	47	4.2	0.6 ± 0.1	
2,4-dihydroxy-butanal	87	1.1	0.6 ± 01	
total VOCs			88.7	
CO	(FT-IR)	17.4	2.5 ± 0.3	
CO_2	(FT-IR)	40.7	5.8 ± 0.2	
total			**97.0**	

A. Part of the discrepancy may also be explained by cyclohexanone formation via route B (see Scheme 4). HCO elimination from an acyclic β-carbonyl alkoxy radical has been previously observed as a dominant reaction pathway.[18] The same process may occur for cyclohexoxy carbonyl radicals. The presence of interfering species at *m*/*z* 99 may also partly explain the discrepancy in cyclohexanone yields. A fraction of the ion signal at *m*/*z* 99 may derive from 6-nitrooxy-hexanal ($[MH - HNO_3]^+$). Traces of the molecular ion (MH^+) at *m*/*z* 162 have been observed, suggesting that this species is present. Takagi et al.[25] report an overall acyclic nitrate yield of 11% from cyclohexane photooxidation. Acyclic nitrates are believed to consist mainly of 6-nitrooxy-hexanal, 6-hydroxy-3-nitrooxy-hexanal, and 3-hydroxy-5-nitrooxy-pentanal (see Scheme 4). A minor (<1%) fraction of the carbon yield at *m*/*z* 99 may be attributed to cyclohexyl nitrate ($[MH - HNO_2]^+$), if CI pathways are assumed to be similar to those observed for alkyl nitrates. 3-Hydroxypentane-1,5-dial may also give rise to a signal at *m*/*z* 99 ($[MH - H_2O]^+$). This compound may be formed from the decomposition of 3-hydroxyhexane-1,6-dial (see below).

