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An FT-IR study of the isomerization of 1-butoxy radicals under atmospheric conditions[☆]

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Dedicated to Professor R.P. Wayne.

Abstract

Relative rate-studies of the reactions of 1-butoxy radicals have been carried out using a 47 L static reactor with detection of end products by FT-IR spectroscopy. Experiments were performed at 700 torr total pressure and over the temperature range 253–295 K. The chemistry of 1-butoxy is characterized by a competition between reaction with oxygen $CH_3CH_2CH_2CH_2O^{\bullet} + O_2 \rightarrow n\text{-}C_3H_7CHO + HO_2$ (R2), which yields butanal and isomerization $CH_3CH_2CH_2CH_2O^{\bullet} \rightarrow {}^{\bullet}CH_2CH_2CH_2CH_2OH$ (R3), to form a hydroxylated carbonyl-product. A reference spectrum attributed to the product of 1-butoxy isomerization was obtained and used to determine the competition between 1-butoxy isomerization versus reaction with oxygen. The results indicate that isomerization is the dominant fate of 1-butoxy radicals at ambient temperature and pressure and that its importance decreases with decreasing temperature. The rate-coefficient ratio k_3/k_2 (molecule cm^{-3}) = $5.5 \times 10^{23} \exp[(-25.1 \pm 0.9\,\text{kJmol}^{-1})/RT]$ was obtained. This agrees with other estimates based on methods without monitoring of the isomerization product.

Keywords: 1-Butoxy; Isomerization; Tropospheric oxidation

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1. Introduction

Alkoxy radicals (RO) play an important role in the atmospheric degradation of volatile organic compounds (VOC) [1]. Under tropospheric conditions, they exhibit three main modes of reaction: (i) reaction with oxygen; (ii) decomposition; (iii) isomerization [1–5]. These three reaction pathways are illustrated in Scheme 1 for the 1-butoxy radical. The competition between (i) and (iii) determines the products formed from the photo-oxidation of a given VOC and has important implications in terms of ozone, smog and aerosol generation. Generally, the structure of an alkoxy radical determines which reactions are favoured under given conditions of temperature and pressure. For example, reaction with oxygen, which yields a carbonyl-compound and HO_2, proceeds via abstraction of an α-hydrogen and is available only to primary and secondary radicals. The rate of decomposition by C–C scission can span over several orders of magnitude and typically increases with increasing substitution of the α- or β-carbon. Isomerization, in which the O radical centre abstracts a H-atom in position four or five relative to the C–O group, proceeds via formation of a 6- or 7-membered transition state and requires a straight chain of at least four carbons. The importance of isomerization increases with the length of the carbon chain and can be the dominant fate for alkoxy radicals $\geq C_6$ [6,7].

The main challenge to the study of the isomerization of alkoxy radicals lies in the detection and quantification of the high molecular weight multifunctional carbonyl-products of this reaction. Recently, two different methods have been employed: derivatization of the carbonyl-group with analysis by chromatography [8–11] and in situ atmospheric pressure ionization mass spectrometry (APIMS) analysis of the protonated molecular ion $[M+H]^+$, the fragment ion $[M+H-H_2O]^+$ and as the NO_2^- adduct [6,7,12]. An alternative approach is to detect the products of isomerization by fourier transform infrared spectroscopy (FT-IR). This method was employed by Niki et al. [13] who

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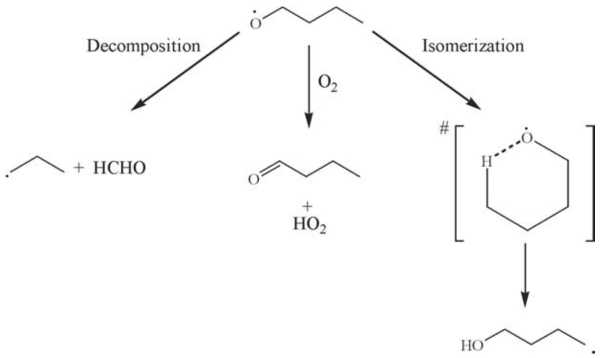


Scheme 1.

identified features in the residual spectrum of the photolysis of 1-butylnitrite/N_2/O_2 mixtures that were attributed to the product of 1-butoxy isomerization. 1-butoxy is the simplest radical that can undergo isomerization and is a useful model for the isomerization of larger alkoxy radicals. In the majority of published studies, the competition between isomerization and reaction with oxygen for 1-butoxy has been estimated from measurements of the yields of butanal, the product of the reaction with O_2, as a function of oxygen pressure [13–17]. The present study was undertaken to extend the work of Niki et al. [13] and to determine a reference spectrum for the product of 1-butoxy isomerization by FT-IR spectroscopy so as to obtain a more direct determination of the relative rate-coefficient for isomerization versus reaction with oxygen for this radical.

