1 **Kinetics of the Reactions of OH Radicals with n-Butyl, Isobutyl,**

2 **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, $k_{BTN} = 1.0 \times 10^{-13}$ $(T/298)^{3.36}$ exp(838/T) (T = 288-500 K), $k_{IBN} = 2.8 \times 10^{-14}$ $(T/298)^{4.09}$ exp(1127/T) (T = 283-500 K), $k_{PTN} = 1.26 \times 10^{-12}$ $(T/298)^{4.56}$ exp(45/T) (T = 298-496 K) and $k_{3M1BN} = 8.47 \times 10^{-14}$ $(T/298)^{3.52}$ exp(1069/T) $cm^3 molecule^{-1}s^{-1}$ (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:

$$OH + n\text{-}C_4H_9ONO_2 \rightarrow products \tag{1}$$

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

$$OH + n\text{-}C_5H_{11}ONO_2 \rightarrow products \tag{3}$$

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

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

74   temperature dependence of the rate constants of the reactions (1) - (4) and the yields of the

75   carbonyl compounds, n-butanal (n-C_3H_7CHO) and isobutanal ((CH_3)$_2$CHCHO), resulting

76   from the abstraction by OH of an α-hydrogen atom in n-butyl and isobutyl nitrates, followed

77   by corresponding α-substituted alkyl radical decomposition, at T = 300 K.

2. Experimental section

79   Experiments were carried out at 1 Torr total pressure of helium in a discharge flow

81   reactor combined with a modulated molecular beam mass spectrometer (MS). Depending on

82   the temperature range, two different flow reactors were used. The first one, thermostated

83   Pyrex tube (45 cm length and 2.4 cm i.d.) covered with halocarbon wax (Bedjanian et al.,

84   1999a, b; Romanias et al., 2015) was employed at low temperatures (283 – 358 K). The

85   second, high temperature reactor (Fig. S1, Supplementary data) consisting of a Quartz tube

86   (45 cm length and 2.5 cm i.d.) with an electrical heater and water-cooled extremities (Morin

87   et al., 2016; Morin et al., 2015) was used at temperatures up to 538 K.

88   OH radicals were generated by reacting hydrogen atoms, produced in a microwave

89   discharge of H_2/He mixture, with NO_2:

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

91   NO_2 was always used in excess over H atoms. OH radicals were detected as $HOBr^+$ (m/z =

92   96/98) after scavenging by an excess of Br_2 ([Br_2] $\approx$ 5×10^{13} molecule cm^{-3}, added at the end

93   of the reactor, 5 cm upstream of the sampling cone) via reaction:

94   OH + Br_2 $\rightarrow$ HOBr + Br   (6)
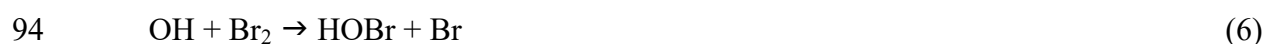
95   This method for OH detection was preferred to the direct detection of these radicals at m/z =

96   17 (OH^+) due to significant background signal at this mass. Similarly, the chemical

97   conversion of OH to HOBr was used for the measurements of the absolute concentrations of

98   the radicals: [OH] = [HOBr] = Δ[Br_2], i.e. concentrations of OH were determined from the

99   consumed fraction of [Br_2]. [Br_2] was determined from the measured flow rate of known

100 Br_2/He mixtures. The possible influence of secondary chemistry on this method of HOBr

101 detection and their absolute calibration procedure was discussed in details in previous papers

102 from this group (Bedjanian et al., 1999a, b).

