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Kinetics of the Reactions of OH Radicals with n-Butyl, Isobutyl, n-Pentyl and 3-Methyl-1-Butyl Nitrates

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ABSTRACT

The kinetics of the reactions of n-butyl (BTN), isobutyl (IBN), n-pentyl (PTN) and 3-methyl-1-butyl (3M1BN) nitrates with OH radicals has been studied using a low pressure flow tube reactor combined with a quadrupole mass spectrometer. The rate constants of the title reactions were determined under pseudo-first order conditions from kinetics of OH consumption in high excess of the nitrates. The overall rate coefficients, $k_{BTN} = 1.0\times10^{-13} (T/298)^{3.36} \exp(838/T)$ (T = 288-500 K), $k_{IBN} = 2.8\times10^{-14} (T/298)^{4.09} \exp(1127/T)$ (T = 283-500 K), $k_{PTN} = 1.26\times10^{-12} (T/298)^{4.56} \exp(45/T)$ (T = 298-496 K) and $k_{3M1BN} = 8.47\times10^{-14} (T/298)^{3.52} \exp(1069/T)$ $cm^3molecule^{-1}s^{-1}$ (T = 288-538 K) (with conservative 15% uncertainty), were determined at a total pressure of 1 Torr of helium. The yields of the carbonyl compounds, n-butanal (n-C_3H_7CHO) and isobutanal ($(CH_3)_2CHCHO$), resulting from the abstraction by OH of an α-hydrogen atom in n-butyl and isobutyl nitrates, followed by α-substituted alkyl radical decomposition, were determined at T = 300 K to be 0.10 ± 0.02 and 0.15 ± 0.03, respectively. The calculated tropospheric lifetimes of BTN, IBN, PTN and 3M1BN indicate that reaction of these nitrates with OH represents an important sink of these compounds in the atmosphere.

Keywords: alkyl nitrates, OH, kinetics, rate constant, atmospheric lifetime

1. Introduction

Organic nitrates are the intermediates of the atmospheric oxidation of volatile organic compounds in the presence of nitrogen oxides. They are formed in the minor (addition) channel of the reaction of peroxy radicals with NO and also in the NO_3-initiated oxidation of unsaturated organic compounds (Finlayson-Pitts and Pitts, 2000). Organic nitrates are temporary reservoirs of NO_x with a tropospheric lifetime from a few days to a few weeks, depending on their reactivity toward OH radicals and photolysis rate (Atkinson et al., 2006; Clemitshaw et al., 1997; Talukdar et al., 1997a; Talukdar et al., 1997b). Due to their chemical stability (relatively long atmospheric lifetime) the nitrates can undergo long-range transport in the troposphere thus suppling NO_x to the remote regions. Hence, organic nitrates significantly influence the distribution of NO_x and the concentration of ozone at a regional scale. Assessing of the atmospheric impact of organic nitrates requires the information on both their lifetime, which determines their ability to transport reactive nitrogen over long distances, and the mechanism of their oxidation in the atmosphere leading to recycling of NO_x.

In the present work, we report the results of the experimental investigation of the reactions of n-butyl (n-$C_4H_9ONO_2$, BTN), isobutyl ($(CH_3)_2CHCH_2ONO_2$, IBN), n-pentyl (n-$C_5H_{11}ONO_2$, PTN), and 3-methyl-1-butyl ($(CH_3)_2CHCH_2CH_2ONO_2$, 3M1BN) nitrates with OH radicals:

$$OH + n\text{-}C_4H_9ONO_2 \rightarrow \text{products} \quad (1)$$

$$OH + (CH_3)_2CHCH_2ONO_2 \rightarrow \text{products} \quad (2)$$

$$OH + n\text{-}C_5H_{11}ONO_2 \rightarrow \text{products} \quad (3)$$

$$OH + (CH_3)_2CHCH_2CH_2ONO_2 \rightarrow \text{products} \quad (4)$$

The available data on the rate constants of the reactions (1) - (4) are limited to a few studies at room temperature (Atkinson and Aschmann, 1989; Becker and Wirtz, 1989; Nielsen et al., 1991; Treves and Rudich, 2003). In the present paper, we report the first measurements of the

temperature dependence of the rate constants of the reactions (1) - (4) and the yields of the carbonyl compounds, n-butanal (n-C_3H_7CHO) and isobutanal ($(CH_3)_2CHCHO$), resulting from the abstraction by OH of an α-hydrogen atom in n-butyl and isobutyl nitrates, followed by corresponding α-substituted alkyl radical decomposition, at T = 300 K.

