# Direct investigations of reactions of 1-butoxy and 1-pentoxy radicals using laser pulse initiated oxidation: reaction with $O_2$ and isomerisation at 293 K and 50 mbar

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The reactions of 1-butoxy and 1-pentoxy radicals were studied using time-resolved and simultaneous measurement of NO<sub>2</sub> and OH concentrations in laser pulse initiated oxidation studies followed by numerical simulations of the concentration profiles. The alkoxy radicals were produced selectively by the excimer-laser photolysis of 1-butyl bromide and 1-pentyl bromide at 248 nm and subsequent reaction of the 1-alkyl radicals with O<sub>2</sub> and NO. Whereas NO<sub>2</sub> was detected by cw-LIF, OH was monitored by laser long-path absorption at 308 nm. All experiments were performed at 293  $\pm$  3 K and a total pressure of 50 mbar. The reactions with O<sub>2</sub> and the isomerisations *via* a 1,5-H-shift, *viz.*,

 $CH_{3}CH_{2}CH_{2}CH_{2}O + O_{2} \rightarrow CH_{3}CH_{2}CH_{2}CHO + HO_{2}$ (5)

$$CH_{3}CH_{2}CH_{2}CH_{2}O \rightarrow CH_{2}CH_{2}CH_{2}CH_{2}OH$$
(6)

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}O + O_{2} \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}CHO + HO_{2}$$

$$(25)$$

$$CH_3CH_2CH_2CH_2CH_2O \rightarrow CH_3CHCH_2CH_2CHOH$$
 (26)

were investigated. Their rate coefficients were varied, utilizing the FACSIMILE integrator, until the best fits were obtained. Whereas in the case of 1-butoxy radicals absolute rate coefficients  $k_5 = (1.4 \pm 0.7) \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_6 = (3.5 \pm 2) \times 10^4$  s<sup>-1</sup> could be derived, only limiting values for the 1-pentoxy radical reactions  $k_{25} \le 1 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_{26} \ge 1.0 \times 10^5$  s<sup>-1</sup> were obtained.

## 1 Introduction

The oxidative degradation of VOCs (volatile organic compounds) in the presence of high  $NO_x$  levels is responsible for the generation of tropospheric ozone. Its concentration during photochemical smog episodes is of great concern because ozone is highly toxic, not only to humans but also to animals and plants. As a consequence, VOC oxidation has been the subject of intensive research in recent decades. This research activity led to a fairly comprehensive understanding of various processes involved in VOC oxidation, *e.g.*, the initial attack of OH radicals or  $O_3$  (during day time) or  $NO_3$  radicals (during night time) on the VOC.<sup>1-3</sup>

However, the corresponding database for alkoxy radical reactions is far from being complete, although alkoxy radicals represent a major branching point in VOC oxidation mechanisms.

It is known that alkoxy radicals show three distinct competitive reaction pathways, depending on their structure and on environmental and experimental conditions.<sup>4–6</sup> These reactions are (i) reaction with O<sub>2</sub>, generating an aldehyde or a ketone and HO<sub>2</sub>, (ii) unimolecular decomposition, forming an aldehyde or a ketone and a shorter alkyl radical, and (iii) isomerisation (1,5-H-shift) *via* a six-membered and nearly strain-free transition state. This isomerisation forms a  $\delta$ hydroxyalkyl radical, which is further oxidized. After addition of O<sub>2</sub> and reaction with NO, it produces a  $\delta$ -hydroxyalkoxy radical. These radicals are believed to undergo a second 1,5-H-shift rather than to react with O<sub>2</sub> or to decompose, ultimately yielding  $\delta$ -hydroxycarbonyl compounds after subsequent H-abstraction by O<sub>2</sub>.<sup>7</sup> The reactions are shown schematically in Fig. 1 using 1-pentoxy radicals as example. Whereas the reaction of alkoxy radicals with  $O_2$  is chain terminating, decomposition and isomerisation produce carbon centered radicals. Therefore, the branching ratio of alkoxy radical reactions is the crucial parameter for the final distribution and yield of oxidation products. It affects the number of NO/NO<sub>2</sub> conversions and hence the concentration of NO<sub>2</sub>. Since NO<sub>2</sub> is readily photolysed, the branching ratio of



Fig. 1 Reactions of 1-pentoxy radicals under atmospheric conditions. Note that there is a second isomerisation following the formation of the 4-hydroxy-2-pentoxy radical (in general:  $\delta$ -hydroxyalkoxy radical).

alkoxy radical reactions has a direct effect on the production of ozone during photochemical smog episodes.

There are a number of differences between studies of alkoxy radical reactions performed previously and the present work. All investigations of butoxy and pentoxy radicals reported in the literature have been indirect and/or relative measurements, e.q., product studies using the FTIR technique.<sup>8</sup> Moreover, it was generally not possible to generate alkoxy radicals selectively. In a typical smog chamber experiment, the oxidation is initiated by the photolytic production of OH radicals, which then react with the VOC under investigation. As a consequence, the analysis of the experiment is complicated since the multitude of all possible alkoxy radicals has to be taken into account. Hence the determination of individual rate constants is difficult and sometimes speculative. In this paper, we present an investigation of the reactions of 1-butoxy and 1-pentoxy radicals with oxygen [reactions (5) and (25)] and of their isomerisations by 1,5-H-shift [reactions (6) and (26)], viz.,

$$CH_{3}CH_{2}CH_{2}CH_{2}O + O_{2} \rightarrow CH_{3}CH_{2}CH_{2}CHO + HO_{2}$$
(5)

 $CH_3CH_2CH_2CH_2O \rightarrow CH_2CH_2CH_2OH$  (6)

 $CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}O + O_{2} \rightarrow$ 

$$CH_3CH_2CH_2CH_2CHO + HO_2$$
 (25)

$$CH_3CH_2CH_2CH_2CH_2O \rightarrow CH_3CHCH_2CH_2CH_2OH$$
 (26)

(for reaction numbering, see Tables 1 and 2) using direct and time-resolved monitoring of the formation of  $NO_2$  and OH radicals in the laser flash initiated oxidation of 1-butyl and 1-pentyl radicals. This technique has previously been applied to studies of 2-butoxy radicals.<sup>9</sup>

## 2 Experimental

The general method applied in this work was the timeresolved and simultaneous monitoring of NO<sub>2</sub> and of OH radicals during the flash initiated oxidation of VOCs in the presence of O<sub>2</sub> and NO<sub>x</sub>. Since the temporal behaviour of the experimentally observed concentration vs. time profiles reflects the rate determining steps of NO<sub>2</sub> and OH producing and consuming processes, absolute rate coefficients can be extracted from the profiles using numerical simulations.