103   The nitrates were introduced into the flow reactor from a 10L flask containing nitrate-He

104 mixture or by passing helium through a thermostated glass bubbler containing liquid nitrate

105 and were detected by mass spectrometry at their fragment peaks at $m/z = 76$ ($CH_2ONO_2^+$),

106 which were much more intensive than the parent ones. All other species were detected at their

107 parent peaks: $m/z = 72$ (n-butanal, $C_3H_7CHO^+$), 72 (isobutanal, $(CH_3)_2CHCHO^+$), 160 (Br_2^+),

108 96/98 ($HOBr^+$), 46 (NO_2^+). The absolute concentrations of the nitrates as well as of other

109 stable species in the reactor were calculated from their flow rates obtained from the

110 measurements of the pressure drop of mixtures of the species with helium in calibrated

111 volume flasks.

112   The purities and origin of the gases used were as follows: He >99.9995% (Alphagaz),

113 was passed through liquid nitrogen traps; H_2 > 99.998% (Alphagaz); Br_2 >99.99% (Aldrich);

114 NO_2 > 99% (Alphagaz); n-butanal > 99.0% (Aldrich); isobutanal > 99.0% (Aldrich); n-butyl

115 nitrate > 99% (Chemos); isobutyl nitrate 96% (Aldrich); n-pentyl nitrate > 98% (TCI Europe);

116 3-methyl-1-butyl nitrate > 98% (TCI Europe). All the nitrates were degassed before use.

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118 **3. Results**

119 *3.1. Measurements of the rate constants*

120   The measurements of the rate constants of the reactions (1) – (4) were carried out under

121 pseudo-first order conditions in excess of nitrates over OH radicals. The initial concentration

122 of OH radicals was nearly 5×10^{11} molecule cm^{-3}. Initial concentrations of the nitrates are

123 shown in Table S1 (Supplementary data). The flow velocity in the reactor was in the range

124 (1150-2300) cm s^{-1}. Examples of the exponential decays of OH in reaction (1) are shown in

125 Fig. 1.

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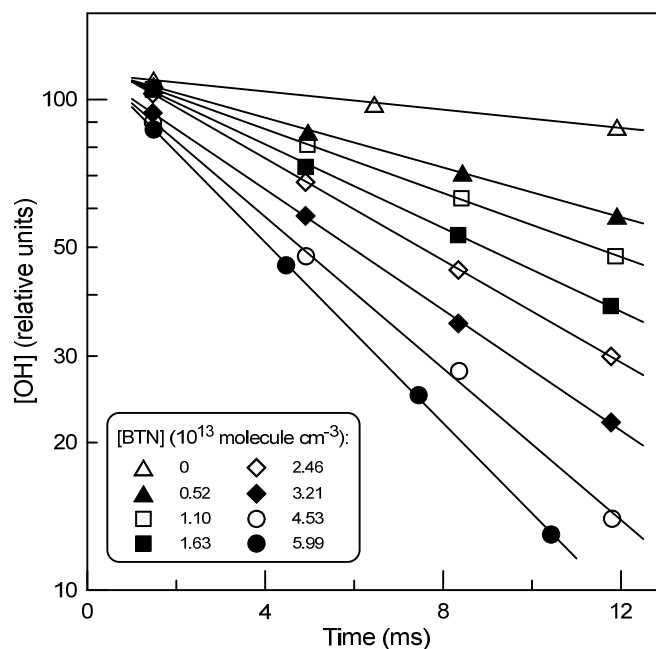
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128 **Fig. 1.** Examples of the exponential decays of OH in reaction with n-butyl nitrate: T = 500 K.

129 Fig. 2 and S2 – S4 (Supplementary data) show examples of the dependencies of the pseudo-

130 first order rate constant, $k' = k[\text{nitrate}] + k_w$, on concentration of the corresponding nitrate. k_w

131 represents the rate of OH decay in the absence of nitrate in the reactor and was measured in