2. Experimental section

Experiments were carried out at 1 Torr total pressure of helium in a discharge flow reactor combined with a modulated molecular beam mass spectrometer (MS). Depending on the temperature range, two different flow reactors were used. The first one, thermostated Pyrex tube (45 cm length and 2.4 cm i.d.) covered with halocarbon wax (Bedjanian et al., 1999a, b; Romanias et al., 2015) was employed at low temperatures (283 – 358 K). The second, high temperature reactor (Fig. S1, Supplementary data) consisting of a Quartz tube (45 cm length and 2.5 cm i.d.) with an electrical heater and water-cooled extremities (Morin et al., 2016; Morin et al., 2015) was used at temperatures up to 538 K.

OH radicals were generated by reacting hydrogen atoms, produced in a microwave discharge of H_2/He mixture, with NO_2:

$$H + NO_2 \rightarrow OH + NO \qquad (5)$$

NO_2 was always used in excess over H atoms. OH radicals were detected as $HOBr^+$ (*m*/*z* = 96/98) after scavenging by an excess of Br_2 ($[Br_2] \approx 5\times10^{13}$ molecule cm^{-3}, added at the end of the reactor, 5 cm upstream of the sampling cone) via reaction:

$$OH + Br_2 \rightarrow HOBr + Br \qquad (6)$$

This method for OH detection was preferred to the direct detection of these radicals at *m*/*z* = 17 (OH^+) due to significant background signal at this mass. Similarly, the chemical conversion of OH to HOBr was used for the measurements of the absolute concentrations of the radicals: $[OH] = [HOBr] = \Delta[Br_2]$, i.e. concentrations of OH were determined from the

consumed fraction of [Br_2]. [Br_2] was determined from the measured flow rate of known Br_2/He mixtures. The possible influence of secondary chemistry on this method of HOBr detection and their absolute calibration procedure was discussed in details in previous papers from this group (Bedjanian et al., 1999a, b).

The nitrates were introduced into the flow reactor from a 10L flask containing nitrate-He mixture or by passing helium through a thermostated glass bubbler containing liquid nitrate and were detected by mass spectrometry at their fragment peaks at *m*/*z* = 76 ($CH_2ONO_2^+$), which were much more intensive than the parent ones. All other species were detected at their parent peaks: *m*/*z*= 72 (n-butanal, $C_3H_7CHO^+$), 72 (isobutanal, $(CH_3)_2CHCHO^+$), 160 (Br_2^+), 96/98 ($HOBr^+$), 46 (NO_2^+). The absolute concentrations of the nitrates as well as of other stable species in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of mixtures of the species with helium in calibrated volume flasks.

The purities and origin of the gases used were as follows: He >99.9995% (Alphagaz), was passed through liquid nitrogen traps; H_2 > 99.998% (Alphagaz); Br_2 >99.99% (Aldrich); NO_2 > 99% (Alphagaz); n-butanal > 99.0% (Aldrich); isobutanal > 99.0% (Aldrich); n-butyl nitrate > 99% (Chemos); isobutyl nitrate 96% (Aldrich); n-pentyl nitrate > 98% (TCI Europe); 3-methyl-1-butyl nitrate > 98% (TCI Europe). All the nitrates were degassed before use.

3. Results

3.1. Measurements of the rate constants

The measurements of the rate constants of the reactions (1) – (4) were carried out under pseudo-first order conditions in excess of nitrates over OH radicals. The initial concentration of OH radicals was nearly 5×10^{11} molecule cm^{-3}. Initial concentrations of the nitrates are shown in Table S1 (Supplementary data). The flow velocity in the reactor was in the range

(1150-2300) cm s^{-1}. Examples of the exponential decays of OH in reaction (1) are shown in Fig. 1.

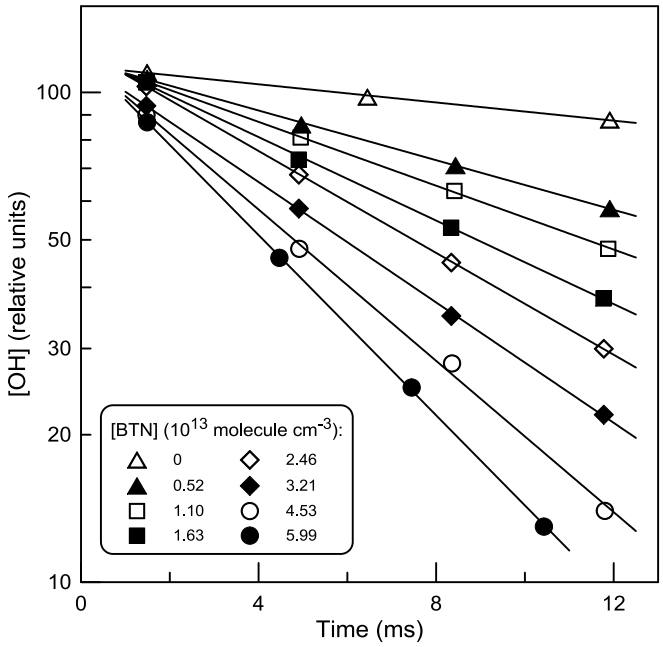

Fig. 1. Examples of the exponential decays of OH in reaction with n-butyl nitrate: T = 500 K.