The experiments were pulse initiated by the excimer-laser photolysis of a 1-bromoalkane, *i.e.*, 1-bromobutane (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br) or 1-bromopentane (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>Br), at 248 nm. With an initial 1-bromoalkane concentration of  $(1-2) \times 10^{14}$  molecules cm<sup>-3</sup>, and a laser fluence of typically 30–40 mJ cm<sup>-2</sup>, the initial concentration of 1-alkyl radicals was estimated to be of the order of  $10^{10}$ – $10^{11}$ molecules cm<sup>-3</sup>. In the presence of O<sub>2</sub> and NO, the photolytically generated alkyl radicals are converted into primary alkoxy radicals on a time-scale of <1 ms.

We cannot completely exclude that H atoms are a byproduct of the excimer-laser photolysis of the bromoalkane radical precursor. However, in a study of the photochemistry of iodoalkanes, Ross and Johnston<sup>10</sup> were able to show that only I atoms and alkyl radicals are produced at 248 nm. By analogy, therefore, it may be assumed that the photolysis of bromoalkanes also produces Br atoms and alkyl radicals exclusively. However, even if H atoms in small yield were to be produced in the photolysis of bromoalkanes, this would not significantly change the results since the major species to initiate formation of NO<sub>2</sub> and OH is the alkyl radical.

 $NO_2$  was detected by cw-laser induced fluorescence (LIF) after excitation at 488 nm by means of the direct output of a 10 W Ar<sup>+</sup> laser. In order to increase the excitation volume,

the excitation beam was coupled into a White cell. The detection limit of this arrangement is approximately  $1 \times 10^{10}$  molecules cm<sup>-3</sup>. It should be noted that NO<sub>2</sub> impurities in the NO gas mixture were measured prior to the oxidation experiment by the NO<sub>2</sub> detection system, thus defining the baseline for the LIF measurement. Therefore, only NO<sub>2</sub> produced in the course of the oxidation is observed in the oxidation experiments.

OH detection was achieved by laser long-path absorption (LLPA) using an Ar<sup>+</sup> laser pumped ring-dye laser. The dye laser was equipped with an intracavity SHG unit which supplied the detection wavelength of 308.417 nm. This corresponds to the Q<sub>1</sub>(4) line of the A<sup>2</sup>\Sigma<sup>+</sup>-X<sup>2</sup>\Pi (0,0) transition of OH radicals. Again, mirrors in White configuration were used to maximize the detection limit with a typical absorption pathlength of 40 m, which resulted in a detection limit of approximately  $1 \times 10^9$  molecules cm<sup>-3</sup>.

The experiments were performed in a slow-flow reactor with the linear flow rate (approximately 70 cm s<sup>-1</sup>) chosen such that the reaction mixture was completely exchanged between consecutive experiments (repetition rate 1 Hz) in order to avoid accumulation of oxidation products. Details of the experimental arrangement have been described elsewhere.<sup>9,11</sup>

The gaseous compounds  $O_2$ ,  $N_2$  and NO were directly taken as delivered by the manufacturer (Messer-Griesheim). Their purities were 99.995, 99.999 and 99.5%, respectively, with the main impurities in the NO being NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>. Since additional NO<sub>2</sub> is accounted for by the NO<sub>2</sub> detection system and since these impurities are of the order of 0.5%, they play no significant role in the oxidation experiments. Gas mixtures of 1-bromobutane and 1-bromopentane were prepared by expanding 10–20 mbar bromoalkane vapour into a 20 l storage bulb and filling the bulb with N<sub>2</sub> up to a total pressure of 1000 mbar. The reaction mixture consisted of O<sub>2</sub>, NO, 1-bromoalkane and N<sub>2</sub> (in the case of 1-bromopentane oxidation only). 1-Bromobutane (Aldrich,  $\geq$ 99% purity) and 1-bromopentane (Fluka,  $\geq$ 98% purity) were used without further purification.

Typical concentrations were  $[N_2] = (0-1.2) \times 10^{18}$ ,  $[O_2] = (0.02-1.2) \times 10^{18}$ ,  $[NO] = (2.0-5.0) \times 10^{14}$ , [1-bromobutane] =  $(0.5-2.0) \times 10^{14}$  and [1-bromopentane] =  $(1.0-1.5) \times 10^{14}$  molecules cm<sup>-3</sup>. All experiments were performed at 293  $\pm$  3 K and a total pressure of 50 mbar.

## **3** Sensitivity analysis

The method used to analyse the experimentally obtained  $NO_2$ and OH concentration-time profiles was to simulate numerically the profiles with complete chemical mechanisms. The major advantage of this method is that individual radical reactions can be investigated even if the reactions of interest are part of a complex reaction scheme, *e.g.*, an oxidation mechanism which may consist of more than 20 reactions occuring simultaneously. In order to use this method, two conditions have to be fulfilled: (i) the rate coefficients of the major part of the mechanism have to be known and (ii) the reactions under investigation must participate significantly in the production and/or consumption of the two species observed.

The first condition is largely fulfilled because the oxidation of VOCs has been the subject of intensive research for at least two decades. This activity led to a fairly comprehensive understanding of the overall mechanisms of a variety of different VOC classes, *e.g.*, alkanes and alkenes.<sup>12,13</sup> In addition, unknown rate coefficients can be deduced from analogous reactions. For instance, the oxygen reaction of 1-propoxy radicals will not be significantly slower or faster than that of 1butoxy radicals. Moreover, there are a number of SARs (structure–activity relationships) for different reactions involved in VOC oxidation.<sup>14,15</sup> In summary, rate constants for the majority of reactions occuring in 1-butyl and 1-pentyl oxidation can be found in the literature.

Of course, if the reactions of 1-butoxy and 1-pentoxy radicals do not participate in the formation or the consumption of NO<sub>2</sub> and OH, no information about their rate constants can be drawn from the profiles. Whether this condition, *i.e.*, sufficient sensitivity of the profiles towards the rate coefficients under investigation, is fulfilled must be verified by simulations. Such sensitivity tests are based on the mechanisms shown schematically in Figs. 2 and 3 and in Tables 1 and 2. The calculations were carried out with the GEPASI program (version 3.20).<sup>16,17</sup>

## 3.1 Reactions of 1-butoxy and 1-pentoxy radicals

As shown in Figs. 2 and 3, there are three competitive reaction channels for 1-butoxy and 1-pentoxy radicals. They can react with  $O_2$ , yielding butanal and pentanal, respectively, and  $HO_2$ . For this type of reaction a rate constant of  $9.5 \times 10^{-15}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> has been predicted previously.<sup>7</sup> They may also isomerize via a 1,5-H-shift generating a  $\delta$ hydroxybutyl or -pentyl radical. These radicals subsequently add  $O_2$  and react with NO to form  $\delta$ -hydroxybutoxy or -pentoxy radicals. Although there are a number of studies dealing with 1-butoxy isomerisation,<sup>7,8,21–23</sup> we could not find any study on 1-pentoxy isomerisation in the literature. Moreover, the investigations of 1-butoxy isomerisation reported in the literature were performed at around 1000 mbar,