2. Experimental

All experiments were conducted in a 2-m long, 47-L stainless steel chamber, interfaced to a BOMEM DA3.01 fourier transform infrared spectrometer [18]. The chamber is equipped with Hanst-type multipass optics which provided an IR analysis beam path length of 32.6 m. Chilled ethanol (from a NESLAB Model EX-250HT cooler) was circulated around the cell to control the temperature, which was varied over the range (253–295 K) and was monitored by eight thermocouples along the length of the cell.

All experiments involved the photolysis of mixtures of: 1-butylnitrite, ($(1.6 \pm 0.1) \times 10^{15}$ molecule cm^{-3}); NO, ($(7.4 \pm 0.7) \times 10^{14}$ molecule cm^{-3}); O_2 (10–600 Torr); N_2 (100–700 Torr) at a total pressure of (700 ± 10) Torr. Minor components of the gas mixtures were flushed into the cell with N_2 from smaller calibrated volumes, which were part of a standard greaseless vacuum system. A cw Xe-arc lamp, filtered with a Corning 7–54 filter to provide radiation in the near UV (350 ± 50 nm), was used for photolysis of the gas mixtures and the temporal profiles of starting material and oxidation products were monitored by FT-IR spectroscopy. Spectra were recorded at intervals of 5 min over the range 800–3000 cm^{-1} at a spectral resolution of 1 cm^{-1} and were obtained from the co-addition of 200 scans. Mixtures were irradiated for 25–30 min and the photolytic intensity corresponded to an observed decay for 1-butylnitrite of $(1.0 \pm 0.2) \times 10^{-4}$ s^{-1}.

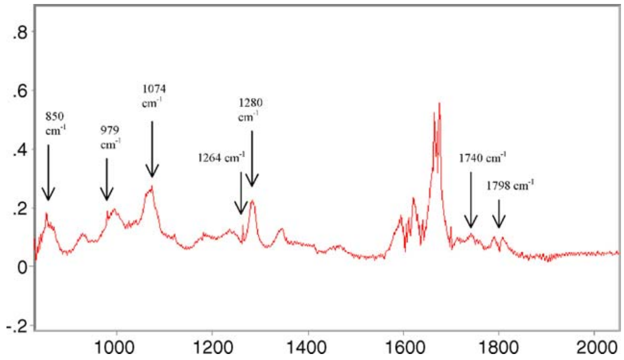


Fig. 1. Residual spectrum from the photolysis of 1-butylnitrite/NO/O_2/N_2 mixtures in 11 Torr oxygen, 700 Torr total pressure at 295 K.

Concentrations of reactants and products were determined by spectral subtraction of reference spectra, which were recorded in the presence of 700 Torr of nitrogen. A reference spectrum for 4-hydroxybutanal (Fig. 1) was obtained from the residual spectrum from the photolysis of 1-butylnitrite and NO mixtures in 2% oxygen at a total pressure of 700 Torr made up with nitrogen. Under these conditions, the branching ratio for the isomerization reaction, $k_3/(k_2 + k_3)$, is predicted to be ≥95% [2,3]. The concentration of 4-hydroxybutanal was determined from a mass balance with an overall estimated error of ±20%, mainly due to uncertainties in the quantification of Δ[1-butylnitrite] and Δ[4-hydroxybutylnitrate], the major expected side product in the conversion of the $CH_2CH_2CH_2CH_2OH$ radical to 4-hydroxybutanal. The spectrum in Fig. 1 is very similar to the product spectrum reported by Niki et al. [13]. Two sharp features at 979 and 1074 cm^{-1}, which correspond to a C-OH stretching band (1000–1100 cm^{-1}) and a few broad bands were observed. In particular, a carbonyl-type absorption band near 1740 cm^{-1} was present. The two bands at 850 and 1280 cm^{-1} are characteristic of nitrates, the feature at 1264 cm^{-1} is that of HONO and the absorption centred at 1798 cm^{-1} was due to an NOCl impurity present in the chamber. NO_2 and 1-butylnitrite absorb strongly in the region 1500–1700 cm^{-1} and no spectral information was obtained in this region. The residual spectrum of Fig. 1 was tested against the product spectrum from the photo-oxidation of cyclopentane, which yields 4-hydroxybutanal [19,20]. Mixtures of cyclopentane (2.1×10^{15} molecule cm^{-3}), Cl_2 (1.4×10^{15} molecule cm^{-3}), NO (7.4×10^{14} molecule cm^{-3}) and 11 Torr O_2 in 700 Torr N_2 were photolyzed in the FT-IR chamber over a period of 20–30 min at two different temperatures (271 and 340 K). A band comprising two IR spectral features at 979 and 1074 cm^{-1} showed similar relative intensity and contours to those observed in Fig. 1 hence this region was used to quantify 4-hydroxybutanal.