Fig. 2 and S2 – S4 (Supplementary data) show examples of the dependencies of the pseudo-first order rate constant, $k' = k[\text{nitrate}] + k_w$, on concentration of the corresponding nitrate. k_w represents the rate of OH decay in the absence of nitrate in the reactor and was measured in separate experiments.

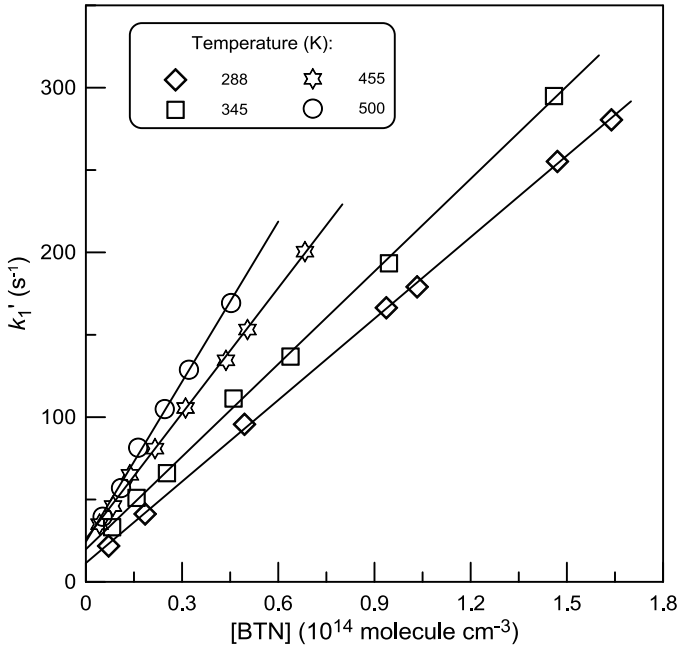

Fig. 2. Example of pseudo-first order plots obtained from OH decays in excess of n-butyl nitrate.

All the measured values of k' were corrected for axial and radial diffusion of OH (Kaufman, 1984). The diffusion coefficient of OH in He was calculated using the following expression: $D_0 = 640 \times (T/298)^{1.85}$ Torr cm^2 s^{-1} (Bedjanian et al., 2010; Ivanov et al., 2007). Corrections on k' were generally less than 10%, however, in a few kinetic runs they were somewhat higher (up to 15%). The slopes of the straight lines in Fig. 2 and S2 – S4 provide the values of the rate constants at respective temperatures. The intercepts were generally in agreement in the range of the experimental uncertainty with the corresponding OH loss rate measured in the absence of nitrates in the reactor: k_w was in the range 7 -20 s^{-1} depending rather on state of the reactor surface than on temperature.

All the results obtained for the rate constants of reactions (1) – (4) at different temperatures are shown in Table S1. The lowest temperature in the rate constant measurements was limited by impact of the heterogeneous chemistry which was manifested in an anomalous increase of the measured rate constant with decreasing temperature. Highest temperature of the study (around 500 K) was limited by thermal decomposition of the nitrates.

In order to check for the possible impact on the measurements of the rate constants of the secondary chemistry, the reaction rate was measured as a function of initial concentration of OH radicals. Fig. S5 and S6 (Supplementary data) shows the results of the measurements of k_1' and k_2' at fixed concentrations of BTN and IBN, respectively, and varied initial concentration of OH. Independence of the reaction rate of concentration of OH for $[OH]_0 < 10^{12}$ molecule cm^{-3} indicates the negligible contribution of the secondary chemistry to OH loss under experimental conditions of the study ($[OH]_0 \approx 5\times10^{11}$ molecule cm^{-3}). Similar picture was also observed in the case of OH reaction with PTN and 3M1BN.

Temperature dependences of the rate constants of the reactions of OH with BTN, IBN, PTN and 3M1BN are shown in Fig. 3, 4, 5 and 6, respectively. The combined uncertainty on the measurements of the rate constants was estimated to be nearly 15%, including statistical error (within a few percent) and those on the measurements of the flows (5%), pressure (2%), temperature (1%) and the absolute concentrations of the nitrates (~ 10%).