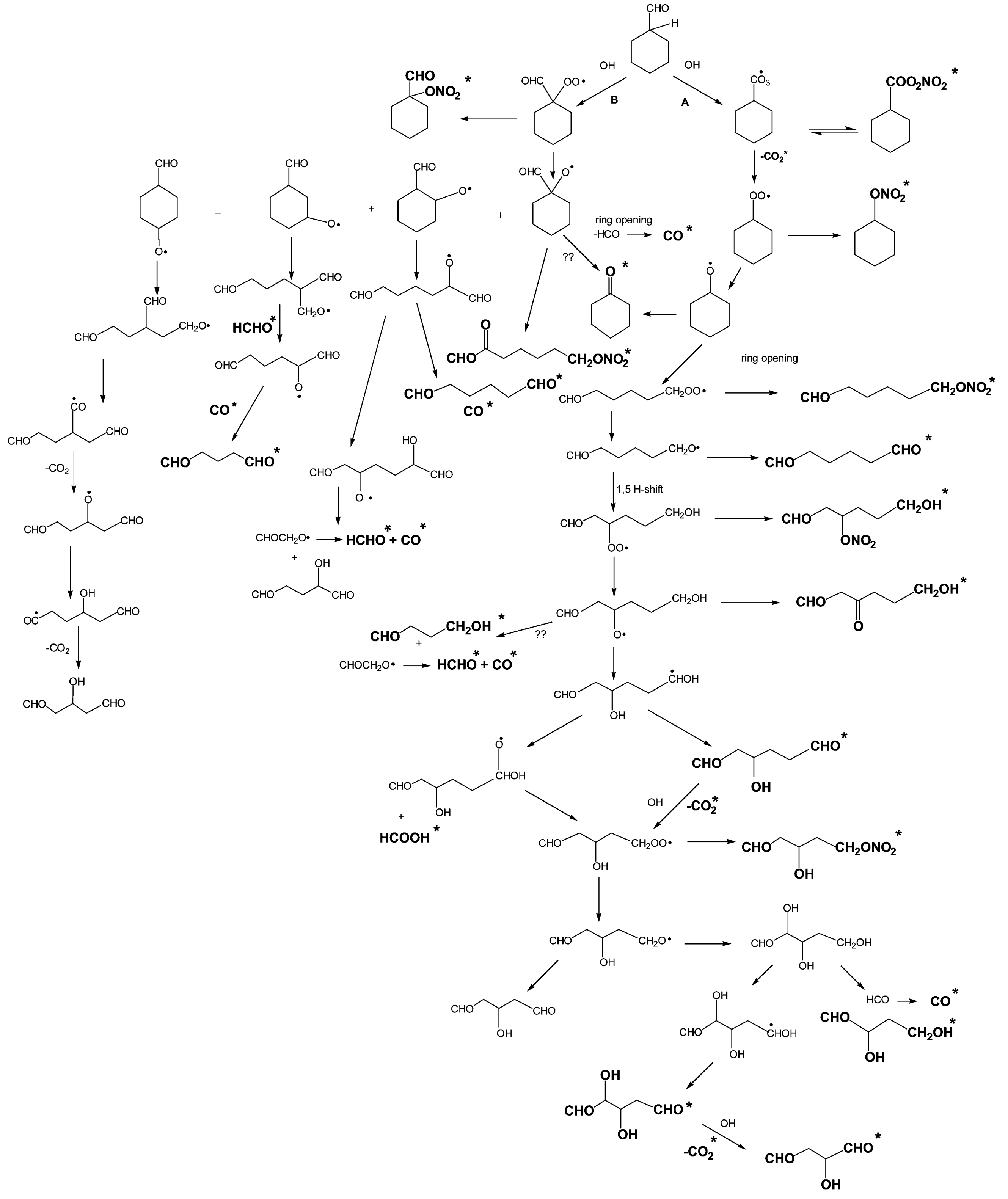
Another relevant cyclic product is cyclohexyl nitrate observed at *m*/*z* 83 ($[MH - HNO_3]^+$) and its hydrate at *m*/*z* 101 with a total carbon yield of 13.2%. The NPCCH contribution to the ion signal at *m*/*z* 83 has been subtracted. Again, the nitrate yield has a higher uncertainty as minor CI pathways have not been taken into account. A minor fraction of the *m*/*z* 101 signal may be attributable to pentane-1,5-dial and to 3-hydroxy-5-nitrooxy-pentanal ($[MH - HNO_3]^+$). Traces of the molecular ion (MH^+) at *m*/*z* 164 have been observed, suggesting that 3-hydroxy-5-nitrooxy-pentanal is present. The cyclohexyl nitrate yield relative to cyclohexyl radical loss is 65%, again significantly higher than previously reported values: 16 ± 2,[17] 16 ± 1,[74] 16 ± 4,[21] and 15 ± 4%.[20] This discrepancy may again be explained by the presence of interfering species at *m*/*z* 83 and by the fact that the SAR method[16] underestimates the fractional abundance of route A. Hanson et al.[18] report a significantly lower cyclohexyl nitrate yield of 3.2%, but HNO_3 loss in their PTR-MS study was not considered as a possible CI pathway for cyclohexyl nitrate.

CO and CO_2 account for 2.4 and 5.8% of the carbon yield, respectively. CO_2 arises primarily from the decomposition of cyclohexylcarboxy radicals. Possible pathways for minor CO formation via route B are shown in Scheme 4.

Some minor acyclic products have also been detected. However, compound assignment is ambiguous.

