

1 **Reactions of OH Radicals with 2-Methyl-1-Butyl, Neopentyl and 1-Hexyl**
2 **Nitrates. Structure-Activity Relationship for Gas-Phase Reactions of OH**
3 **with Alkyl Nitrates: an Update**

4
5
6 **Yuri Bedjanian,* Julien Morin,¹ Manolis N. Romanias²**

7
8
9 Institut de Combustion, Aérodynamique, Réactivité et Environnement (ICARE), CNRS and Université
10 d'Orléans, 45071 Orléans Cedex 2, France
11

12
13
14
15
16
17
18
19
20
21
22
23
24
25

* Corresponding author. CNRS/ICARE, , 45071 Orléans Cedex 2, France.

26 E-mail: yuri.bedjanian@cnrs-orleans.fr (Y. Bedjanian)

27 ¹ Now at Aix Marseille Université, CNRS, LCE, 13331, Marseille, France.

28 ² Now at IMT Lille Douai, SAGE, F-59508, Douai, France.
29

30 **ABSTRACT**

31 The kinetics of the reactions 2-methyl-1-butyl (2M1BNT), neopentyl (NPTNT) and 1-hexyl
32 nitrates (1HXNT) with OH radicals has been studied using a low pressure flow tube reactor
33 combined with a quadrupole mass spectrometer. The rate constants of the title reactions were
34 determined under pseudo-first order conditions from kinetics of OH consumption in excess of
35 nitrates. The overall rate coefficients, $k_{2M1BNT} = 1.54 \times 10^{-14} (T/298)^{4.85} \exp(1463/T)$ (T = 278-
36 538 K), $k_{NPTNT} = 1.39 \times 10^{-14} (T/298)^{4.89} \exp(1189/T)$ (T = 278-500 K) and $k_{1HXNT} = 2.23 \times 10^{-13}$
37 $(T/298)^{2.83} \exp(853/T)$ cm³molecule⁻¹s⁻¹ (T = 306-538 K) (with conservative 15%
38 uncertainty), were determined at a total pressure of 1 Torr of helium. The yield of
39 trimethylacetaldehyde ((CH₃)₃CCHO), resulting from the abstraction by OH of an α-
40 hydrogen atom in neopentyl nitrate, followed by α-substituted alkyl radical decomposition,
41 was determined as 0.31 ± 0.06 at T = 298 K. The calculated tropospheric lifetimes of
42 2M1BNT, NPTNT and 1HXNT indicate that reaction of these nitrates with OH represents an
43 important sink of these compounds in the atmosphere. Based on the available kinetic data, we
44 have updated the structure-activity relationship (SAR) for reactions of alkyl nitrates with OH
45 at T = 298 K. Good agreement (within 20%) is obtained between experimentally measured
46 rate constants (total and that for H-atom abstraction from α carbon) and those calculated from
47 SAR using new substituents factors for almost all the experimental data available.

48

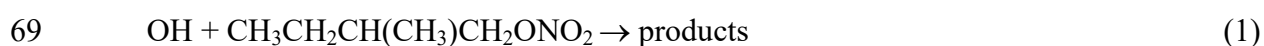
49

50 **Keywords:** Alkyl nitrates, OH, Kinetics, Atmospheric lifetime, Structure-activity relationship
51 (SAR).
52

53 1. Introduction

54 Organic nitrates are important atmospheric species which are formed during oxidation of
55 volatile organic compounds in the atmosphere through addition channel of the reaction of
56 peroxy radicals with NO and also in the NO₃-initiated oxidation of unsaturated organics
57 (Finlayson-Pitts and Pitts, 2000). Being temporary reservoirs of NO_x with atmospheric
58 lifetimes from a few days to a few weeks (Atkinson et al., 2006; Clemitshaw et al., 1997;
59 Talukdar et al., 1997a; Talukdar et al., 1997b), organic nitrates play a key role in the
60 distribution of reactive nitrogen by undergoing long-range transport in the free troposphere.
61 The assessing of the atmospheric impact of organic nitrates requires the information on both
62 their lifetime and the mechanism of their oxidation in the atmosphere leading NO_x recycling.