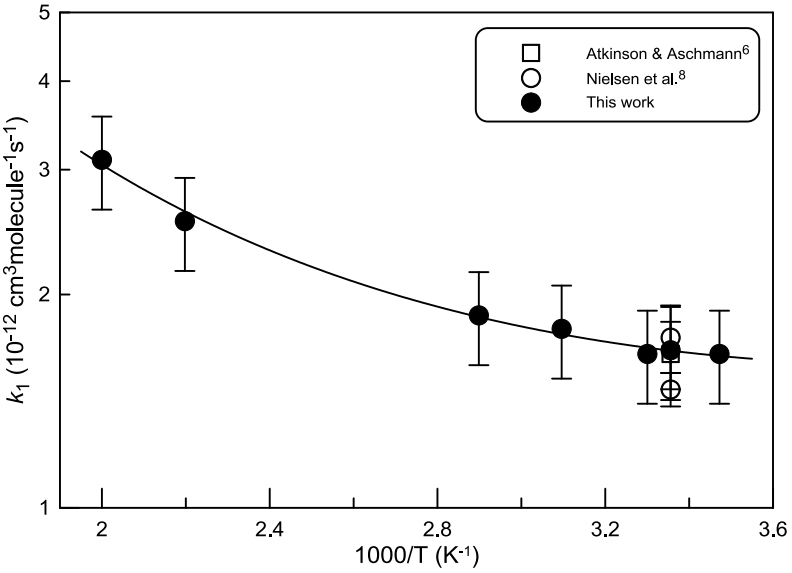

Fig. 3. Summary of the measurements of the rate constant of the reaction OH + n-butyl nitrate.

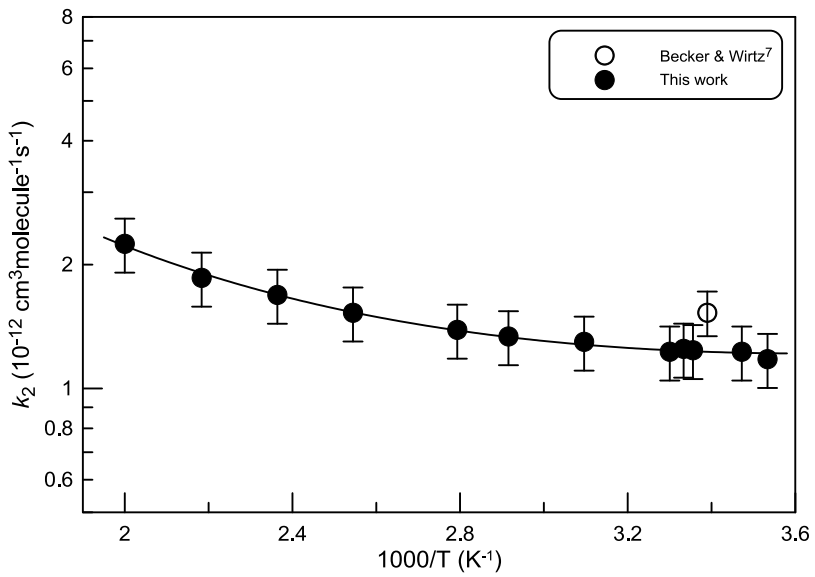

Fig. 4. Summary of the measurements of the rate constant of the reaction OH + isobutyl nitrate.

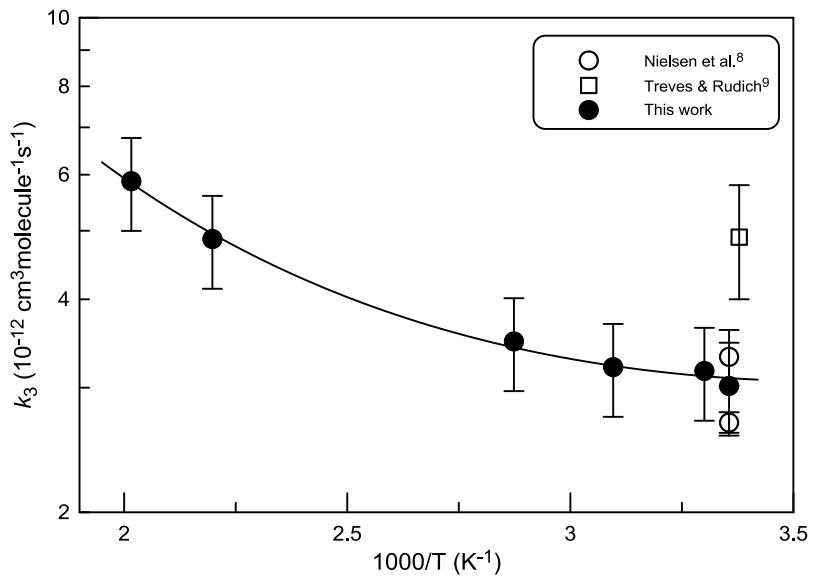

Fig. 5. Summary of the measurements of the rate constant of the reaction OH + n-pentyl nitrate.