Aschmann et al.[17] and Hanson et al.[18] identified 3-hydroxyhexane-1,6-dial as a major decomposition product of cyclohexoxy radicals applying similar CI methods as those used here. In both studies, which involved the OH-radical- and Cl-atom-initiated oxidation of cyclohexane, 3-hydroxyhexane-1,6-dial was predominantly detected at *m*/*z* 113 ($[MH - H_2O]^+$). In the present study, the reactant cyclohexanecarbaldehyde produced an intense ion signal at *m*/*z* 113 (MH^+), hindering the detection of 3-hydroxyhexane-1,6-dial. However, cyclohexanecarbaldehyde also formed an ion signal at *m*/*z* 95 ($[MH - H_2O]^+$) and the *m*/*z* 113:*m*/*z* 95 signal ratio remained constant throughout the reaction with OH radicals. Considering the uncertainty in this analysis, it can be concluded that no products with a carbon yield ≥2% were formed at *m*/*z* 113. Additional experiments were performed under the same experimental conditions using cyclohexane as a reactant. A reactive intermediate product was observed at *m*/*z* 113 with only low yield. In addition to the *m*/*z* 113 ion signal, Hanson et al.[18] assigned fragment ion signals at *m*/*z* 71 and *m*/*z* 85 to 3-hydroxyhexane-1,6-dial. In the present study, the two ion signals account for 2.1 and 3.4% of the carbon yield, respectively. Increasing *m*/*z* 85:*m*/*z* 113 and *m*/*z* 71:*m*/*z* 113 ion signal ratios were observed in the OH−cyclohexane experiments, suggesting the presence of additional species at *m*/*z* 85 and *m*/*z* 71. A potential compound with a *m*/*z* 85 signal is 2-hydroxybutane-1,4-dial ($[MH - H_2O]^+$) which arises from the decomposition of 3-hydroxyhexane-1,6-dial. The ion signal at *m*/*z* 71 may derive from 4-hydroxy-butanal ($[MH - H_2O]^+$). The carbon yields of 2.1, 3.4, and ≤2.0% for *m*/*z* 71, *m*/*z* 85, and *m*/*z* 113, respectively, result in an upper limit of 7.5% carbon yield for 3-hydroxyhexane-1,6-dial for the OH−cyclohexanecarbaldehyde reaction. This corresponds to an upper limit of 36.7% for the 3-hydroxyhexane-1,6-dial yield relative to cyclohexyl radical decomposition, which is similar to the 39% yield reported by Hanson et al.[18] However, 3-hydroxyhexane-1,6-dial loss due to secondary reaction with OH has to be considered. The OH−cyclohexanecarbaldehyde reaction rate coefficient is 3.75×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (this work), and the OH−3-hydroxyhexane-1,6-dial rate coefficient is estimated to be 8.04×10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[16,75] This results in a corrected 3-hydroxyhexane-1,6-dial yield of 76.7% at 50% cyclohexanecarbaldehyde conversion. Secondary reactions are

SCHEME 4: Degradation Paths in the OH-Initiated Oxidation of Cyclohexanecarbaldehyde



insignificant in the study of Hanson et al.[18] Again, the discrepancy suggests that the SAR method[16] used underestimates the fractional abundance of route A.

Ion signals at *m*/*z* 115 (MH^+) and *m*/*z* 97 ($[MH - H_2O]^+$) with a total carbon yield of 5.9% have been assigned to hexane-1,6-dial. The given hexane-1,6-dial yield should, however, be regarded as an upper limit, since other species are expected to contribute significantly to the signal at *m*/*z* 115: 6-hydroxy-3-nitrooxy-hexanal ($[MH - HNO_3]^+$), 6-nitrooxy-hexanal ($[MH - HNO_2]^+$), and also 2,3-dihydroxypentane-1,5-dial ($[MH - H_2O]^+$), which is the main decomposition product of 3-hydroxyhexane-1,6-dial.

Traces of several other compounds have been detected. Signals at *m*/*z* 31 and *m*/*z* 47 are assigned to HCHO (MH^+) and HCOOH (MH^+) with a carbon yield of 1.0 and 0.6%, respectively. The ion signal at *m*/*z* 87 accounts for a carbon yield of 0.6% and has been tentatively assigned to 2,4-dihydroxy-butanal ($[MH - H_2O]^+$).

The signal at *m*/*z* 129 accounting for a carbon yield of 2.8% corresponds to the unidentified *m*/*z* 87, *m*/*z* 101, and *m*/*z* 115 signals observed for C_3-C_5 cycloalkanecarbaldehydes and will be discussed later.

As discussed above, the decomposition via route A was calculated to amount to 57% using the SAR method.[16] However, the observed cyclohexanone and cyclohexyl nitrate yields relative to cyclohexyl radical decomposition are all well above reported literature values, indicating that the SAR method[16] underestimates the fractional abundance of route A. Quantitative estimates of the cyclohexyl radical decomposition products are thus difficult, also because unambiguous product identification is not possible. It can just be concluded that a relevant fraction of the OH−cyclohexanecarbaldehyde reaction proceeds via H_{ald} abstraction, giving NPCCH as the major reaction product with a yield of ∼33%. The major products arising from cyclohexylperoxy radicals are cyclohexyl nitrate and cyclohexanone. The minor products of route A are discussed in detail above.