132 separate experiments.
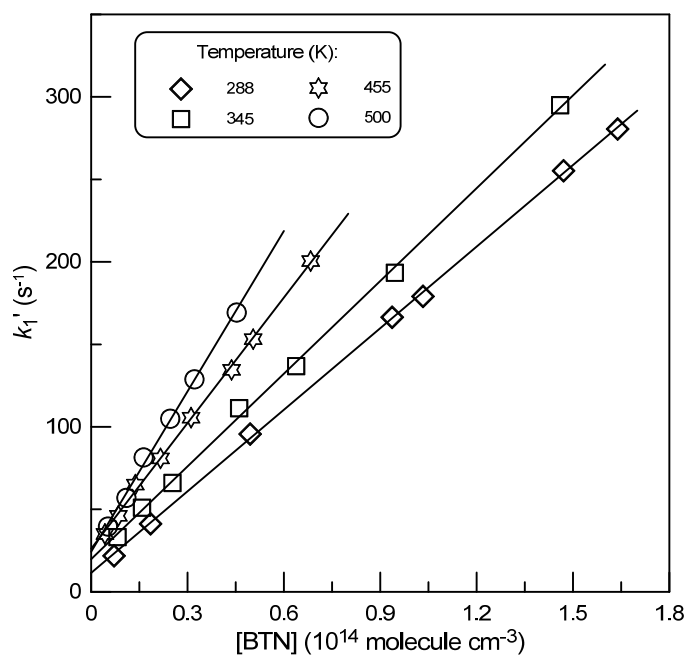
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134   **Fig. 2.** Example of pseudo-first order plots obtained from OH decays in excess of n-butyl nitrate.

135   All the measured values of k' were corrected for axial and radial diffusion of OH (Kaufman,

136   1984). The diffusion coefficient of OH in He was calculated using the following expression:

137    $D_0 = 640 \times (T/298)^{1.85}$ Torr cm^2 s^{-1} (Bedjanian et al., 2010; Ivanov et al., 2007). Corrections

138   on k' were generally less than 10%, however, in a few kinetic runs they were somewhat higher

139   (up to 15%). The slopes of the straight lines in Fig. 2 and S2 – S4 provide the values of the

140   rate constants at respective temperatures. The intercepts were generally in agreement in the

141   range of the experimental uncertainty with the corresponding OH loss rate measured in the

142   absence of nitrates in the reactor: k_w was in the range 7 -20 s^{-1} depending rather on state of the

143   reactor surface than on temperature.

144   All the results obtained for the rate constants of reactions (1) – (4) at different

145   temperatures are shown in Table S1. The lowest temperature in the rate constant

146   measurements was limited by impact of the heterogeneous chemistry which was manifested in

147   an anomalous increase of the measured rate constant with decreasing temperature. Highest

148   temperature of the study (around 500 K) was limited by thermal decomposition of the nitrates.

149   In order to check for the possible impact on the measurements of the rate constants of the

150   secondary chemistry, the reaction rate was measured as a function of initial concentration of

151   OH radicals. Fig. S5 and S6 (Supplementary data) shows the results of the measurements of

152   k_1' and k_2' at fixed concentrations of BTN and IBN, respectively, and varied initial

153   concentration of OH. Independence of the reaction rate of concentration of OH for $[OH]_0 <$

154   10^{12} molecule cm^{-3} indicates the negligible contribution of the secondary chemistry to OH

155   loss under experimental conditions of the study ($[OH]_0 \approx 5\times10^{11}$ molecule cm^{-3}). Similar

156   picture was also observed in the case of OH reaction with PTN and 3M1BN.

157   Temperature dependences of the rate constants of the reactions of OH with BTN, IBN,

158   PTN and 3M1BN are shown in Fig. 3, 4, 5 and 6, respectively. The combined uncertainty on

159   the measurements of the rate constants was estimated to be nearly 15%, including statistical

160   error (within a few percent) and those on the measurements of the flows (5%), pressure (2%),