**Fig. 2** Detailed mechanism used for numerical simulations of the 1butoxy oxidation. Second-order rate coefficients in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and first-order rate coefficients in s<sup>-1</sup> are taken from the literature. The major fluxes predicted for  $[O_2] = 1.2 \times 10^{18}$  and  $[NO] = 5.0 \times 10^{14}$  molecules cm<sup>-3</sup> are indicated by the size of the arrows.

whereas our experiments were conducted at 50 mbar. This makes a comparison difficult because the isomerisation rate coefficient is expected to be pressure dependent. However, a recent combined *ab initio*–**RRKM** study of unimolecular reactions of primary and secondary  $C_2$ – $C_5$  alkoxy radicals performed by our group<sup>24</sup> indicates rate constants for the isomerisation at 290 K and 50 mbar of  $2.7 \times 10^4$  and  $7.5 \times 10^5$  s<sup>-1</sup> for 1-butoxy and 1-pentoxy radicals, respectively.

The same theoretical analysis<sup>24</sup> reveals a rate constant for the isomerisation of the  $\delta$ -hydroxy alkoxy radicals occuring in 1-butyl and 1-pentyl oxidation, *viz.*,

$$OCH_2CH_2CH_2CH_2OH \rightarrow HOCH_2CH_2CH_2CHOH$$
 (12)  
 $CH_3CH(O)CH_2CH_2CH_2OH \rightarrow$ 

# CH<sub>3</sub>CH(OH)CH<sub>2</sub>CH<sub>2</sub>CHOH (32)

(cf., Tables 1 and 2) of  $3.2 \times 10^6 \text{ s}^{-1}$  at 290 K and 50 mbar. This value is in agreement with the SAR for alkoxy and  $\delta$ -hydroxyalkoxy radical isomerisations given by Atkinson,<sup>7</sup> who estimates  $6.4 \times 10^6 \text{ s}^{-1}$  at 290 K and atmospheric pressure. However, this fast isomerisation prohibits the determination of  $k_{12}$  and  $k_{32}$  in our work because the profiles measured only reflect the rate determining steps of NO<sub>2</sub> and OH formation and consumption for which reactions (12) and (32) are not rate determining. Therefore, the profiles are insensitive towards  $k_{12}$  and  $k_{32}$  and no information about these rate constants can be extracted.

Under our experimental conditions, *i.e.*, at high NO concentrations, 1-butoxy and 1-pentoxy radicals may also react with NO. This reaction has two pathways, either addition of NO to form an organic nitrite or H atom abstraction generating HNO + butanal or pentanal, respectively. However, the exact loss process of the 1-alkoxy radicals due to reaction with NO is of little importance as far as the numerical simulations of the profiles observed are concerned. As a consequence, the two pathways were treated as if they were a single NO reaction.

In principal, primary alkoxy radicals can show a fourth reaction pathway, namely decomposition to form formaldehyde and an alkyl radical containing one C atom less than the parent VOC. The only primary alkoxy radicals for which decomposition rate constants at room temperature are available from the literature are ethoxy, 1-propoxy and 1-butoxy. Reported decomposition rate constants at 298 K and at around atmospheric pressure are (in units of s<sup>-1</sup>)  $4.8 \times 10^{-2}$ ,  $^{25}$   $3.9 \times 10^{-3}$ ,  $^{22}$   $7.7 \times 10^{-2}$ ,  $^{26}$   $7.1 \times 10^{-3}$   $^{27}$  and 0.31 <sup>7</sup> for ethoxy, 116,  $^{25}$  0.18  $^{22}$  and 49 <sup>7</sup> for 1-propoxy and 0.225  $^{22}$  for 1-butoxy radicals. These rate constants, if compared with the reaction rates of the other pathways, were considered to be too slow to be of any importance. Hence the decomposition was neglected in the mechanisms used for the simulations.

**1-Butoxy radicals.** The sensitivity of the profiles towards  $k_5$ , the rate constant for the O<sub>2</sub> reaction of 1-butoxy radicals, *viz.*,

$$CH_3CH_2CH_2CH_2O + O_2 \rightarrow CH_3CH_2CH_2CHO + HO_2$$
 (5)

was tested, using the mechanism displayed in Fig. 2 and summarized in Table 1, by varying the rate constant and simulating the system. The resulting profiles and changes in absolute concentration and temporal behaviour are shown in Fig. 4. This figure reveals that significant changes in absolute yield occur for OH only, whereas changes in the NO<sub>2</sub> profile are too small to be considered significant. It follows that no information about  $k_5$  can be drawn from the NO<sub>2</sub> profile.

For the simulations the following concentrations and rate coefficients were used:  $[O_2] = 1.2 \times 10^{18}$ ,  $[NO] = 5.0 \times 10^{14}$  and [1-bromobutane] =  $2.0 \times 10^{14}$  molecules cm<sup>-3</sup>,  $k_5 = 9.5 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_8 = 2.7 \times 10^4$  s<sup>-1</sup>. These



**Fig. 3** Detailed mechanism used for numerical simulations of the 1pentoxy oxidation. Second-order rate coefficients in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and first-order rate coefficients in s<sup>-1</sup> are taken from the literature. The major fluxes predicted for  $[O_2] = 1.2 \times 10^{18}$  and  $[NO] = 5.0 \times 10^{14}$  molecules cm<sup>-3</sup> are indicated by the size of the arrows.

concentrations and rate coefficients yield branching ratios for the 1-butoxy radical reactions of 0.31 for reaction with NO, 0.52 for the isomerisation and 0.17 for the  $O_2$  reaction. Therefore, reaction with  $O_2$  plays only a minor role and isomerisation and reaction with NO are the dominant pathways. Since  $k_5$  has no significant effect on the NO<sub>2</sub> profile, NO<sub>2</sub>



Fig. 4 Sensitivity of the NO<sub>2</sub> (top) and OH (bottom) profiles towards  $k_5$ , the rate constant for reactions of 1-butoxy with O<sub>2</sub> ([O<sub>2</sub>] =  $1.2 \times 10^{18}$  molecules cm<sup>-3</sup>).

cannot be formed by reaction (5) followed by reaction (15):

$$HO_2 + NO \rightarrow OH + NO_2$$
 (15)