63 In our recent work (Bedjanian et al., 2017; Morin et al., 2016; Romanias et al., 2015) we
64 have studied reaction of OH radicals with a series of alkyl nitrates containing from 2 to 5
65 carbon atoms. In the present work, we report new experimental data on the reactions of OH
66 with three other nitrates, two C₅ alkyl nitrates of different structure, 2-methyl-1-butyl
67 (CH₃CH₂CH(CH₃)CH₂ONO₂, 2M1BNT) and neopentyl ((CH₃)₃CCH₂ONO₂, NPTNT), and a
68 linear C₆, 1-hexyl (1-C₆H₁₃ONO₂, 1HXNT), nitrate:



72 The available data on the rate constants of the reactions (1) - (2) are limited to one room
73 temperature study for each reaction (Atkinson et al., 1984; Becker and Wirtz, 1989). Reaction
74 (3), to our knowledge, has not been studied previously. In the present paper, we report the
75 first measurements of the temperature dependence of the rate constants of the reactions (1) -
76 (3) and the yield of trimethylacetaldehyde ((CH₃)₃CCHO), resulting from the abstraction by

77 OH of an α -hydrogen atom in neopentyl nitrate, followed by the formed α -substituted alkyl
78 radical decomposition, at T = 298 K.

79 Finally, based on the kinetic data from this group (including those from the present study)
80 and those available in the literature, we have updated the structure-activity relationship (SAR)
81 for reactions of alkyl nitrates with OH at T = 298 K. In particular, it is shown that SAR, newly
82 updated in this work, allows to reproduce the rate constants of most investigated reactions of
83 OH with alkyl nitrates within 20% accuracy, and, potentially, can be used to predict not only
84 the total rate constants but also primary products of the unknown (not yet investigated
85 experimentally) reactions of OH with alkyl nitrates, i.e. to determine the atmospheric lifetime
86 and first steps of the oxidation mechanism of these important atmospheric species.

87

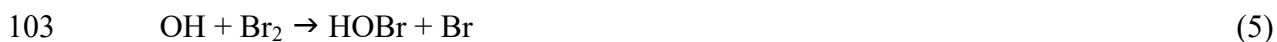
88 **2. Experimental Section**

89 Experiments were carried out at 1 Torr total pressure of helium using a modulated
90 molecular beam mass spectrometer (MS) combined with a discharge-flow system. Depending
91 on temperature of the measurements two flow reactors were used. The first one (thermostated
92 Pyrex tube of 45 cm length and 2.4 cm i.d. covered with halocarbon wax) was employed at
93 low temperatures of the study (278 – 345 K) (Bedjanian et al., 1999a, b; Romanias et al.,
94 2015). The second flow reactor, a Quartz tube (45 cm length and 2.5 cm i.d.) with an
95 electrical heater and water-cooled extremities (Fig. S1, Supplementary Data) (Morin et al.,
96 2016; Morin et al., 2015), was used at higher temperatures (455 – 538) K.

97 OH radicals were produced in a fast reaction of hydrogen atoms, generated in a
98 microwave discharge of H₂/He mixture, with excess NO₂:



100 and detected as HOBr^+ ($m/z = 96/98$) (Bedjanian et al., 1999a, b) after being scavenged with
101 an excess of Br_2 ($[\text{Br}_2] \approx 5 \times 10^{13}$ molecule cm^{-3}), added at the end of the reactor 5 cm
102 upstream of the sampling cone of the mass spectrometer (Figure S1), via reaction:



104 The chemical conversion of OH to HOBr was also used for the measurements of the absolute
105 concentrations of the radicals: $[\text{OH}] = [\text{HOBr}] = \Delta[\text{Br}_2]$ (Bedjanian et al., 1999a, b), i.e.
106 concentrations of OH were determined from the consumed fraction of $[\text{Br}_2]$.

107 The nitrates were synthesized in the laboratory via slow mixing of the corresponding
108 alcohol with $\text{H}_2\text{SO}_4:\text{HNO}_3$ (1:1) mixture at temperature $< 5^\circ\text{C}$ (Boschan et al., 1955; Morin et
109 al., 2016). The synthesized nitrate was degassed before use. Gas chromatographic analysis of
110 the degassed nitrates has shown that impurities were less than 0.1%. The nitrates were
111 introduced into the flow reactor from a 10L flask containing nitrate-He mixture or by passing
112 helium through a thermostated glass bubbler containing liquid nitrate and were detected by
113 mass spectrometry at their fragment peaks at $m/z = 76$ ($\text{CH}_2\text{ONO}_2^+$), which were much more
114 intensive than the parent ones. All other species were detected at their parent peaks: $m/z = 86$
115 (trimethylacetaldehyde ($(\text{CH}_3)_3\text{CCHO}^+$), 160 (Br_2^+), 96/98 (HOBr^+), 46 (NO_2^+). The absolute
116 concentrations of the nitrates as well as of other stable species in the reactor were calculated
117 from their flow rates determined by measuring a pressure drop over time of their mixtures
118 with helium from known volume flasks. Another method employed for the absolute
119 calibration of mass spectrometer for nitrates consisted in injecting of the known volume of
120 liquid nitrate inside the flow tube, and recording its mass peak intensity. The integrated area
121 of the mass spectrometric signals corresponding to the known total number of nitrate
122 molecules injected into the reactor allowed the determination of the calibration factor. Two
123 methods of the determination of the absolute concentrations of nitrates, by measurements of

124 their flow rates and direct injection of liquid nitrate in the reactor, were consistent within 10-
 125 15%.