A detailed degradation scheme of route B is given in the Supporting Information (Scheme VIIS). Most of the possible reaction products of route B are identical to those formed along route A: 2- and 3-hydroxy-pentane-1,5-dial, hexane-1,6-dial, and pentane-1,5-dial. The ion signal at *m*/*z* 127 accounting for 1.4% of the carbon yield seems to be the only signal unequivocally attributable to route B. It has been tentatively assigned to 2-keto-7-nitrooxy-heptanal ($[MH - HNO_3]^+$) or isomeric species with the sum formula $C_{12}H_{11}O_5N$. This is consistent with the finding that no *m*/*z* 127 ion signal was observed in the OH−cyclohexane experiment. Signal traces at *m*/*z* 174 may derive from nitrooxy-cyclohexanecarbaldehyde. HNO_2 loss from this species would also produce an ion signal at *m*/*z* 127.

The formation of large multifunctional compounds in the reaction of OH radicals with cyclohexanecarbaldehyde, the largest of the studied aldehydes, may lead to gas-to-particle conversion. Particle formation was monitored using a differential mobility particle analyzer. The aerosol yield was found to be insignificant under the given experimental conditions.

Conclusions

The rate coefficients for the gas phase reaction of NO_3 and OH radicals with C_3-C_6 cycloalkanecarbaldehydes have been measured for atmospheric conditions. Quantitative product analyses of the OH−cycloalkanecarbaldehyde reactions were carried out using FT-IR spectroscopy and PTR-MS. The measured carbon balance was in the range 89−97%.

The identified reaction products include mainly NPCCAs, followed by cycloalkyl nitrates and cycloketones. Ring opening produces carbonyl alkoxy radicals, $CHO(CH_2)_nO^{\bullet}$, which depending on the number of carbons of the aliphatic chain undergo unimolecular decomposition (C−C fragmentation, observed only for C_3), reaction with O_2, or isomerization (intramolecular H shift). Isomerization prevails when the number of carbon atoms is ≥ 4.[51,54,58−60,65,66,71,76] This is confirmed by the high carbon yield of 3-hydroxy-propanal in the degradation of cyclobutanecarbaldehyde. Unimolecular decomposition through −CHO elimination was found to be the dominant reaction pathway for β-carbonyl alkoxy radicals, $CHOCH(O^{\bullet})CH_2CH_2CH_2OH$.

Remarkably large yields of CO and HCHO have been found in the decomposition of cyclopropanecarbaldehyde and are only partly attributable to secondary OH chemistry. CO and HCHO formation from NPCCPr decomposition with the UV lights off provided experimental evidence for the unimolecular decomposition of $CHOCH_2CH_2O^{\bullet}$ radicals. For larger carbonyl alkoxy radicals, unimolecular decomposition was not observed.

Acyclic and cyclic nitrates have been observed. While it was difficult to quantify the yield of acyclic nitrates, the yield of cycloalkyl nitrates was found to increase with the ring size: cyclopropyl nitrate (<1%), cyclobutyl nitrate (<1%), cyclopentyl nitrate (3.7%), and cyclohexyl nitrate (13.2%). A similar trend has been observed for *n*-alkyl nitrates.[77] Cycloketone yields were also found to increase with ring size, but accurate quantification was hindered by the presence of interfering species.

Ring opening was found to be the only reaction pathway for the cyclopropoxy and cyclobutoxy radicals formed during OH degradation of the respective cycloalkanecarbaldehydes. For the cyclopentoxy radical, ring opening is the dominant decomposition pathway, as already reported by Orlando et al.,[20] Hanson et al.,[18] and Takagi et al.[25] For the cyclohexoxy radical, competition between ring opening and the formation of cyclohexanone was observed.[17,18,20]

The reaction of OH radicals with cycloalkanecarbaldehydes may occur via H abstraction from the aldehydic group (route A) or to a lesser extent via H abstraction from the ring (route B). Using the SAR developed by Kwok and Atkinson,[16] the fractional contribution of route B was calculated to be ∼1, 11, 30, and 43% for cyclopropanecarbaldehyde, cyclobutanecarbaldehyde, cyclopentanecarbaldehyde, and cyclohexanecarbaldehyde, respectively. The experimental data did not allow evaluation of the relative contribution of route B. However, in the C_5 and C_6 cycloalkanecarbaldehyde experiments, observed product yields relative to cycloalkyl radical decomposition were well above reported literature values, indicating that the SAR method[16] overestimates the fractional abundance of route B.