Rather, the major part of  $NO_2$  is generated by the conversion of organic peroxy radicals into oxy radicals, *i.e.*,

$$\rm CH_3CH_2CH_2CH_2O_2 + \rm NO \rightarrow$$

$$CH_3CH_2CH_2CH_2O + NO_2 \quad (3)$$

 $\rm O_2CH_2CH_2CH_2OH + NO \rightarrow$ 

$$OCH_2CH_2CH_2CH_2OH + NO_2$$
 (9)

for which the rate of formation of NO<sub>2</sub> is independent of  $k_5$ . A closer look at the OH profile reveals that significant changes in total yield occur only for  $k_5 \ge 1.0 \times 10^{-14}$  cm<sup>3</sup>

Table 1Reaction system used to simulate 1-bromobutane oxidation at 293  $\pm$  3 K and 50 mbar

No.	Reaction	k <sup>a</sup>	Ref.
1 2 2	$CH_{3}CH_{2}CH_{2}CH_{2}Br + hv \rightarrow CH_{3}CH_{2}CH_{2}CH_{2} + Br$ $CH_{3}CH_{2}CH_{2}CH_{2} + O_{2} \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}O_{2}$ $CH_{3}CH_{2}CH_{2}CH_{2}O_{2} \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}O_{2} \rightarrow O_{2}$	$7.5 \times 10^{-12}$	18
3 4 <sup>b</sup> 5	$CH_{3}CH_{2}CH_{2}CH_{2}O_{2} + NO \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}O + NO_{2}$ $CH_{3}CH_{2}CH_{2}CH_{2}O_{2} + NO \rightarrow CH_{3}CH_{2}CH_{2}ONO_{2}$ $CH_{3}CH_{2}CH_{2}CH_{2}O + O_{2} \rightarrow butanal + HO_{2}$ $CH_{2}CH_{2}CH_{2}O + O_{2} \rightarrow butanal + HO_{2}$	$4.9 \times 10^{-12}$ $1.1 \times 10^{-14}$ Varied	13
7 8 9	$CH_{3}CH_{2}CH_{2}CH_{2}O + NO \rightarrow products$ $CH_{3}CH_{2}CH_{2}CH_{2}OH + O_{2} \rightarrow O_{2}CH_{2}CH_{2}CH_{2}OH$ $O_{2}CH_{2}CH_{2}CH_{2}OH + NO \rightarrow OCH_{2}CH_{2}CH_{2}OH$	$4.6 \times 10^{-11} \\ 7.5 \times 10^{-12} \\ 4.9 \times 10^{-12}$	13 18 13
10 <sup>b</sup> 11 12	$O_2CH_2CH_2CH_2CH_2CH_2OH + NO \rightarrow O_2NOCH_2CH_2CH_2CH_2OH - NO_2 OCH_2CH_2CH_2CH_2CH_2OH + O_2 \rightarrow CHOCH_2CH_2CH_2CH_2OH + O_2 OCH_2CH_2CH_2CH_2OH + O_2 \rightarrow CHOCH_2CH_2CH_2OH + HO_2 OCH_2CH_2CH_2CH_2OH - HOCH_2CH_2CH_2OH - HOCH_2CH_2OH - HOCH_2OH - H$	$ \begin{array}{r}     1.5 \times 10^{-14} \\     1.1 \times 10^{-14} \\     9.5 \times 10^{-15} \\     3.2 \times 10^{6} \end{array} $	7 24
13 14 15	OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH + NO $\rightarrow$ products HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHOH + O <sub>2</sub> $\rightarrow$ HOCH <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub> HO <sub>2</sub> + NO $\rightarrow$ OH + NO <sub>2</sub>	$4.6 \times 10^{-11} 3 \times 10^{-11} 8.1 \times 10^{-12}$	13 19 12
16 17 18	$HO_{2}^{2} + OH \rightarrow H_{2}O + O_{2}^{2}$ OH + NO $\rightarrow$ HONO OH + NO <sub>2</sub> $\rightarrow$ HNO <sub>3</sub>	$ \begin{array}{r} 1.1 \times 10^{-10} \\ 7.6 \times 10^{-13} \\ 2.0 \times 10^{-12} \end{array} $	12 12 12
19 20	$OH \rightarrow diffusion$ $CH_3CH_2CH_2CH_2Br + OH \rightarrow products$	$\frac{10}{1.9 \times 10^{-12}}$	20 20

<sup>*a*</sup> First-order rate coefficients in  $s^{-1}$ , second-order rate coefficients in cm<sup>3</sup> molecule<sup>-1</sup>  $s^{-1}$ . <sup>*b*</sup> Branching ratio for RO<sub>2</sub> + NO reactions calculated after ref. 3.

Table 2 Reaction system used to simulate 1-bromopentane oxidation at 293  $\pm$  3 K and 50 mbar

No.	Reaction	k <sup>a</sup>	Ref.
21	$CH_3CH_2CH_2CH_2CH_2Br + hv \rightarrow CH_3CH_2CH_2CH_2CH_2 + Br$		
22	$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2} + O_{2} \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}O_{2}$	$7.5 \times 10^{-12}$	18
23	$CH_{3}CH_{5}CH_{7}CH_{7}CH_{7}O_{7} + NO \rightarrow CH_{4}CH_{7}CH_{7}CH_{7}CH_{7}O + NO_{7}O_{7}O_{7}O_{7}O_{7}O_{7}O_{7}O_{7}$	$4.9 \times 10^{-12}$	13
24 <sup>b</sup>	$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}O_{2} + NO \rightarrow nitrate$	$3.1 \times 10^{-14}$	
25	$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}O + O_{2} \rightarrow pentanal + HO_{2}$	Varied	
26	$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}O \rightarrow CH_{3}CHCH_{2}CH_{2}CH_{2}OH$	Varied	
27	$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}O + NO \rightarrow \text{products}$	$4.6 \times 10^{-11}$	13
28	$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}OH + O_{2} \rightarrow CH_{3}CH(O_{2})CH_{2}CH_{2}OH$	$1.7 \times 10^{-11}$	18
29	$CH_{3}CH(O_{2})CH_{2}CH_{2}CH_{2}OH + NO \rightarrow CH_{3}CH(O)CH_{2}CH_{2}OH + NO_{2}OH$	$4.7 \times 10^{-12}$	13
30 <sup>b</sup>	$CH_{3}CH(O_{2})CH_{2}CH_{2}CH_{2}OH + NO \rightarrow nitrate$	$7.5 \times 10^{-14}$	
31	$CH_{3}CH(O)CH_{2}CH_{2}CH_{2}OH + O_{2} \rightarrow CH_{3}COCH_{2}CH_{2}OH + HO_{2}$	$8 \times 10^{-15}$	7
32	$CH_{3}CH(O)CH_{2}CH_{2}CH_{2}OH \rightarrow CH_{3}CH(OH)CH_{2}CH_{2}CHOH$	$3.2 \times 10^{5}$	24
33	$CH_{3}CH(O)CH_{2}CH_{2}CH_{2}OH + NO \rightarrow products$	$4.1 \times 10^{-11}$	12
34	$CH_{3}CH(OH)CH_{2}CH_{2}CHOH + O_{2} \rightarrow CH_{3}CH(OH)CH_{2}CH_{2}CHO + HO_{2}$	$3 \times 10^{-11}$	19
15	$HO_2 + NO \rightarrow OH + NO_2$	$8.1 \times 10^{-12}$	12
16	$HO_2 + OH \rightarrow H_2O + O_2$	$1.1 \times 10^{-10}$	12
17	$OH + NO \rightarrow HONO$	$7.6 \times 10^{-13}$	12
18	$OH + NO_2 \rightarrow HNO_3$	$2.0 \times 10^{-12}$	12
19	$OH \rightarrow diffusion$	10	20
35	$CH_3CH_2CH_2CH_2CH_2Br + OH \rightarrow products$	$3.5 \times 10^{-12}$	20