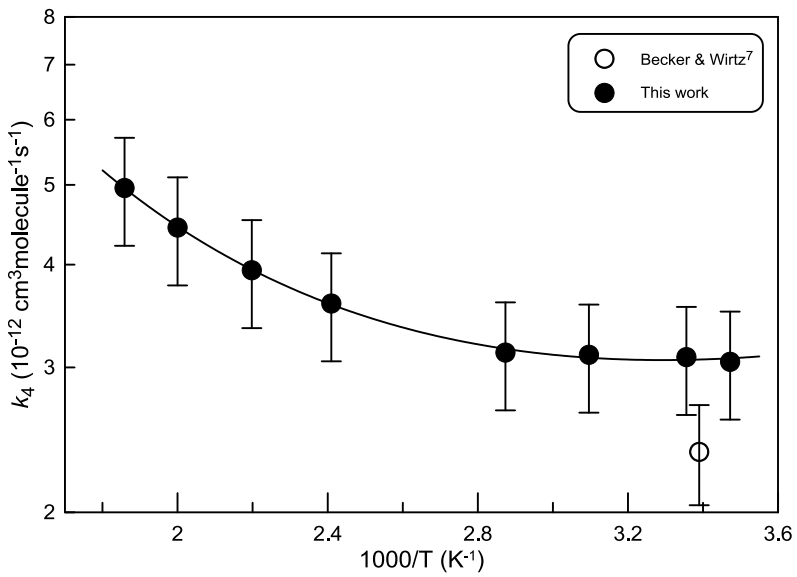

Fig. 6. Summary of the measurements of the rate constant of the reaction OH + 3-methyl-1-butyl nitrate.

As one can see, the temperature dependence of the measured rate constants deviates from a simple Arrhenius behavior as could be expected considering that the overall rate constant is the sum of those for H-atom abstraction channels proceeding through breaking of different C-H bonds. The experimental data were fitted with a three-parameter expression, leading to the following results:

$k_1 = 1.0\times10^{-13}\ (T/298)^{3.36}\ \exp(838/T)$ cm^{3}molecule^{-1}s^{-1} (T = 288-500 K),

$k_2 = 2.8\times10^{-14}\ (T/298)^{4.09}\ \exp(1127/T)$ cm^{3}molecule^{-1}s^{-1} (T = 268-500 K)

$k_3 = 1.26\times10^{-12}\ (T/298)^{4.56}\ \exp(45/T)$ cm^{3}molecule^{-1}s^{-1} (T = 298-496 K),

$k_4 = 8.47\times10^{-14}\ (T/298)^{3.52}\ \exp(1069/T)$ cm^{3}molecule^{-1}s^{-1} (T = 288-538 K)

with conservative independent of temperature 15% uncertainty on the rate constant.

3.2. α-hydrogen atom abstraction channel in reactions (1) and (2)

Abstraction by OH of an hydrogen atom from α-carbon in organic nitrates leads to the formation of an α-substituted alkyl radicals:

$$OH + R_1R_2CHONO_2 \rightarrow R_1R_2C^{\bullet}ONO_2 + H_2O$$

These radicals are known to be unstable, dissociating spontaneously without an energetic barrier to form a carbonyl compound and NO_2 (Vereecken, 2008):

$$R_1R_2C^{\bullet}ONO_2 \rightarrow R_1R_2C{=}O + NO_2$$

There is an experimental evidence (Romanias et al., 2015) that the rate of the prompt $R_1R_2C^{\bullet}ONO_2$ radical decomposition under atmospheric conditions is much higher than the rate of its possible stabilization and/or reaction with O_2, in agreement with the conclusion of the theoretical study of Vereecken (2008) that the radical decomposition occurs on timescales that are too short for any chemical process to compete. The measurements of the yield of carbonyl compound formed upon decomposition of $R_1R_2C^{\bullet}ONO_2$ radical provide the information on the extent of H-atom abstraction from α carbon. In the present paper, we have determined at T = 300 K the yields of n-butanal and isobutanal resulting from the abstraction by OH of an α-hydrogen atom in n-butyl and isobutyl nitrates, respectively, followed by corresponding α-substituted alkyl radical decomposition. Example of the kinetics of the product formation along with the kinetics of OH consumption is shown in Fig. 7.

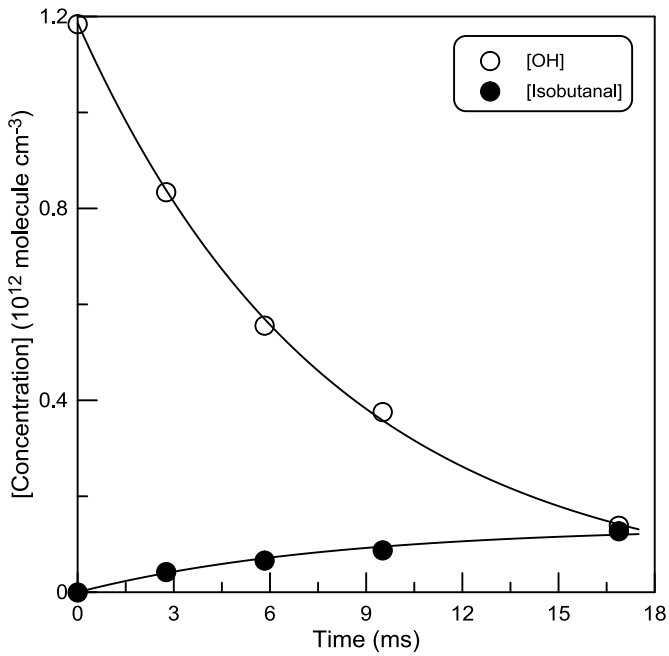

Fig. 7. Example of kinetics of OH consumption and isobutanal formation in the reaction of OH radicals with isobutyl nitrate: T = 300K; [IBN] = 8.2×10^{13} molecule cm^{-3}.