For cyclopropanecarbaldehyde and cyclobutanecarbaldehyde, the individual contributions of characteristic reaction products arising from route B (e.g., keto-dialdehydes or keto-nitrooxy-aldehydes) are expected to be below the 1% signal-based yield limit set for inclusion in the data analysis. An unambiguous identification of such low-yield products goes beyond the analytical capabilities of the PTR-MS technique.

For cyclopentanecarbaldehyde and cyclohexanecarbaldehyde, the fractional contribution of route B is expected to be substantial. However, the same product ion signals or even the same products may be formed via both reaction routes. The only product ion signal clearly attributable to route B was observed in the cyclohexanecarbaldehyde experiment. The ion signal at *m*/*z* 127 accounted for 1.4% carbon yield and has been tentatively assigned to 2-keto-7-nitrooxy-heptanal.

The origin of the signal series *m*/*z* 87, *m*/*z* 101, *m*/*z* 115, and *m*/*z* 129 observed in the oxidation of cyclopropanecarbaldehyde, cyclobutanecarbaldehyde, cyclopentanecarbaldehyde, and cyclohexanecarbaldehyde has not been identified. Their contribution in terms of carbon yield is steadily increasing from 0.9% for cyclopropanecarbaldehyde to 2.8% for cyclohexanecarbaldehyde. Thermal decomposition studies indicate that the signals cannot be associated with NPCCAs or peroxyalkyl nitrate species. However, a rapid decay was observed when additional NO was added at the end of the experiment and UV lights were off. Such decay would be expected only for NPCCAs or peroxyalkyl nitrate species. The identity of these signals remains unknown.

This work demonstrates the applicability of PTR-MS for quantitative detection of volatile organic reaction products which cannot be achieved using other CI methods (e.g., API-MS) or traditional analytical techniques unless authentic calibration standards are used. However, PTR-MS is not a truly species-specific method of analysis and unambiguous compound identification is difficult.

Acknowledgment. A.W. thanks the Verein zur Förderung der wissenschaftlichen Ausbildung und Tätigkeit von Südtirolern an der Landesuniversität Innsbruck for postdoctoral support. The authors thank the anonymous referees for their extensive comments and valuable suggestions.

Supporting Information Available: Possible degradation paths in the OH-initiated oxidation of cyclobutanecarbaldehyde, cyclopentanecarbaldehyde, and cyclohexanecarbaldehyde; plot of the time evolution for reagent and major products in the cyclobutanecarbaldehyde−OH radical reaction; and PTR-MS product ion signals, relative signal abundances, and sensitivities of target compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinebrecher, R.; Tallamaraju, R.; Taylor, J.; Zimmermann, P. *J. Geophys. Res., [Atmos.]* **1995**, *100*, 8873.

(2) Atkinson, R.; Aschmann, S. M. *J. Atmos. Chem.* **1993**, *16*, 337.

(3) Bonn, B.; Schuster, G.; Moortgat, G. K. *J. Phys. Chem. A* **2002**, *106*, 2869.

(4) Calogirou, A.; Larsen, B. R.; Kotzias, D. *Atmos. Environ.* **1999**, *33*, 1423.

(5) Griffin, R. J.; Cocker, D. R., III.; Flagan, R. C.; Seinfeld, J. H. *J. Geophys. Res., [Atmos.]* **1999**, *104*, 3555.

(6) Hakola, H.; Arey, J.; Aschmann, S. M.; Atkinson, R. *J. Atmos. Chem.* **1994**, *18*, 75.

(7) Hoffmann, T.; Odum, J. R.; Bowman, F.; Collins, D.; Klockow, D.; Flagan, R. C.; Seinfeld, J. H. *J. Atmos. Chem.* **1997**, *26*, 189.

(8) Larsen, B. R.; Di Bella, D.; Glasius, M.; Winterhalter, R.; Jensen, N. R.; Hjorth, J. *J. Atmos. Chem.* **2001**, *38*, 231.

(9) Jang, M.; Kamens, R. M. *Atmos. Environ.* **1998**, *33*, 459.

(10) Novakov, P., Penner, J. *Nature* **1993**, *265*, 823.