161   temperature (1%) and the absolute concentrations of the nitrates ($\sim$ 10%).
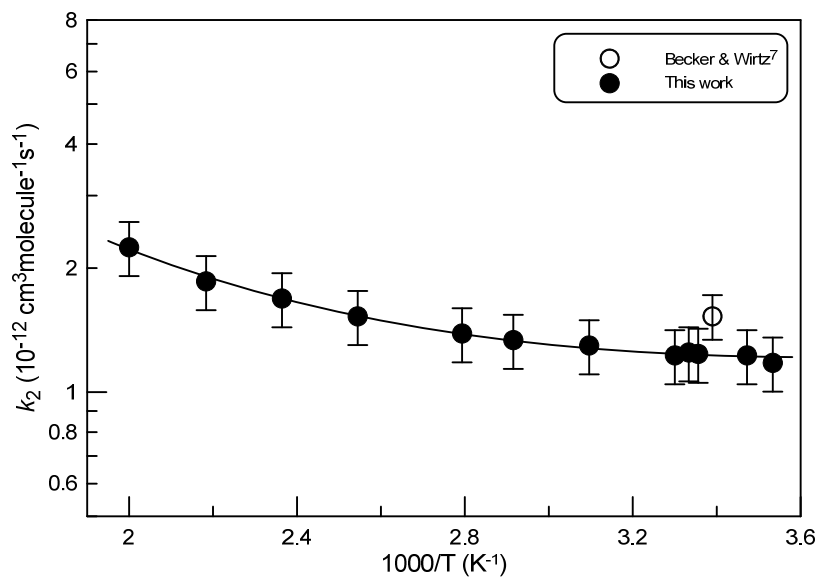
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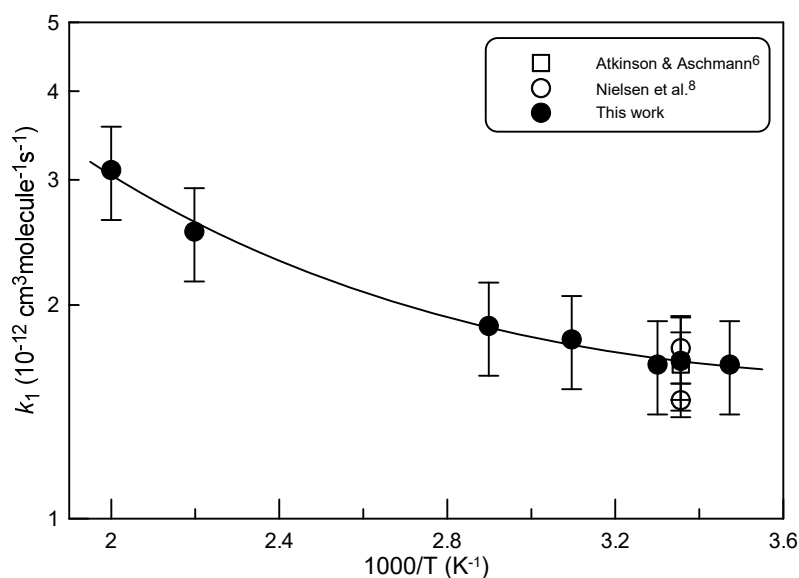
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164   **Fig. 3.** Summary of the measurements of the rate constant of the reaction OH + n-butyl nitrate.
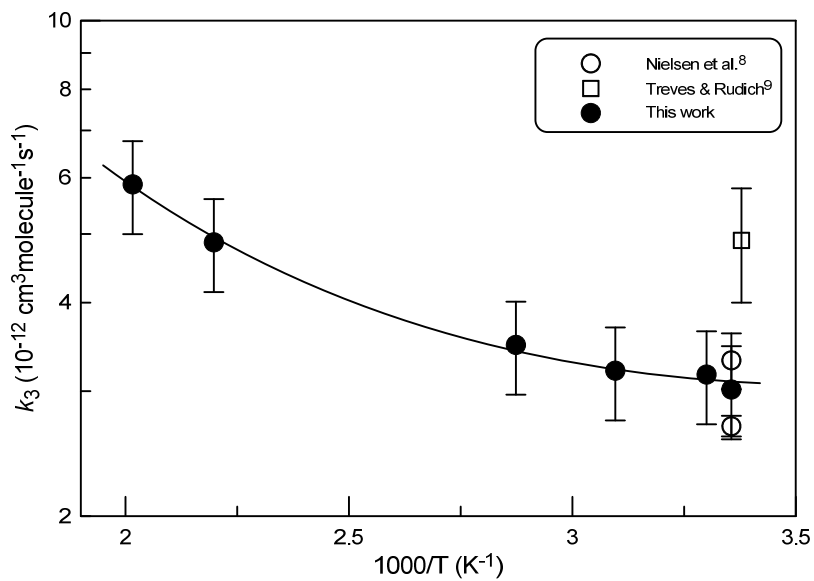
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166　**Fig. 4.** Summary of the measurements of the rate constant of the reaction OH + isobutyl nitrate.
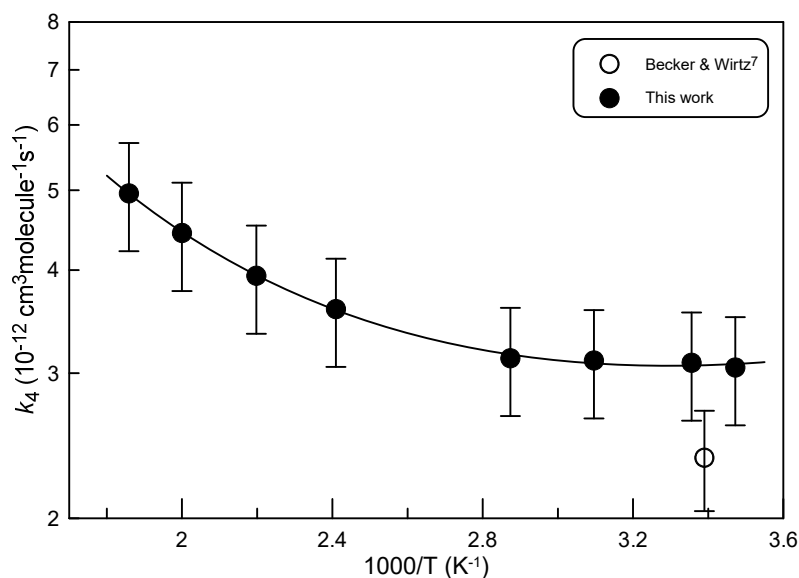
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169　**Fig. 5.** Summary of the measurements of the rate constant of the reaction OH + n-pentyl nitrate.