Continuous lines in Fig. 7 represent the simulation of the experimental profiles of OH (exponential function) and isobutanal. Temporal profile of isobutanal is fitted with the following equation:

$$[\text{isobutanal}] = \alpha\times(k' - k_w')/k'\times[\text{OH}]_0\times(1 - \exp(-k't),$$

where α is the product yield, k' and k_w' are the first order rate constants of OH consumption in the presence and in the absence (heterogeneous loss) of nitrate in the reactor (determined experimentally), respectively. α was the only fitting parameter. The value of α obtained from the best fit to the isobutanal profile in Fig. 7 is 0.143.

The bulk of the experiments on the determination of the yields of n-butanal and isobutanal in reactions (1) and (2) consisted in the monitoring of the consumed [OH] and [n-C_3H_7CHO] (or [$(CH_3)_2CHCHO$]) formed at a fixed reaction time (6 – 30 ms). The concentration ranges used in these experiments were [OH] = $(0.5\text{-}3.5)\times10^{12}$, [BTN] = = $(0.3 – 0.7)\times10^{14}$ and [IBN] = $(0.3 – 1.9)\times10^{14}$ molecule cm^{-3}. Concentration of OH consumed in reaction with nitrate was determined as a difference between initial concentration of the radicals (measured in the absence of nitrate and presence of Br_2 in the main reactor) and concentration of OH recorded in the presence of nitrate in the reactor (Br_2 being added at the end of the reactor). The relative contribution of the wall loss to consumed [OH] depended on concentration of nitrates (up to 30% at lowest concentrations of the nitrates) and was taken into account. The experimental data are shown in Fig. 8 and 9. Error bars in Fig. 8 and 9 correspond to 10% and 15% uncertainties on the measurements of the concentrations of OH and reaction products, respectively. Higher uncertainty on the measurements of the concentrations of n-butanal and isobutanal is due to important contribution to their peaks at m/z = 72 of n-butyl and isobutyl nitrates upon their fragmentation in the ion source of the mass spectrometer which was operated at 25-30 eV energy. The slopes of the straight lines in

Fig. 8 and 9 provide the yields of n-butanal and isobutanal in reactions (1) and (2) at T = 300K: 0.10 ± 0.02 and 0.15 ± 0.03, respectively. The estimated nearly 20% uncertainty on the measurements arises mainly from the combined errors on the measurements of the concentrations of OH and reaction product.

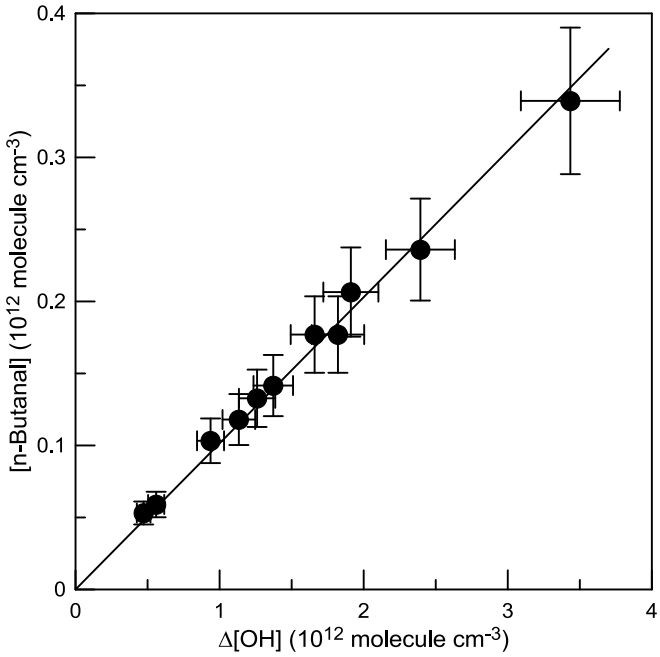

Fig. 8. Concentration of n-butanal formed in reaction (1) as a function of the consumed concentration of OH.