(11) Yu, J.; Cocker, D. R., III; Griffin, R. J.; Flagan, R. C.; Seinfeld, J. H. *J. Atmos. Chem.* **1999**, *34*, 207.

(12) Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Hurley, M. D.; Goto, M.; Kawasaki, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2189.

(13) Tuazon, E. C.; Aschmann, S. M.; Nguyen, M. V.; Atkinson, R. *Int. J. Chem. Kinet.* **2003**, *35*, 415.

(14) D'Anna, B.; Bakken, V.; Are Beukes, J.; Nielsen, C. J.; Brudnik, K.; Jodkowski, J. T. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1790.

(15) Cameron, M.; Sivakumaran, V.; Dillon, T. J.; Crowley, J. N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3628.

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

(17) Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **1997**, *101*, 8042.

(18) Hanson, D.; Orlando, J.; Noziere, B.; Kosciuch, E. *Int. J. Mass Spectrom.* **2004**, *239*, 147.

(19) McEwen, C. N.; Druliner, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 8579.

(20) Orlando, J. J.; Iraci, L. T.; Tyndall, G. S. *J. Phys. Chem. A* **2000a**, *104*, 5072.

(21) Platz, J.; Sehested, J.; Nielsen, O. J.; Wallington, T. J. *J. Phys. Chem. A* **1999**, *103*, 2688.

(22) Rowley, D. M.; Lesclaux, R.; Lightfoot, P. D.; Noziere, B.; Wallington, T. J.; Hurley, M. D. *J. Phys. Chem.* **1992**, *96*, 4889.

(23) Rowley, D. M.; Lightfoot, P. D.; Lesclaux, R.; Wallington, T. J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3221.

(24) Rowley, D. M.; Lightfoot, P. D.; Lesclaux, R.; Wallington, T. J. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1369.

(25) Takagi, H.; Washida, N.; Bandow, H.; Akimoto, H.; Okuda, M. *J. Phys. Chem.* **1981**, *85*, 2701.

(26) D'Anna, B.; Andresen, O.; Gefen, Z.; Nielsen, C. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3057.

(27) Ballesteros, B.; Jensen, N. R.; Hjorth, J. *J. Atmos. Chem.* **2002**, *43*, 135.

(28) Griffith, D. W. T. *Appl. Spectrosc.* **1996**, *50*, 59.

(29) Rothman, L. S.; Rinsland, C. P.; Goldman, A.; Massie, S. T.; Edwards, D. P.; Flaud, J. M.; Perrin, A.; Camy-peyret, C.; Dana, V.; Mandin, J. Y.; Schroeder, J.; McCann, A.; Gamache, R. R.; Wattson, R. B.; Yoshino, K.; Chance, K. V.; Jucks, K. W.; Brown, L. R.; Nemtchinov, V.; Varanasi, P. *J. Quant. Spectrosc. Radiat. Transfer* **1998**, *60*, 665.

(30) Lindinger, W.; Jordan, A. *Chem. Soc. Rev.* **1998**, *27*, 347.

(31) Hewitt, C. N.; Hayward, S.; Tani, A. *J. Environ. Monit.* **2003**, *5*, 1.

(32) Jensen, N. R. V., J.; Karl, T.; Prazeller, P.; Wisthaler, A.; Larsen, B. R.; Seufert, G.; Hjorth, J. *Contributions: 1st International Conference on Proton-Transfer Reaction Mass Spectrometry and Its Applications*, 2003.

(33) De Gouw, J.; Warneke, C.; Karl, T.; Eerdekens, G.; van der Veen, C.; Fall, R. *Int. J. Mass Spectrom.* **2003**, *223*−*224*, 365.

(34) Kwok, E. S. C.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **1995b**, *29*, 2467.

(35) Wisthaler, A. Unpublished results.

(36) Kames, J.; Schurath, U.; Flocke, F.; Volz-Thomas, A. *J. Atmos. Chem.* **1993**, *16*, 349.

(37) Hansel, A.; Wisthaler, A. *Geophys. Res. Lett.* **2000**, *27*, 895.

(38) Hatakeyama, S.; Tanonaka, T.; Weng, J.; Bandow, H.; Takagi, H.; Akimoto, H. *Environ. Sci. Technol.* **1985**, *19*, 935.