1-Butylnitrite was synthesized by the reaction of 1-butanol with nitrous acid. Peroxy-*n*-butyrylnitrate, PnBN, (n-$C_3H_7C(O)OONO_2$) was prepared in ppm concentrations in the long path cell by the Cl-initiated oxidation of butanal in the presence of NO_2. Irradiation of a mixture containing butanal (4.4×10^{14} molecule cm^{-3}), NO (4.4×10^{14} molecule cm^{-3}) and Cl_2 (1.4×10^{15} molecule cm^{-3}), in 700 Torr air over a period of 12 min resulted in 75% conversion of butanal to n-$C_3H_7C(O)OONO_2$. Other chemicals were obtained commercially: butanal Aldrich, 99%; 1-butylnitrate Aldrich, >95%; NO 99%, Linde; O_2 99.99%, U.S. Welding, UHP; N_2, boil-off from LN_2 dewar, U.S. Welding.

3. Results and discussion

Following the irradiation of 1-butylnitrite/NO/O_2/N_2 mixtures, the main reactions that are expected to take place are as follows:

$$CH_3CH_2CH_2CH_2ONO + h\nu \rightarrow CH_3CH_2CH_2CH_2(O^\bullet) + NO \quad (1)$$

$$CH_3CH_2CH_2CH_2(O^\bullet) + O_2 \rightarrow n\text{-}C_3H_7CHO + HO_2 \quad (2)$$

$$CH_3CH_2CH_2CH_2(O^\bullet) \rightarrow {}^\bullet CH_2CH_2CH_2CH_2OH \quad (3)$$

$${}^\bullet CH_2CH_2CH_2CH_2OH + O_2 \rightarrow CH_2(O_2{}^\bullet)CH_2CH_2CH_2OH \quad (4)$$

$$CH_2(O_2{}^\bullet)CH_2CH_2CH_2OH + NO \rightarrow CH_2(O^\bullet)CH_2CH_2CH_2OH + NO_2 \quad (5a)$$

$$CH_2(O_2{}^\bullet)CH_2CH_2CH_2OH + NO \rightarrow CH_2(ONO_2)CH_2CH_2CH_2OH \quad (5b)$$

$$CH_2(O^\bullet)CH_2CH_2CH_2OH \rightarrow CH_2(OH)CH_2CH_2(C^\bullet)HOH \quad (6)$$

$$CH_2(OH)CH_2CH_2(C^\bullet)HOH + O_2 \rightarrow CH_2(OH)CH_2CH_2CHO + HO_2 \quad (7)$$

$$CH_3CH_2CH_2CH_2(O^\bullet) + NO_2 \rightarrow CH_3CH_2CH_2CH_2ONO_2 \quad (8)$$

Decomposition of 1-butoxy, although possible, is too slow to compete and is believed to be negligible under our experimental conditions [5]. The main products observed included butanal, 4-hydroxybutanal and nitrate compounds. Small amounts of peroxy n-butyrylnitrate (PnBN), formaldehyde, formic acid, CO and CO_2 were also measured and NO_2, HONO, HNO_3 were detected, but not quantified. At 295 K, (90 ± 15)% of the reacted 1-butylnitrite could be accounted for in all the experiments. At 253 K, the lowest temperature studied, this fraction was smaller, (70 ± 10)%, possibly due to wall losses of compounds of lower volatility and to the formation of small amounts of peroxynitrates. In Fig. 2 typical FT-IR spectra of mixtures of 1-butylnitrite/NO/O_2/N_2 in 700 Torr total pressure before and after 30 min irradiation are shown in A and B. Spectrum C is the residual spectrum resulting from the subtraction of A from B.