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

172   As one can see, the temperature dependence of the measured rate constants deviates from a

173   simple Arrhenius behavior as could be expected considering that the overall rate constant is

174   the sum of those for H-atom abstraction channels proceeding through breaking of different C-

175   H bonds. The experimental data were fitted with a three-parameter expression, leading to the

176   following results:

177    $k_1 = 1.0 \times 10^{-13} (T/298)^{3.36} \exp(838/T)$ cm^{3}molecule^{-1}s^{-1} (T = 288-500 K),

178    $k_2 = 2.8 \times 10^{-14} (T/298)^{4.09} \exp(1127/T)$ cm^{3}molecule^{-1}s^{-1} (T = 268-500 K)

179    $k_3 = 1.26 \times 10^{-12} (T/298)^{4.56} \exp(45/T)$ cm^{3}molecule^{-1}s^{-1} (T = 298-496 K),

180    $k_4 = 8.47 \times 10^{-14} (T/298)^{3.52} \exp(1069/T)$ cm^{3}molecule^{-1}s^{-1} (T = 288-538 K)

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

182

183   *3.2. α-hydrogen atom abstraction channel in reactions (1) and (2)*

184   Abstraction by OH of an hydrogen atom from α-carbon in organic nitrates leads to the

185   formation of an α-substituted alkyl radicals:

186   OH + R$_1$R$_2$CHONO$_2$ → R$_1$R$_2$C$^\bullet$ONO$_2$ + H$_2$O

187 These radicals are known to be unstable, dissociating spontaneously without an energetic

188 barrier to form a carbonyl compound and NO_2 (Vereecken, 2008):

189 $$R_1R_2C^\bullet ONO_2 \rightarrow R_1R_2C=O + NO_2$$

190 There is an experimental evidence (Romanias et al., 2015) that the rate of the prompt

191 $R_1R_2C^\bullet ONO_2$ radical decomposition under atmospheric conditions is much higher than the

192 rate of its possible stabilization and/or reaction with O_2, in agreement with the conclusion of

193 the theoretical study of Vereecken (2008) that the radical decomposition occurs on timescales

194 that are too short for any chemical process to compete. The measurements of the yield of

195 carbonyl compound formed upon decomposition of $R_1R_2C^\bullet ONO_2$ radical provide the

196 information on the extent of H-atom abstraction from α carbon. In the present paper, we have

197 determined at T = 300 K the yields of n-butanal and isobutanal resulting from the abstraction

198 by OH of an α-hydrogen atom in n-butyl and isobutyl nitrates, respectively, followed by

199 corresponding α-substituted alkyl radical decomposition. Example of the kinetics of the

200 product formation along with the kinetics of OH consumption is shown in Fig. 7.
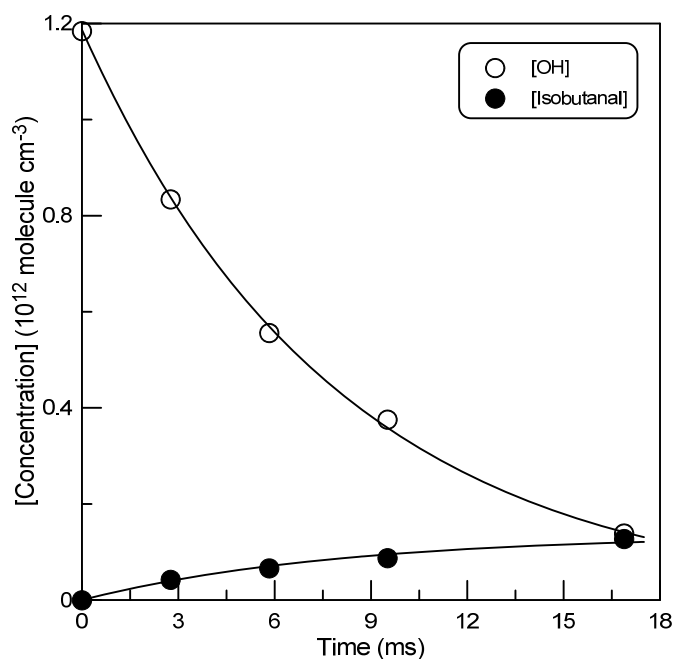
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202 **Fig. 7.** Example of kinetics of OH consumption and isobutanal formation in the reaction of OH radicals

203 with isobutyl nitrate: T = 300K; [IBN] = 8.2×10^{13} molecule cm^{-3}.

11

204

205   Continuous lines in Fig. 7 represent the simulation of the experimental profiles of OH

206   (exponential function) and isobutanal. Temporal profile of isobutanal is fitted with the

207   following equation:

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

209   where α is the product yield, k' and k_w' are the first order rate constants of OH consumption in

210   the presence and in the absence (heterogeneous loss) of nitrate in the reactor (determined

211   experimentally), respectively. α was the only fitting parameter. The value of α obtained from

212   the best fit to the isobutanal profile in Fig. 7 is 0.143.