<sup>*a*</sup> First-order rate coefficients in  $s^{-1}$ , second-order rate coefficients in cm<sup>3</sup> molecule<sup>-1</sup>  $s^{-1}$ . <sup>*b*</sup> Branching ratio for RO<sub>2</sub> + NO reactions calculated after ref. 3.

molecule<sup>-1</sup> s<sup>-1</sup>. For smaller values of  $k_5$  the resulting changes in the OH profile are too small to be recognized in an experimental profile (*cf.*, Figs. 12 and 13). As a consequence, an absolute value for  $k_5$  can only be extracted if  $k_5 \ge 1.0 \times 10^{-14}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, otherwise only an upper limit can be derived.

To estimate the relative error of  $k_5$ , the NO<sub>2</sub> concentration at infinite reaction time,  $[NO_2]_{\infty}$ , and the maximum OH concentration,  $[OH]_{max}$ , are plotted against  $k_5$  in Fig. 5. The error bars shown represent the 10% uncertainty of the NO<sub>2</sub> and OH detection systems. Clearly, the NO<sub>2</sub> profile is insensitive towards  $k_5$ . The OH profile, however, is sensitive towards  $k_5$  but the changes in absolute concentration are within the errors of the OH detection system. Therefore, the relative error of  $k_5$  is estimated to be 50%.

In a similar way as described above, the sensitivity of the profiles towards  $k_6$ , the rate constant for the isomerisation of 1-butoxy radicals, was verified. The profiles obtained and the resulting changes are shown in Fig. 6. As opposed to  $k_5$ , Fig. 6 reveals significant sensitivity of both profiles towards  $k_6$  if it is varied around its expected value of approximately  $2.7 \times 10^4$  s<sup>-1</sup>. Since  $k_5$  is not reflected by the NO<sub>2</sub> profile, the NO<sub>2</sub> profile can be used to derive  $k_6$ . The procedure to obtain



**Fig. 5** Dependence of the NO<sub>2</sub> concentration at infinite reaction time,  $[NO_2]_{\infty}$  (left ordinate), and of the maximum OH concentration,  $[OH]_{max}$  (right ordinate), on  $k_5$ . The error bars shown represent 10% uncertainty of the NO<sub>2</sub> and OH detection systems.

absolute values for  $k_5$  and  $k_6$ , therefore, is to fit  $k_6$  to the NO<sub>2</sub> profile first and in a second step to fix  $k_5$  using the OH profile.

The relative error of  $k_6$  can be estimated from Fig. 7, in which  $[NO_2]_{\infty}$  and  $[OH]_{max}$  are shown as functions of  $k_6$ .  $[NO_2]_{\infty}$  and  $[OH]_{max}$  both increase with increasing  $k_6$  but apparently reach a limiting value.  $[NO_2]_{\infty}$  approaches an upper limit of approximately  $6 \times 10^{11}$  molecules cm<sup>-3</sup> at  $k_6 > 1 \times 10^5$  s<sup>-1</sup>. Hence the sensitivity drops, finally reaching zero, if  $k_6$  is larger than  $1 \times 10^5$  s<sup>-1</sup>. Since the expected value of  $k_6$  is well below this "sensitivity threshold", an absolute value for  $k_6$  can be extracted from the profile.



Fig. 6 Sensitivity of the NO<sub>2</sub> (top) and OH (bottom) profiles towards  $k_6$ , the rate constant for isomerisation of 1-butoxy ([O<sub>2</sub>] =  $1.2 \times 10^{18}$  molecules cm<sup>-3</sup>).



Fig. 7 Dependence of the NO<sub>2</sub> concentration at infinite reaction time,  $[NO_2]_{\infty}$  (left ordinate), and of the maximum OH concentration,  $[OH]_{max}$  (right ordinate), on  $k_6$ . The error bars shown represent 10% uncertainty of the NO<sub>2</sub> and OH detection systems.

The dependence of  $[NO_2]_{\infty}$  and  $[OH]_{max}$  on  $k_6$  can be easily understood by considering the mechanism in Fig. 2. As long as the isomerisation rate is comparable to the rate determining steps of the straight downward route in Fig. 2, *i.e.*, the peroxy/oxy conversions [reactions (3), (9) and (15)], the sensitivity of the profiles towards  $k_6$  is large because the profiles reflect the rate determining steps of NO<sub>2</sub> and OH production or consumption. However, if rapid isomerisation leaves the peroxy/oxy conversions as the only rate determining steps, the sensitivity of the profiles toward  $k_6$  drops, ultimately reaching zero.

Since the changes in  $[NO_2]_{\infty}$  are of the order of the experimental uncertainty of the NO<sub>2</sub> detection at around the expected value of  $k_6$ , its relative error is estimated to be 50% as long as  $k_6$  is in the range (0–5) × 10<sup>4</sup> s<sup>-1</sup>. Otherwise, only a lower limit for  $k_6$  can be derived.



**Fig. 9** Dependence of the NO<sub>2</sub> concentration at infinite reaction time,  $[NO_2]_{\infty}$  (left ordinate), and of the maximum OH concentration,  $[OH]_{max}$  (right ordinate), on  $k_{25}$ . The error bars shown represent 10% uncertainty of the NO<sub>2</sub> and OH detection systems.

**1-Pentoxy radicals.** The mechanism displayed in Fig. 3 and in Table 2 was used to test the sensitivity of the profiles towards  $k_{25}$ , the rate constant for the reaction of 1-pentoxy radicals with  $O_2$ , viz.,

$$CH_3CH_2CH_2CH_2CH_2O + O_2 \rightarrow pentanal + HO_2$$
 (25)

The concentrations and rate coefficients used are  $[O_2] = 1.2 \times 10^{18}$ ,  $[NO] = 5.0 \times 10^{14}$  and [1-bromopentane]  $= 1.5 \times 10^{14}$  molecules cm<sup>-3</sup>,  $k_{25} = 9.5 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_{26} = 7.5 \times 10^5$  s<sup>-1</sup>. They produce branching ratios for the 1-pentoxy radical reactions of 0.05 for reaction with NO, 0.92 for isomerisation and 0.03 for reaction with O<sub>2</sub>. Clearly, isomerisation is by far the dominant reaction pathway.