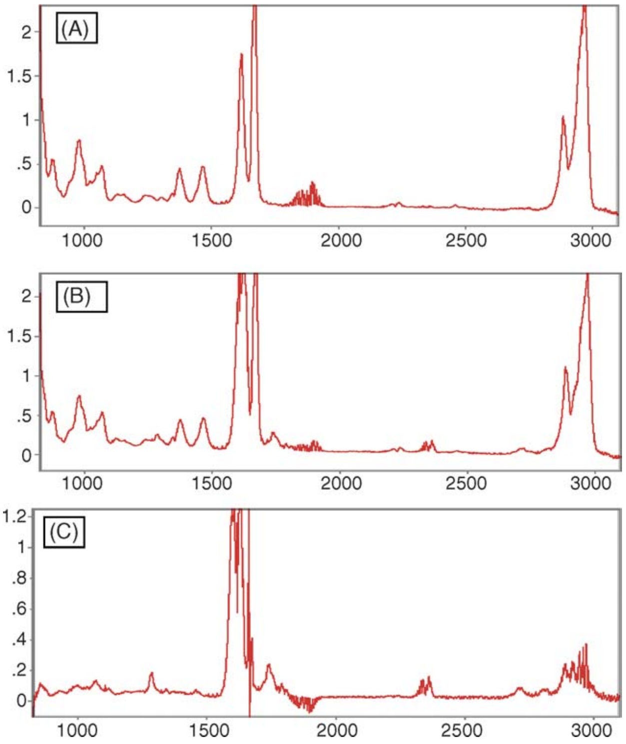


Fig. 2. IR spectra acquired before (A) and after (B) 30 min irradiation of mixtures of 1-butylnitrite/NO/O_2/N_2 at 271 K. (C) is the residual spectrum after subtraction of the starting material.

Butanal was quantified by virtue of its absorption band centered at 2712 cm^{-1} in yields that increased with increasing oxygen concentration and decreasing temperature. The opposite trend was observed for 4-hydroxybutanal. Figs. 3 and 4 show the yield at 295 K of butanal and 4-hydroxybutanal respectively plotted as a function of $\Delta[CH_3CH_2CH_2CH_2ONO]$ for different oxygen concentrations. The relative intensity distribution among the various absorption features attributed to 4-hydroxybutanal was found to be dependent on temperature and oxygen concentration. It is possible that, under our experimental conditions, some of the 4-hydroxybutanal isomerized to form 2-hydroxytetrahydrofuran, with subsequent conversion to

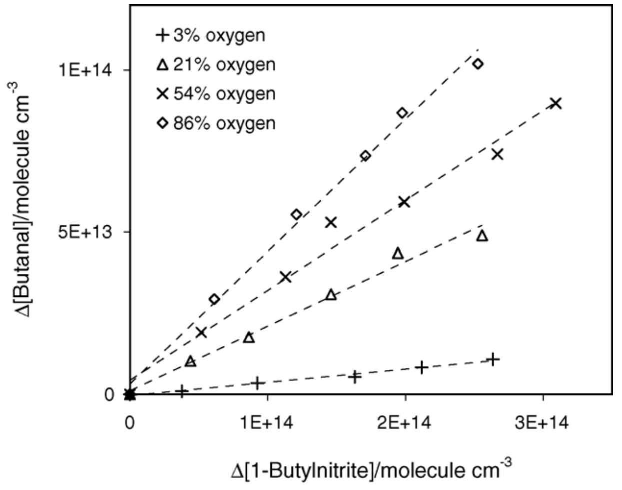


Fig. 3. Plots of the observed butanal concentration as a function of the loss of 1-butylnitrite in the photolysis of 1-butylnitrite/NO/O_2/N_2 mixtures at 700 Torr and 295 K.

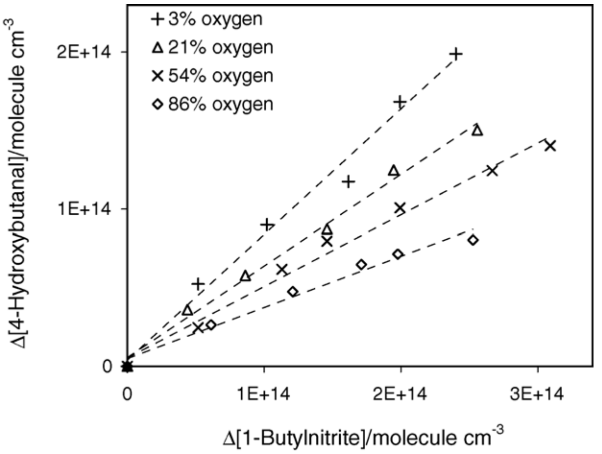
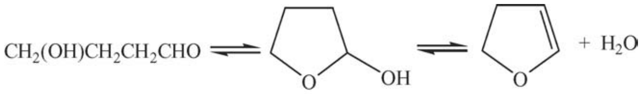


Fig. 4. Plots of 4-Hydroxybutanal concentration as a function of the loss of 1-butylnitrite in the photolysis of 1-butylnitrite/NO/O_2/N_2 mixtures at 700 Torr and 295 K.