213   The bulk of the experiments on the determination of the yields of n-butanal and

214   isobutanal in reactions (1) and (2) consisted in the monitoring of the consumed [OH] and [n-

215   C_3H_7CHO] (or [$(CH_3)_2CHCHO$]) formed at a fixed reaction time (6 – 30 ms). The

216   concentration ranges used in these experiments were [OH] = $(0.5\text{-}3.5) \times 10^{12}$, [BTN] = = $(0.3 -$

217     $0.7) \times 10^{14}$ and [IBN] = $(0.3 - 1.9) \times 10^{14}$ molecule cm^{-3}. Concentration of OH consumed in

218   reaction with nitrate was determined as a difference between initial concentration of the

219   radicals (measured in the absence of nitrate and presence of Br_2 in the main reactor) and

220   concentration of OH recorded in the presence of nitrate in the reactor (Br_2 being added at the

221   end of the reactor). The relative contribution of the wall loss to consumed [OH] depended on

222   concentration of nitrates (up to 30% at lowest concentrations of the nitrates) and was taken

223   into account. The experimental data are shown in Fig. 8 and 9. Error bars in Fig. 8 and 9

224   correspond to 10% and 15% uncertainties on the measurements of the concentrations of OH

225   and reaction products, respectively. Higher uncertainty on the measurements of the

226   concentrations of n-butanal and isobutanal is due to important contribution to their peaks at

227   m/z = 72 of n-butyl and isobutyl nitrates upon their fragmentation in the ion source of the

228   mass spectrometer which was operated at 25-30 eV energy. The slopes of the straight lines in

229   Fig. 8 and 9 provide the yields of n-butanal and isobutanal in reactions (1) and (2) at T =

230   300K: 0.10 ± 0.02 and 0.15 ± 0.03, respectively. The estimated nearly 20% uncertainty on the

231   measurements arises mainly from the combined errors on the measurements of the

232   concentrations of OH and reaction product.
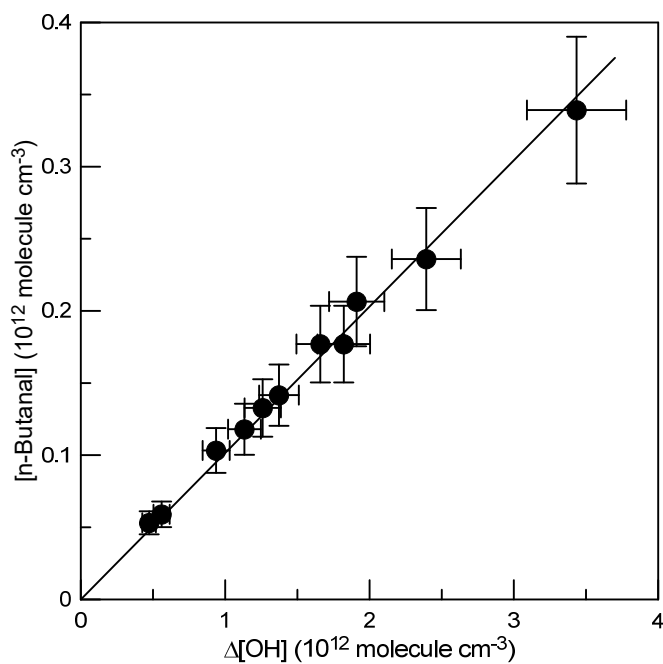
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234   **Fig. 8.** Concentration of n-butanal formed in reaction (1) as a function of the consumed concentration of
235   OH.
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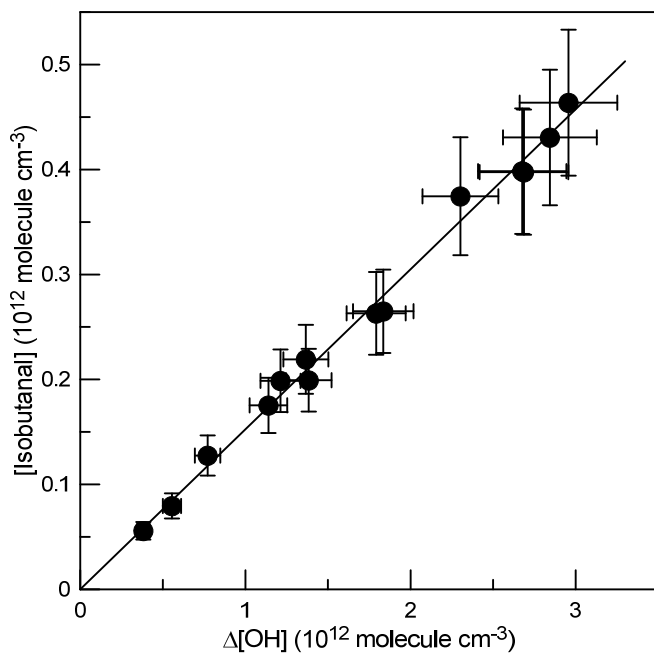
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238   **Fig. 9.** Concentration of isobutanal formed in reaction (2) as a function of the consumed concentration of
239   OH.
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4. Discussion