Fig. 8 summarizes the changes in the profiles if  $k_{25}$  is varied. As can be seen, if  $k_{25}$  is in the range  $(0-1.0) \times 10^{-13}$  cm<sup>3</sup>



**Fig. 8** Sensitivity of the NO<sub>2</sub> (top) and OH (bottom) profiles towards  $k_{25}$ , the rate constant for reaction of 1-pentoxy with O<sub>2</sub> ([O<sub>2</sub>] =  $1.2 \times 10^{18}$  molecules cm<sup>-3</sup>). Both profiles are insensitive towards  $k_{25}$  if it is varied around its expected value of  $1 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

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Fig. 10 Sensitivity of the NO<sub>2</sub> (top) and OH (bottom) profiles towards  $k_{26}$ , the rate constant for isomerisation of 1-pentoxy with  $([O_2] = 1.2 \times 10^{18} \text{ molecules cm}^{-3})$ . No significant changes occur if  $k_{26} \ge 1.0 \times 10^5 \text{ s}^{-1}$ .



**Fig. 11** Dependence of the NO<sub>2</sub> concentration at infinite reaction time,  $[NO_2]_{\infty}$  (left ordinate), and of the maximum OH concentration,  $[OH]_{max}$  (right ordinate), on  $k_{26}$ . The error bars shown represent 10% uncertainty of the NO<sub>2</sub> and OH detection systems. The diagram clearly shows the "sensitivity threshold" of approximately  $k_{26} \ge 1.0 \times 10^5 \text{ s}^{-1}$ .

molecule<sup>-1</sup> s<sup>-1</sup>, both profiles are insensitive towards  $k_{25}$ . The changes that occur are too small to be recognized in an experimental profile. Only if  $k_{25}$  is larger than approximately  $5 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is the sensitivity increased (Fig. 9). The changes are much smaller than the experimental uncertainties of the NO<sub>2</sub> and OH detection systems, if  $k_{25}$  is varied around its expected value of approximately  $1 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. As a consequence, only an upper limit for  $k_{25}$  can be extracted. Unfortunately, it is not possible to shift the branching ratio of the 1-pentoxy radical reactions in favour of the oxygen reaction because the assumed  $[O_2] = 1.2 \times 10^{18}$  molecules cm<sup>-3</sup> corresponds to a pressure of 50 mbar, which is the maximum pressure allowing NO<sub>2</sub> fluorescence to be detected.

The sensitivity of the NO<sub>2</sub> and OH profiles towards  $k_{26}$ , the isomerisation rate constant of 1-pentoxy radicals, is shown in Fig. 10. Although there are significant interrelations, they only occur if  $k_{26}$  is in the range  $(0-1.0) \times 10^5 \text{ s}^{-1}$ . If  $k_{26}$  is larger than  $1.0 \times 10^5 \text{ s}^{-1}$ , the changes in the profiles are much too small to be considered significant. This "sensitivity threshold" also was noticed for  $k_6$ , the 1-butoxy isomerisation rate constant.

Since the expected value of  $k_{26}$  is  $7.5 \times 10^5$  s<sup>-1</sup>, only a lower limit for that rate coefficient can be derived. Fig. 11 shows the dependence of  $[NO_2]_{\infty}$  and  $[OH]_{max}$  on  $k_{26}$ . The figure reveals large changes, and hence a good sensitivity for  $k_{26} < 1.0 \times 10^5$  s<sup>-1</sup>. If  $k_{26} \ge 1.0 \times 10^5$  s<sup>-1</sup>,  $[NO_2]_{\infty}$  and  $[OH]_{max}$  reach a plateau with no significant dependence on  $k_{26}$ . The explanation of the "sensitivity threshold" is the same as discussed for the 1-butoxy isomerisation in the preceding section.

# 4 Results and discussion

Experiments with a variety of reactant concentrations were performed. The concentrations of  $NO_2$  and of OH were measured simultaneously, and the FACSIMILE program was used to reproduce the concentration-time profiles. For that purpose again the mechanisms shown in Figs. 2 and 3 and in Tables 1 and 2 were utilized. In contrast to the sensitivity tests, in the FACSIMILE simulations the rate coefficients under investigation were varied, until the simulated profiles.

Typical examples for the agreement between experiment and simulation are shown in Figs. 12 and 13 for 1-butoxy and 1-pentoxy, respectively. As can be seen, the mechanisms are able to reproduce the experiments. Also included in these figures are the sensitivities of the calculated profiles towards



Fig. 12 Comparison between experimentally obtained and simulated concentration-time profiles for the 1-butoxy system.  $k_5$  and  $k_6$  were varied until the best fit was reached. In each case one of these rate constants was held fixed at its best value while the other one was varied. Experimental conditions:  $[O_2] = 1.2 \times 10^{18}$ ,  $[NO] = 5.0 \times 10^{14}$  and  $[1\text{-bromobutane}] = 2.0 \times 10^{14}$  molecules cm<sup>-3</sup>, T = 293 K, p = 50 mbar, photolysis wavelength  $\lambda = 248$  nm.



Fig. 13 Comparison between experimentally obtained and simulated concentration-time profiles for the 1-pentoxy system.  $k_{25}$  and  $k_{26}$  were varied until the best fit was reached. In each case one of these rate constants was held fixed at its best value while the other one was varied. Experimental conditions:  $[O_2] = 1.2 \times 10^{18}$ ,  $[NO] = 5.0 \times 10^{14}$  and [1-bromopentane] =  $1.5 \times 10^{14}$  molecules cm<sup>-3</sup>, T = 293 K, p = 50 mbar, photolysis wavelength  $\lambda = 248$  nm.

the rate coefficients varied, as discussed in detail in Section 3. Note that while  $k_5$  and  $k_{25}$  were varied in this sensitivity test,  $k_6$  and  $k_{26}$  were held at their best fit values and vice versa.

Although in this work we performed a series of simulations covering a variety of different experimental conditions, we present only one comparison for each radical system investigated owing to limited space. These simulations are available on request either as diagrams or in tabular form. The best fits provide the following rate constants:  $k_5 = (1.4 \pm 0.7) \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,  $k_6 = (3.5 \pm 2) \times 10^4$  s<sup>-1</sup>,  $k_{25} \le 1.0 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_{26} \ge 5.0 \times 10^5$  s<sup>-1</sup>.