4,5-dihydrofuran, via loss of a water molecule:

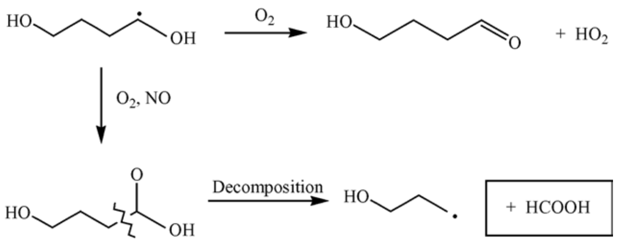


The cyclization of 1,4- and 1,5-hydroxycarbonyls to hemiacetals has been studied in the liquid phase and it is known to be catalyzed by the presence of traces of a strong acid [21]. The extent of cyclization of 1,4-hydroxycarbonyls in the gas phase is a function of relative humidity: Martin et al. [22] have recently shown that in dry N_2 5-hydroxy-2-pentanone cyclizes rapidly, with a first-order rate-constant of $2.5 \times 10^{-4}\,s^{-1}$, to form 4,5-dihydro-2-methylfuran, but that the process reverses in air at 5% relative humidity at 298 K. Evidence for the cyclization of 1,4-hydroxycarbonyls has been observed in other studies: Zabel and co-workers [23], who studied the reactions of 1-butoxy with an environmental chamber coupled to an FT-IR, identified 2-hydroxytetrahydrofuran as one of the products of 1-butoxy isomerization from a residual spectrum similar to the one we observed (Fig. 1) and Eberhard et al. [8] observed both 5-hydroxyhexan-2-one and 2,3-dihydro-2,5-dimethylfuran from a study of the reactions of 2-hexoxy radicals. Although the compound we quantified might be a mixture of tautomers, the product of 1-butoxy isomerization is referred to, for convenience, as 4-hydroxybutanal in the remaining part of this paper.

The small amounts of HCHO, HCOOH, CO, CO_2 are probably the result of secondary chemistry involving the OH radical (generated from the reaction of HO_2 with NO following reactions (2) and (7)). HCHO, for example, can be formed from the reaction of OH with 1-butylnitrite:

$$CH_3CH_2CH_2CH_2ONO + OH \xrightarrow{O_2,NO} CH_3CH_2CH(O^{\bullet})CH_2ONO + H_2O \quad (9)$$

$$CH_3CH_2CH(O^{\bullet})CH_2ONO \rightarrow CH_3CH_2CHO + HCHO + NO \quad (10)$$



Scheme 2.

Formaldehyde was identified from its absorption features at $1745\,cm^{-1}$ and was observed in yields that varied with temperature (from ∼7% at 295 K to ∼2% at 253 K), but were independent of oxygen concentration. Formic acid, which absorbs at $1776\,cm^{-1}$, was observed in small yields in all product spectra with concentrations that decreased with increasing oxygen partial pressure and decreasing temperature. For example, at 295 K, formic acid yields varied from ∼5% in the presence of 11 Torr of oxygen to ≤2% at 600 Torr of O_2. At 253 K, HCOOH was measured in yields of ≤2.5% at 15 Torr of oxygen and <1% at higher oxygen concentrations. Two possible sources were identified for HCOOH. One was the reaction of HCHO with HO_2:

$$HCHO + HO_2 \rightleftharpoons HOCH_2OO \quad (11)$$

$$HOCH_2OO + NO \rightarrow HOCH_2O + NO_2 \quad (12)$$

$$HOCH_2O + O_2 \rightarrow HCOOH + HO_2 \quad (13)$$

However, this source would be expected to be more important at low temperature, contrary to what is observed. The second source involved the chemistry occurring after isomerization of the 1-butoxy radical (Scheme 2) as there is evidence that formic acid might be formed from the reaction of R-CHOH radicals (where R is an organic fragment) with O_2 [19]. Since, the source is unknown, no corrections were made to the yield of 4-hydroxybutanal for the HCOOH observed, introducing a potential maximum error of ∼5%, but probably much less.