(39) Hansel, A.; Singer, W.; Wisthaler, A.; Schwarzmann, M.; Lindinger, W. *Int. J. Mass Spectrom. Ion Processes* **1997**, *167*/*168*, 697.

(40) Noyes, W. A. *Org. Synth.* **1943**, *Coll. Vol. 2*, 108.

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

(42) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(43) Johnson, M. R.; Rickborn, B. *Org. Synth.* **1971**, *51*, 11.

(44) York, D. *Can. J. Phys* **1966**, *44*, 1079.

(45) 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* **1999**, *28*, 191.

(46) Prinn, R. G.; Huang, J.; Weiss, R. F.; Cunnold, D. M.; Fraser, P. J.; Simmonds, P. G.; McCulloch, A.; Harth, C.; Salameh, P.; O'Doherty, S.; Wang, R. H. J.; Porter, L.; Miller, B. R. *Science* **2001**, *292*, 1882.

(47) Allan, B. J.; Plane, J. M. C.; Coe, H.; Shillito, J. *J. Geophys. Res., [Atmos.]* **2002**, *107*, ACH11/1.

(48) Atkinson, R. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459.

(49) 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.

(50) Ferenac, M. A.; Davis, A. J.; Holloway, A. S.; Dibble, T. S. *J. Phys. Chem. A* **2003**, *107*, 63.

(51) Devolder, P. *J. Photochem. Photobiol., A* **2003**, *157*, 137.

(52) Mereau, R.; Rayez, M.-T.; Caralp, F.; Rayez, J.-C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3765.

(53) Meunier, N.; Doussin, J. F.; Chevallier, E.; Durand-Jolibois, R.; Picquet-Varrault, B.; Carlier, P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4834.

(54) Baldwin, A. C.; Barker, J. R.; Golden, D. M.; Hendry, D. G. *J. Phys. Chem.* **1977**, *81*, 2483.

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

(56) Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1907.

(57) Orlando, J. J.; Tyndall, G. S.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **2000b**, *104*, 11578.

(58) Jungkamp, T. P. W.; Smith, J. N.; Seinfeld, J. H. *J. Phys. Chem. A* **1997**, *101*, 4392.

(59) Hein, H.; Hoffmann, A.; Zellner, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3743.

(60) Eberhard, J.; Mueller, C.; Stocker, D. W.; Kerr, J. A. *Environ. Sci. Technol.* **1995**, *29*, 232.

(61) Orlando, J. J.; Tyndall, G. S.; Bilde, M.; Ferronato, C.; Wallington, T. J.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **1998**, *102*, 8116.

(62) Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **1999**, *103*, 1768.

(63) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *Chem. Phys. Lett.* **1981**, *80*, 499.

(64) Baker, J.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **2004**, *108*, 7032.

(65) Johnson, D.; Cassanelli, P.; Cox, R. A. *J. Phys. Chem. A* **2004**, *108*, 519.

(66) Mereau, R.; Rayez, M.-T.; Caralp, F.; Rayez, J.-C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4828.

(67) Houk, K. N.; Tucker, J. A.; Dorigo, A. E. *Acc. Chem. Res.* **1990**, *23*, 107.

(68) Francisco, C. G.; Freire, R.; Herrera, A. J.; Perez-Martin, I.; Suarez, E. *Org. Lett.* **2002**, *4*, 1959.

(69) Henon, E.; Bohr, F.; Sokolowski-Gomez, N.; Caralp, F. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5431.

(70) Peeters, J.; Fantechi, G.; Vereecken, L. *J. Atmos. Chem.* **2004**, *48*, 59.

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

(72) IUPAC. http://www.iupac-kinetic.ch.cam.ac.uk/.

(73) Atkinson, R.; Aschmann, S. M.; Arey, J.; Shorees, B. *J. Geophys. Res., [Atmos.]* **1992**, *97*, 6065.

(74) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 1085.

(75) Bradley, W. R.; Wyatt, S. E.; Wells, J. R.; Henley, M. V.; Graziano, G. M. *Int. J. Chem. Kinet.* **2001**, *33*, 108.

(76) Vereecken, L.; Peeters, J. *J. Chem. Phys.* **2003**, *119*, 5159.

(77) Arey, J.; Aschmann, S. M.; Kwok, E. S. C.; Atkinson, R. *J. Phys. Chem. A* **2001**, *105*, 1020.

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