It should be noted that the discrepancy between the measured and simulated OH profiles in the case of 1-pentoxy radicals (Fig. 13) is due to an electronic oscillation superimposed on the OH signal. The same oscillation, although significantly smaller, can be seen in Fig. 12. This oscillation originates from the electronic processing of the absorption signal. However, for the determination of  $k_{25}$  and  $k_{26}$  only the first 3 ms of the OH profile were used. Hence the oscillation did not perturb the extraction of the rate coefficients.

In addition to the rate constants extracted from the profiles, the simulations resulted in a semi-quantitative determination of  $k_3$ ,  $k_9$ ,  $k_{23}$  and  $k_{29}$ , the rate constants for reactions of peroxy radicals with NO. Although having been the subject of research since the beginning of the 1970s, the rate coefficient for this reaction has recently been suggested to be a factor of two larger than previously believed. However, if we used the values for  $k_3$ ,  $k_9$ ,  $k_{23}$  and  $k_{29}$  as determined by Eberhard and Howard,<sup>28,29</sup> we were unable to simulate the experimentally obtained profiles. This applies in particular to the OH profile. Since the simulated profiles are very sensitive towards the different  $k(\mathbf{RO}_2 + \mathbf{NO})s$ , as has been discussed in Section 3, this is a strong indication that the rate constants determined by Eberhard and Howard are significantly too high.

## 4.1 Reactions of 1-butoxy radicals

**Reaction with oxygen.** Since the value of  $k_5$  derived in this work was determined independently of  $k_6$ , it has to be considered as an absolute determination. To our knowledge, there is only one previous investigation of the O<sub>2</sub> reaction of 1-butoxy radicals. Morabito and Heicklen<sup>21</sup> determined the rate coefficient relative to that of nitrite formation. At 293 K they reported  $1.34 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which is in good agreement with our results.

In his recent review of alkoxy radical reactions, Atkinson<sup>7</sup> proposed two SARs for estimating the rate coefficients of reaction with  $O_2$ . In the first one the only distinction made is that between primary and secondary radicals. The SAR for primary alkoxy radicals is

$$k_5 = 6.0 \times 10^{-14}$$
  
  $\times \exp(-550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (36)

from which a rate constant at 293 K of  $9.2 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in satisfactory agreement with the result from

this work, is derived. However, the second SAR,  

$$k_5 = 4.0 \times 10^{-19} \times n \times \exp(-0.28$$
  
 $\times \Delta H_{\odot}/\text{kcal mol}^{-1}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (37)

where *n* is the number of abstractable H atoms, yields a rate coefficient of  $4.0 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 293 K, a factor of 3.5 lower than that found here. This discrepancy might be expected because only methoxy, ethoxy and 2-propoxy radicals were used in the derivation of eqn. (37). Moreover, only for these three radicals are recommended values for their heats of formation available.<sup>13</sup> For butoxy and pentoxy radicals, the heats of formation<sup>30,31</sup> and hence

the enthalpy of the reaction are less certain, contributing to the uncertainty of  $k_5$  calculated by eqn. (37).

The rate coefficient  $k_5$  determined in the present work may also be compared with the rate coefficients of other alkoxy radicals with O<sub>2</sub>. Direct investigations are available for methoxy,<sup>32–38</sup> ethoxy<sup>36,39,40</sup> and propoxy<sup>41,42</sup> radicals. The IUPAC recommended<sup>13</sup> rate constants at 298 K are  $1.9 \times 10^{-15}$ ,  $9.5 \times 10^{-15}$  and  $8 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for methoxy, ethoxy and propoxy (1- and 2-propoxy), respectively. In addition, Mund *et al.*<sup>42</sup> determined rate coefficients of  $1.4 \times 10^{-14}$  and  $6.0 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for 1propoxy and 2-propoxy, respectively, using LIF measurements for the direct detection of the radicals. Moreover, in a recent investigation<sup>9</sup> of the reactions of 2-butoxy radicals, applying the same method as described in this work, we obtained a rate coefficient for the oxygen reaction of  $6.5 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The rate constants of  $C_1-C_4$  alkoxy radicals for reaction with  $O_2$  are summarized in Table 3. The available kinetic data suggest that primary alkoxy radicals tend to have rate constants slightly higher than their secondary analogues. This reactivity trend is confirmed by  $k_5$  determined in this work. Whether this conclusion may be valid for even larger alkoxy radicals is the subject of further investigations in our laboratory.

A previous study of the O<sub>2</sub> reactions of linear chain C<sub>3</sub>-C<sub>8</sub> alkoxy radicals performed by our group<sup>43</sup> indicated rate coefficients of (7.3-8.0) × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. However, in this investigation the oxidation of the parent VOCs was initiated by Cl atoms which led to the simultaneous production of primary and secondary alkoxy radicals and the results obtained were weighted averages for the two types of alkoxy radicals. Nevertheless, the result obtained is consistent with a higher rate coefficient for primary alkoxy radicals ( $k_{O_2} \approx 1 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and a corresponding lower rate coefficient for the secondary radicals ( $k_{O_2} \approx 6 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). Further work is clearly necessary to confirm these conclusions.

**Isomerisation.** Although there are a number of investigations dealing with 1-butoxy isomerisation,  $^{7,8,21-23}$  no absolute rate constants are available in the literature. All previous studies provided rate constant ratios  $k_5/k_6$  from which  $k_6$  can be deduced. However, a direct comparison between previously reported rate coefficients and  $k_6$  as determined in this work should be made carefully for several reasons. First, all studies reported used the relative rate technique to determine the rate

Table 3 Summary of available rate constants for alkoxy radical reactions with O\_2 at 295  $\pm$  3 K

Radical	$\frac{k_{02}}{\text{cm}^3}$ molecule <sup>-1</sup> s <sup>-1</sup>	Method	Ref.
CH <sub>2</sub> O	$1.9 \times 10^{-15}$	Recommendation	13
C,H,O	$9.5 \times 10^{-15}$	SAR <sup>a</sup> , recommendation	7, 13
1-C,H,O	$9.5 \times 10^{-15}$	SAR <sup>a</sup>	7
5,	$8 \times 10^{-15}$	Recommendation	13
	$1.4 \times 10^{-14}$	LIF <sup>b</sup>	42
2-C <sub>3</sub> H <sub>7</sub> O	$8 \times 10^{-15}$	SAR <sup>a</sup> , recommendation	7, 13
5,	$6.0 \times 10^{-15}$	$LIF^{b}$	42
1-C₄H₀O	$9.5 \times 10^{-15}$	SAR <sup>a</sup>	7
<b>-</b> )	$1.34 \times 10^{-14}$	RRS <sup>c</sup>	21
	$(1.4 \pm 0.7) \times 10^{-14}$	$LPO^{d}$	This work
2-C <sub>4</sub> H <sub>9</sub> O	$8 \times 10^{-15}$	SAR <sup>a</sup>	7
<b>-</b> )	$6.5 \times 10^{-15}$	$LPO^{d}$	9
1-C <sub>5</sub> H <sub>11</sub> O	$9.5 \times 10^{-15}$	SAR <sup>a</sup>	7
5 11	$\leq 1.0 \times 10^{-13}$	$LPO^{d}$	This work