CO ($2132\,cm^{-1}$) and CO_2 ($2350\,cm^{-1}$) were present in trace amounts of ∼5% each. CO is a product of the reaction of HCHO with OH:

$$HCHO + OH \rightarrow HCO + H_2O \quad (14)$$

$$HCO + O_2 \rightarrow CO + HO_2 \quad (15)$$

Hydroxyl radicals are scavenged by NO and NO_2 and the IR absorptions of HONO and HNO_3 at $1263\,cm^{-1}$ and $1325\,cm^{-1}$, respectively, provided supportive evidence for the presence of OH radicals:

$$OH + NO + M \rightarrow HONO + M \quad (16)$$

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (17)$$

OH also reacts with butanal to form peroxy-*n*-butyrylnitrate or CO_2, from the NO reaction:

$$n\text{-}C_3H_7CHO + OH \rightarrow n\text{-}C_3H_7C(^{\bullet})O + H_2O \quad (18)$$

$$n\text{-}C_3H_7C(^{\bullet})O + O_2 \rightarrow n\text{-}C_3H_7C(O)O_2(^{\bullet}) \quad (19)$$

$$n\text{-}C_3H_7C(O)O_2(^\bullet) + NO_2 \rightleftharpoons n\text{-}C_3H_7C(O)O_2NO_2 \quad (20)$$

$$n\text{-}C_3H_7C(O)O_2(^\bullet) + NO \rightarrow n\text{-}C_3H_7 + CO_2 + NO_2 \quad (21)$$

The yield of n-$C_3H_7C(O)O_2NO_2$ increased with increasing oxygen mixing ratios and extent of reaction with yields of typically ∼6% in the presence of a fractional concentrations of oxygen >50%. At low temperatures and low oxygen mixing ratios, the yield of PnBN was negligible. To account for this secondary loss, the yields of butanal were corrected for the small amounts of n-$C_3H_7C(O)O_2NO_2$ detected.

Absorption bands characteristic of nitrates at 850 and 1280 cm^{-1} were observed and the overall nitrate yield was quantified by assuming a peak absorption cross section at 1280 cm^{-1} of 1.8×10^{-18} cm^2 $molecule^{-1}$, by analogy to methyl nitrate, with an estimated error of 10%. Alkyl nitrates could be generated from the reaction of NO with 4-hydroxy-n-butylperoxy radicals formed after the isomerization of 1-butoxy radicals:

$$CH_2(O_2{}^\bullet)CH_2CH_2CH_2OH + NO$$
$$\rightarrow CH_2(ONO_2)CH_2CH_2CH_2OH$$

and from the reaction of 1-butoxy radicals with NO_2:

$$CH_3CH_2CH_2CH_2(O^\bullet) + NO_2 \rightarrow CH_3CH_2CH_2CH_2ONO_2$$

Since, isomerization of $CH_2(O^\bullet)CH_2CH_2CH_2OH$ is thought to be much faster than 1-butoxy [3], it is unlikely that nitrate formation could be due to reaction of this radical with NO_2. Formation of 1-butylnitrate in reaction (8) would reduce the amount of 1-butoxy radical available for reaction with oxygen and isomerization, but would not affect the relative yields of butanal and of 4-hydroxybutanal or the data analysis for the relative rate-constant ratio k_3/k_2. In contrast, the formation of 4-hydroxybutylnitrate from reaction (5b) would reduce the yield of 4-hydroxybutanal making it necessary to account for this product in the analysis. Subtraction of the reference spectrum for 1-butylnitrate showed that the absorption feature centred at 1280 cm^{-1} was composed of more than one band, indicating the presence of different types of organic nitrates. Yields were found to be dependent on the extent of reaction, especially at low temperatures and low oxygen partial pressure. The apparent nitrate yield was also found to decrease with increasing $[O_2]$. Since NO_2 is a secondary product in our system, an upper limit to the yield of 4-hydroxybutylnitrate was calculated from the total nitrate yield in the initial stages of an experiment, when the contribution from reaction (8) was assumed to be much smaller relative to that from reaction (5b). We report an upper limit to the fractional yield of 4-hydroxybutylnitrate from reaction (5a) and (5b), that is k_{5b}/k_5 of (0.10 ± 0.03) at 295 K and 700 Torr which can be compared with the value by Arey et al. [24] of 0.07 for the corresponding ratio for 2-hydroxypentylnitrate (with an uncertainty of a factor of 2 in their product yields). No significant temperature-dependence for k_{5b}/k_5 was observed.