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), $k_2 = (1.53 \pm 0.19) \times 10^{-12}$ cm^{3}molecule^{-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 ($k_3 = (2.68 \pm 0.09) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}, newly placed on the absolute basis in Calvert et al. (2011) and absolute rate method ($k_3 = (3.32 \pm 0.30) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}) and in relative rate study of Treves and Rudich (2003) ($k_3 = (4.9 \pm 0.9) \times 10^{-12}$ cm^{3}molecule^{-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, $k_4 = (2.37 \pm 0.33) \times 10^{-12}$ cm^{3}molecule^{-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).

265   In this study, we have determined at T = 300 K the yields of n-butanal and isobutanal

266   resulting from the decomposition of α-substituted alkyl radicals formed upon initial

267   abstraction by OH of an α-hydrogen atom in n-butyl and isobutyl nitrates, respectively. The

268   measured product yields can be considered as the branching ratios for an α-hydrogen atom

269   abstraction pathway of the respective reactions:

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

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

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

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

274   The rate constant data for the reactions of OH radicals with alkyl nitrates obtained in the

275   present work and two previous studies from this group (Morin et al., 2016; Romanias et al.,

276   2015) are shown in Table 1 in comparison with the corresponding values calculated using

277   Structure-Activity Relationship (SAR) of Kwok and Atkinson (with group rate constants for

278   abstraction of primary, secondary, and tertiary H-atoms $k(-CH_3) = 0.136$, $k(-CH_2-) = 0.934$

279   and $k(>CH-) = 1.94 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ and substituent factors $F(-CH_3) = 1$, $F(-CH_2-) =$

280    $F(>CH-) = F(>C<) = 0.23$, $F(-ONO_2) = 0.04$, $F(-CH_2ONO_2) = F(>CHONO_2) = F(\equiv C-ONO_2)$

281   = 0.20) (Kwok and Atkinson, 1995). It can be noted that the total rate constant estimated

282   within SAR is significantly lower than the experimental value for four from seven nitrates.

283   Similarly, the extent of H-atom abstraction from α carbon in alkyl nitrates is considerably

284   underestimated by SAR. Difficulties arising for the prediction of the rate constants of OH

285   reactions with organic nitrates were also highlighted in a more recent development of SAR

286   (Neeb, 2000). Currently, we continue the experimental studies of the kinetics and products of

287   the OH reactions with other alkyl nitrates in order to improve the existing data base and to try

288   to update the substituent factors for the $-ONO_2$ containing groups used in the calculations of

289   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.

Appendix A. Supplementary Data

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

REFERENCES

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397 **Kinetics of the Reactions of OH Radicals with n-Butyl, Isobutyl, n-Pentyl**

398 **and 3-Methyl-1-Butyl Nitrates**

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Highlights

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407 • Reactions of OH radicals with four alkyl nitrates are studied

408 • Rate constants are measured as a function of temperature

409 • Branching ratios for an α-hydrogen atom abstraction in n-butyl and isobutyl nitrates are
410   measured

411 • Tropospheric lifetimes of the four nitrates with respect to their reaction with OH are
412   determined

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