<sup>*a*</sup> Structure-activity relationship;  $9.5 \times 10^{-15}$  and  $8 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for primary and secondary alkoxy radicals, respectively. <sup>*b*</sup> Direct detection of the radicals. <sup>*c*</sup> Relative rate study;  $k_{02}$  determined relative to nitrite formation for which a rate constant of  $3.4 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was adopted. <sup>*d*</sup> Laser Pulse initiated oxidation.

of isomerisation. While Morabito and Heicklen<sup>21</sup> measured  $k_6$  relative to nitrite formation, all other experimental studies used the oxygen reaction as reference.<sup>8,23</sup> Since the reference reactions have their own uncertainties, the error of  $k_6$  is potentially enhanced. Second, because of severe difficulties in producing linear alkoxy radicals with more than three C atoms, it was hitherto not possible to generate the radicals selectively. In typical smog chamber experiments, all possible alkoxy radicals are produced simultaneously, although with characteristic yields according to the relative reactivity of different H atoms in the parent VOC towards OH radicals. This complicates the analysis of product yields, making the extraction of individual rate coefficients difficult and somewhat speculative.

Furthermore, all previous studies were carried out near atmospheric pressure, whereas our experiments were conducted at 50 mbar. Only the work of Morabito and Heicklen<sup>21</sup> was performed at 533 mbar. Since the fall-off behaviour of alkoxy radical isomerisations is not known, a direct comparison with our results is not possible. For that reason, it seems more appropriate to compare  $k_6$  with the results from *ab initio*/RRKM calculations.<sup>24</sup> This theoretical analysis indicates an isomerisation rate constant at 50 mbar of  $2.7 \times 10^4 \text{ s}^{-1}$ , whereas the predicted value for 1000 mbar is  $5.0 \times 10^4 \text{ s}^{-1}$ . The agreement between the theoretically obtained and the measured value for  $k_6$ , as determined in this work, is satisfactory if the fact that an uncertainty of  $\pm 1$  kcal mol<sup>-1</sup> in the calculated energy barrier corresponds to an uncertainty in the predicted rate constant of a factor of approximately 5 is considered.

The available data on 1-butoxy isomerisation are summarized in Table 4. The detailed fall-off curve, as provided in ref. 24, together with experimental data, is shown in Fig. 14.

#### 4.2 Reactions of 1-pentoxy radicals

As the concentration-time profiles are insensitive towards  $k_{25}$ and  $k_{26}$  (as long as they are varied in their expected ranges), only limiting values for these rate coefficients could be obtained in this work. Therefore,  $k_{25}$  and  $k_{26}$  cannot be discussed in detail. To our knowledge, reactions of 1-pentoxy radicals have not been studied experimentally before. However, since 1-pentoxy radicals are primary alkoxy radicals, their rate coefficient for reaction with O<sub>2</sub> can be estimated to be approximately  $1 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Unfortunately, our result of  $k_{25} \le 1.0 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> allows no assessment of the reactivity trends of primary and secondary alkoxy radicals to be made.

Atkinson<sup>7</sup> proposed that isomerisations proceeding via H atom abstraction from a  $CH_2$  group are a factor of approximately 10 faster than isomerisations abstracting H atoms from a  $CH_3$  group. Although the quantitative benefit of the

Table 4 Summary of available isomerisation rate constants of 1-butoxy radicals at 295  $\pm$  3 K

<i>p</i> /mbar	$k_{\rm Isom}/{\rm s}^{-1}$	Method	Ref.
1000	$1.4 \times 10^{5}$	RRS <sup>a</sup>	23
	$1.8 \times 10^{5}$	RRS <sup>a</sup>	8
	$1.6 \times 10^{5}$	SAR <sup>b</sup>	7
533	$2.0 \times 10^{5}$	RRS <sup>c</sup>	21
50	$2.7 \times 10^{4}$	<b>RRKM</b> calculation	24
	$(3.5 \pm 2) \times 10^4$	$LPO^{d}$	This work

<sup>*a*</sup> Relative rate study;  $k_{\rm Isom}$  determined relative to reaction with O<sub>2</sub> for which a rate constant of 9.5 × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> as provided in ref. 7 was adopted. <sup>*b*</sup> Structure-activity relationship;  $k_{\rm Isom} = 2.4 \times 10^{11} \times \exp(-4170/T) \, {\rm s}^{-1}$ . <sup>*c*</sup> Relative rate study;  $k_{\rm Isom}$  determined relative to nitrite formation for which a rate constant of  $3.4 \times 10^{-11} \, {\rm cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> was adopted. <sup>*d*</sup> Laser pulse initiated oxidation.



Fig. 14 Fall-off curve of 1-butoxy radicals obtained by RRKM calculations (T = 290 K)<sup>23</sup> and comparison of isomerisation rate constants derived in this work and those calculated from previous studies using  $9.5 \times 10^{-15} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> as rate coefficient for the O<sub>2</sub> reaction.<sup>7</sup>

value for  $k_{26}$  as derived in this work is limited, our experiments confirm the difference between these two types of isomerisations qualitatively.

#### 5 Conclusion

The technique of time-resolved and simultaneous detection of  $NO_2$  and OH and subsequent numerical simulation of the concentration-time profiles was used to study the reactions of 1-butoxy and 1-pentoxy radicals. The radicals were produced selectively by the excimer-laser photolysis of their respective bromoalkanes in the presence of  $O_2$  and  $NO_x$ . The reactions investigated are reaction with  $O_2$  and isomerisation. The numerical simulations were carried out with the FACSIMILE program, which used complete chemical mechanisms, and the rate coefficients under investigation were varied until the computed profiles best fitted the experimentally obtained profiles. Prior to the determination of individual rate constants, the sensitivity of the simulations towards the rate constants of interest was tested in detail using the GEPASI code.

In the case of 1-butoxy radicals, this method was found to be adequate to extract absolute rate constants, whereas the extremely fast isomerisation of 1-pentoxy radicals led to the determination of limiting values for  $k_{25}$  and  $k_{26}$  only. The rate coefficients obtained in this work confirm the previously expected trends in reactivity for primary and secondary alkoxy radicals such that primary radicals have slightly higher rate coefficients for reaction with O<sub>2</sub> than secondary radicals. Moreover, it was shown that isomerisations abstracting H atoms from a CH<sub>2</sub> group are significantly faster than those which abstract the H atom from a methyl group.

In summary, the technique used in this work must be considered a useful tool to study reactions which are part of a complex reaction mechanism. Therefore, further investigations of alkoxy radical reactions will be carried out in the future in our laboratory.

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