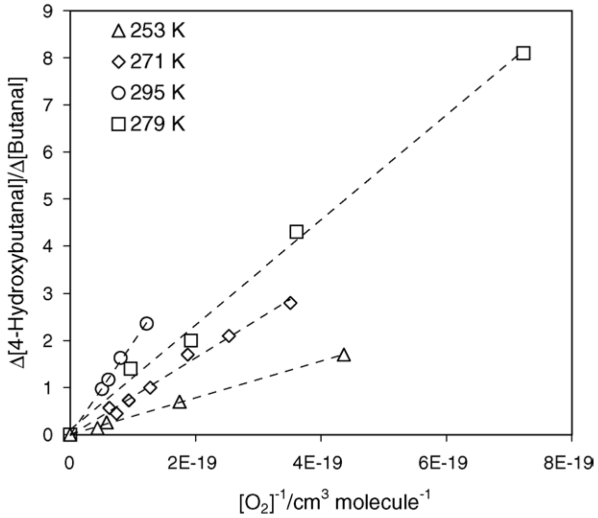


Fig. 5. Plots of Δ[4-Hydroxybutanal]/Δ[butanal] versus $[O_2]^{-1}$ following the irradiation of 1-butylnitrite/NO/O_2/N_2 mixtures as a function of temperature at 700 Torr total pressure.

The yields of 4-hydroxybutanal were corrected for the estimated yield of 4-hydroxybutylnitrate and used to calculate the relative rate-ratio, k_3/k_2 using the following equation:

$$\frac{\Delta[4 - \text{Hydroxybutanal}]}{\Delta[\text{Butanal}]} = \frac{k_3}{k_2}\frac{1}{[O_2]} \quad \text{(i)}$$

In Fig. 5 plots of Δ[4-Hydroxybutanal]/Δ[Butanal] versus $[O_2]^{-1}$ are shown for the four temperatures studied and the rate-constant ratios derived from the slopes of these plots – which were all linear as required by Eq. (i) – are listed in Table 1. Small intercepts of, typically, (0.2 ± 0.5) were observed.

Chemical activation can be important in the chemistry of alkoxy radicals formed from the photolysis (λ∼250 nm) of alkyl nitrite precursors [25,26], resulting in intercepts significantly larger than those predicted by equations equivalent to (i). As pointed out by Wallington et al. [27], we expect an excess energy of the order of 30–40 kJ mol^{-1} to be deposited into the alkoxy radical fragment under our experimental conditions, which is comparable to the isomerization barrier for 1-butoxy [2,17] (although it still falls below the barrier to decomposition [2,28,29]). Based on the intercepts of Fig. 5, however, we observed no evidence for prompt isomerization in this study. It seems therefore that any hot alkoxy radicals, if formed, were quenched before they could react. This is consistent with the results from previous work carried out in the laboratory in Cambridge [17], where the fraction of chemically activated 1-butoxy radicals formed from the photolysis of 1-butylnitrite at similar

Table 1
Temperature-dependence for k_3/k_2 for 1-butoxy radicals (errors quoted are 2σ)

	(253 ± 2) K	(271 ± 1) K	(279 ± 1) K	(295 ± 1) K
$k_3/k_2 \times 10^{-18}$ cm^3 $molecule^{-1}$	3.60 ± 0.46	7.96 ± 1.54	11.1 ± 1.3	19.5 ± 4.1

Table 2
Comparison with literature values of k_3/k_2

k_3/k_2 (10^{-19} molecule cm^{-3})	T/K	p/Torr	Reference
1.6	303	740	Carter et al. [15]
1.5 ± 0.5	296 ± 2	760	Cox et al. [14]
1.9 ± 0.4	298 ± 2	700	Niki et al. [13]
1.8 ± 0.6	298	760	Geiger et al. [16]
2.1 ± 0.5	300 ± 1	760 ± 10	Cassanelli et al. [17]
1.8 ± 1.1	298 ± 1	760 ± 10	Cassanelli et al. [17]

wavelengths was calculated to be of the order of about 10% or less. Hence, by neglecting any chemical activation effect, only a small error well within the overall experimental uncertainty was likely to be introduced.