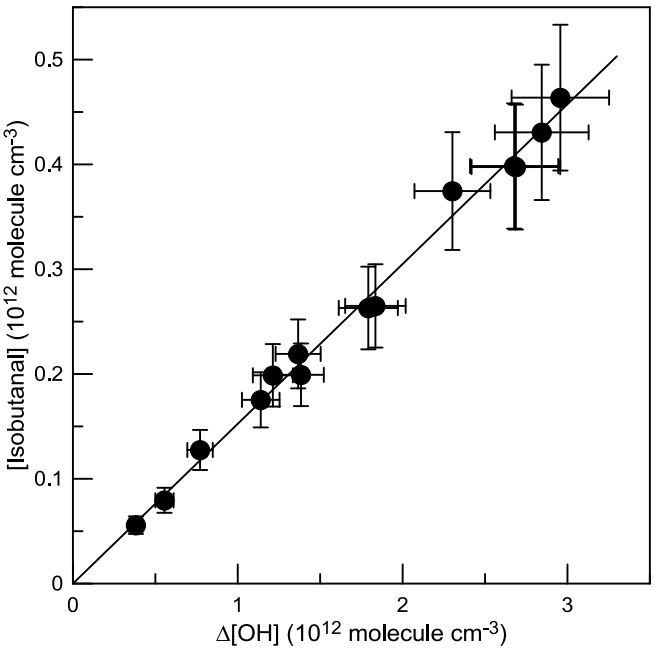

Fig. 9. Concentration of isobutanal formed in reaction (2) as a function of the consumed concentration of OH.

4. Discussion

To our knowledge, this is the first study of the temperature dependence of the rate constant of the title reactions. Previously, the rate constant of reaction (1) was measured in two room temperature studies (Atkinson and Aschmann, 1989; Nielsen et al., 1991) using both relative (Atkinson and Aschmann, 1989; Nielsen et al., 1991) and absolute (Nielsen et al., 1991) rate method. These data (relative rate measurements being placed on the absolute basis using updated rate constants for the reference reactions (Calvert et al., 2011)) are shown in Fig. 3 together with those from the present work. One can note good agreement between the results of the previous studies obtained at total pressure of 1 atm of air and those of the present one measured at nearly 1 Torr pressure of helium as could be expected for a bimolecular reaction proceeding via abstraction of an H atom from the alkyl group. The rate constant of reaction (2), k_2 = (1.53 ± 0.19)×10^{-12} $cm^3molecule^{-1}s^{-1}$ measured by Becker and Wirtz (1989) at T = 295 K using relative rate method and placed on the absolute basis in Calvert et al. (2011) agrees in the range of the reported experimental uncertainties with the present data (Fig. 4). The rate coefficient of the reaction OH + PTN has been measured by Nielsen et al. (1991) at T = 298 K using relative (k_3 = (2.68 ± 0.09)×10^{-12} $cm^3molecule^{-1}s^{-1}$, newly placed on the absolute basis in Calvert et al. (2011) and absolute rate method (k_3 = (3.32 ± 0.30)×10^{-12} $cm^3molecule^{-1}s^{-1}$) and in relative rate study of Treves and Rudich (2003) (k_3 = (4.9 ± 0.9)×10^{-12} $cm^3molecule^{-1}s^{-1}$). The values of k_3 from Nielsen et al. (1991) are in good agreement with our data (Fig. 5), while that of Treves and Rudich (2003) is by a factor of 1.6 higher. Finally, the rate coefficient, k_4 = (2.37 ± 0.33)×10^{-12} $cm^3molecule^{-1}s^{-1}$, measured by Becker and Wirtz (1989) in a relative rate study at T = 295 K and atmospheric pressure, is somewhat lower although in agreement within experimental uncertainties with our value of k_4 (Fig. 6).

In this study, we have determined at T = 300 K the yields of n-butanal and isobutanal resulting from the decomposition of α-substituted alkyl radicals formed upon initial abstraction by OH of an α-hydrogen atom in n-butyl and isobutyl nitrates, respectively. The measured product yields can be considered as the branching ratios for an α-hydrogen atom abstraction pathway of the respective reactions:

$$OH + CH_3CH_2CH_2CH_2ONO_2 \rightarrow CH_3CH_2CH_2CHONO_2 + H_2O \quad (1a)$$

$k_{1a}/k_1 = 0.10 \pm 0.02$,

$$OH + (CH_3)_2CHCH_2ONO_2 \rightarrow (CH_3)_2CHCHONO_2 + H_2O \quad (2a)$$

$k_{2a}/k_2 = 0.15 \pm 0.03$

The rate constant data for the reactions of OH radicals with alkyl nitrates obtained in the present work and two previous studies from this group (Morin et al., 2016; Romanias et al., 2015) are shown in Table 1 in comparison with the corresponding values calculated using Structure-Activity Relationship (SAR) of Kwok and Atkinson (with group rate constants for abstraction of primary, secondary, and tertiary H-atoms $k(\text{-CH}_3) = 0.136$, $k(\text{-CH}_2\text{-}) = 0.934$ and $k(\text{>CH-}) = 1.94\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ and substituent factors $F(\text{-CH}_3) = 1$, $F(\text{-CH}_2\text{-}) = F(\text{>CH-}) = F(\text{>C<}) = 0.23$, $F(\text{-ONO}_2) = 0.04$, $F(\text{-CH}_2\text{ONO}_2) = F(\text{>CHONO}_2) = F(\equiv\text{C-ONO}_2) = 0.20$) (Kwok and Atkinson, 1995). It can be noted that the total rate constant estimated within SAR is significantly lower than the experimental value for four from seven nitrates. Similarly, the extent of H-atom abstraction from α carbon in alkyl nitrates is considerably underestimated by SAR. Difficulties arising for the prediction of the rate constants of OH reactions with organic nitrates were also highlighted in a more recent development of SAR (Neeb, 2000). Currently, we continue the experimental studies of the kinetics and products of the OH reactions with other alkyl nitrates in order to improve the existing data base and to try to update the substituent factors for the -ONO_2 containing groups used in the calculations of the rate constants, at least for reactions of OH with alkyl nitrates.

Table 1
Comparison of the experimental and calculated (within SAR) rate constants for reactions of some alkyl nitrates with OH at T = 298 K.

Nitrate	Total rate constant[a]			k_α/k_{total}[b]		
	Exp.[c]	Calc.[d]	Calc./Exp.	Exp.[c]	Calc.[d]	Calc./Exp.
ethyl	2.01	0.65	0.32	0.77	0.58	0.75
propyl	5.98	4.00	0.67	0.22	0.11	0.50
isopropyl	3.02	1.32	0.44	0.82	0.59	0.72
n-butyl	16.6	15.9	0.96	0.10	0.03	0.30
isobutyl	12.3	7.69	0.63	0.15	0.06	0.40
n-pentyl	30.9	30.0	0.97			
3-methyl-1-butyl	30.6	30.0	0.98			

[a] Units of 10^{-13} $cm^3 molecule^{-1} s^{-1}$.
[b] Branching ratio for α-hydrogen atom abstraction channel.
[c] Experimental data from the present study, except for ethyl (Morin et al., 2016), propyl (Morin et al., 2016) and isopropyl nitrates (Romanias et al., 2015).
[d] calculated using SAR (Kwok and Atkinson, 1995).

Alkyl nitrates are lost in the atmosphere in the following processes: UV photolysis, reactions with atmospheric oxidants (OH, O_3, NO_3) and heterogeneous removal on liquid or solid surfaces. Photolysis of alkyl nitrates and their reaction with OH radicals are expected to be their major loss processes in the atmosphere, considering very low solubility of the nitrates in water. The tropospheric lifetimes of BTN, IBN, PTN and 3M1BN, with respect to their loss in reaction with OH only, calculated using the measured rate constants (at T = 298 K) and a 24h average concentration of the OH radical of 10^6 molecules cm^{-3} are 7.0, 9.4, 3.7 and 3.8 days, respectively. For comparison, the tropospheric lifetimes of BTN, IBN and PTN with respect to their photodissociation reported by Clemitshaw et al.(Clemitshaw et al., 1997) for summer conditions are between 3 and 13 days depending on altitude (0 – 10 km) and latitude (0 – 60°N). These data indicate that reaction with OH radicals is an important atmospheric sink for the four alkyl nitrates considered in the present study, comparable with that due to their photolysis.

5. Conclusion

In this work, we investigated the kinetics of the reaction of OH radicals with n-butyl, isobutyl, n-pentyl and 3-methyl-1-butyl nitrates. Temperature dependences of the rate constants of the title reactions, measured for the first time, were found to deviate from a simple Arrhenius behavior. n-Butanal and isobutanal were directly detected as products of the OH reactions with BTN and IBN for the first time. Their yields measured at T = 300K, 0.10 ± 0.02 and 0.15 ± 0.03, respectively, correspond to the branching ratios for the α-hydrogen atom abstraction pathway of the reactions of OH with BTN and IBN. Comparison of the experimental data with those estimated with Structure-Activity Relationship (SAR) confirms the current view concerning the problems in the SAR based prediction of the rate constants of OH reactions with organic nitrates. Finally, the tropospheric lifetimes of BTN, IBN, PTN and 3M1BN, calculated using the measured rate constants, indicate that reaction of these nitrates with OH represents an important sink of these compounds in the atmosphere.

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Appendix A. Supplementary Data

Supplementary data related to this article can be found at...

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Kinetics of the Reactions of OH Radicals with n-Butyl, Isobutyl, n-Pentyl and 3-Methyl-1-Butyl Nitrates

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Highlights

- Reactions of OH radicals with four alkyl nitrates are studied
- Rate constants are measured as a function of temperature
- Branching ratios for an α-hydrogen atom abstraction in n-butyl and isobutyl nitrates are measured
- Tropospheric lifetimes of the four nitrates with respect to their reaction with OH are determined