The rate-coefficient ratio obtained at 295 K (1.5×10^{19} molecule cm^{-3}) is in good agreement with all previous evaluations of k_3/k_2, which were derived from the yield of butanal as a function of oxygen concentrations at ambient temperature and pressure [13–17] (Table 2). Our results are plotted in Arrhenius form in Fig. 6 and least-squares analysis yields the Arrhenius expression: k_3/k_2 (molecule cm^{-3}) = 5.5×10^{23} exp[(-25.1 ± 0.9 kJ mol^{-1})/RT]. This expression can be compared with a determination for the temperature-dependence of k_3/k_2 obtained in the laboratories in Cambridge using a slow-flow system coupled to a gas chromatograph with FID [17]: 1.98×10^{23} exp[(-22.6 ± 3.9) kJ mol^{-1}/RT] molecule cm^{-3}. The expressions agree within 20% over the range of temperatures studied. The slightly steeper temperature-dependence of the rate-coefficient ratio k_3/k_2 from the FT-IR experiments might be due to a small fraction of the heavier hydroxylated multifunctional compounds lost to the chamber walls at the lower temperatures. This would lead to an underestimate of the Δ[4-Hydroxybutanal]/Δ[Butanal] ratio and therefore k_3/k_2 at these temperatures. It is also of interest to compare our Arrhenius expression with the results from the work of Morabito and Heicklen [30], who measured the temperature-dependence of reactions (2) and (3) relative to reaction with NO. Their results, scaled to the recommended value for ($1-C_4H_9O+NO$) [3], give $k_3/k_2 = 2.5 \times 10^{23}$ exp(-23.6 kJ mol^{-1}/RT) cm^3 molecule^{-1} s^{-1}. The results are also in substantial accord with the most recent theoretical calculations of the activation energies for isomerization [28,31–33].

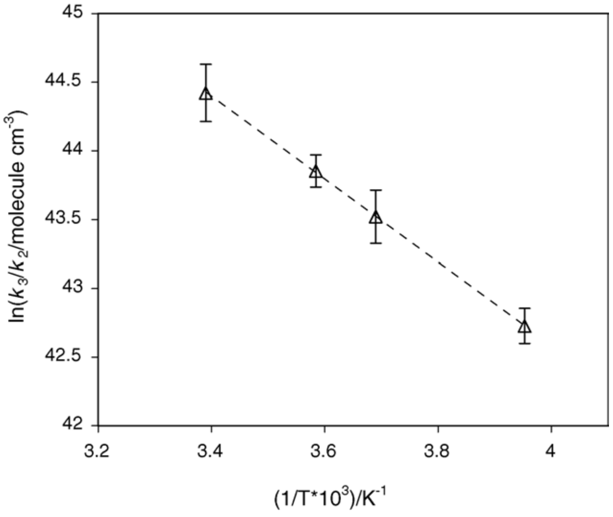


Fig. 6. Rate-coefficient k_3/k_2 plotted in Arrhenius form.

4. Conclusions

The reactions of 1-butoxy radicals have been measured in a temperature-regulated environmental chamber with detection by FT-IR over a range of temperatures relevant to the atmosphere. The two first-generation products from the reactions of 1-butoxy radicals are butanal (from the reaction with O_2) and 4-hydroxybutanal (from its isomerization). The competition between isomerization and reaction with oxygen was quantified over the temperature-range 253–295 K at 700 Torr with k_3/k_2 (molecule cm^{-3}) = 5.5×10^{23} exp[(-25.1 ± 0.9 kJ mol^{-1})/RT]. The reaction rate-coefficient k_3/k_2 at 295 K agrees well with values reported previously at ambient temperature and pressure [13–17], providing confirmation of the less direct measurement of this ratio. Isomerization is the main fate of 1-butoxy at ambient temperature and pressure and it remains a competitive channel at temperatures typical of the upper troposphere (200–230 K). 4-Hydroxybutanal, the product of the isomerization of 1-butoxy, might be converted to its cyclic tautomer, 2-hydroxytetrahydrofuran, which in turn could eliminate water to form 4,5-dihydrofuran. In the atmosphere, 4-hydroxybutanal is removed by reaction with OH at an estimated rate-constant of 3.5×10^{-11} molecule cm^{-3} at 298 K [34,35], leading to the formation of shorter chain hydroxylated aldehydes and dicarbonyls. However, the cyclization of 4-hydroxybutanal could be an important route to the formation of highly substituted oxygenated C_4 products, which maintain the carbon chain even subsequent to atmospheric degradation [1,22]. The higher solubility and lower volatility of these multifunctional products makes these compounds more likely to take part in aqueous phase chemistry and may favour transfer to the aerosol phase at the low temperatures of the upper troposphere.

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