126 3. Results

127 3.1. Measurements of the rate constants.

128 Measurements of the rate constants of the reactions (1) – (3) were carried out under
 129 pseudo-first order conditions in excess of nitrates over OH radicals. Initial concentration of
 130 OH radicals was $(3 - 5) \times 10^{11}$ molecule cm^{-3} , those of the nitrates are shown in Table 1.

131 **Table 1**
 132 Experimental Conditions and Results of the Measurements of the Rate Constants of Reactions
 133 (1) – (3).
 134

T (K)	reactor surface ^a	number of kinetic runs	[nitrate] (10^{13} molecule cm^{-3})	k^b (10^{-12} $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)
OH + 2-methyl-1-butyl nitrate				
278	HW	6	3.56-13.8	2.08
288	HW	9	1.98-14.5	2.09
298	HW	8	1.71-8.14	2.12
318	HW	8	1.50-9.55	2.14
345	HW	8	1.22-11.1	2.19
455	Q	8	0.69-7.43	2.98
500	Q	9	1.14-8.69	3.47
538	Q	9	0.50-5.82	4.15
OH + neopentyl nitrate				
278	HW	6	0.32-1.54	0.70
288	HW	8	0.51-2.56	0.72
298	HW	6	0.24-1.69	0.77
318	HW	9	0.26-2.58	0.81
345	HW	9	0.31-2.39	0.89
455	Q	5	0.25-1.29	1.49
500	Q	8	0.08-1.08	1.89
OH + 1-hexyl nitrate				
306	HW	8	0.42-1.63	3.89
315	HW	8	0.40-2.94	3.90
318	HW	8	0.70-2.64	3.83
331	HW	7	0.36-2.21	4.03

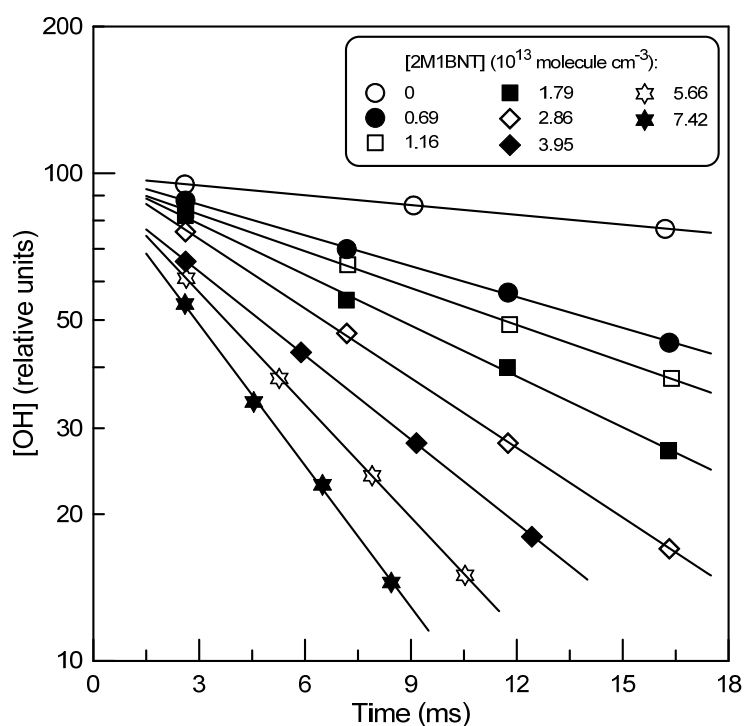
335	HW	8	0.51-2.84	3.92
345	HW	8	0.55-2.67	4.08
455	Q	7	0.20-2.19	4.88
500	Q	8	0.22-2.83	5.08
538	Q	9	0.12-2.16	5.91

135 ^a HW: halocarbon wax, Q: quartz.

136 ^b Estimated uncertainty on k is nearly 15%.

137

138 The flow velocity in the reactor was in the range (840-1890) cm s^{-1} . The concentrations of OH
 139 and nitrates were simultaneously monitored as a function of reaction time. The consumption
 140 of nitrates was unimportant as a result of their high excess over OH radicals and negligible
 141 wall loss. Examples of exponential decays of OH in reaction (1) in accordance with
 142 expression $[\text{OH}] = [\text{OH}]_0 \times \exp(-k' \times t)$ are shown in Fig. 1.

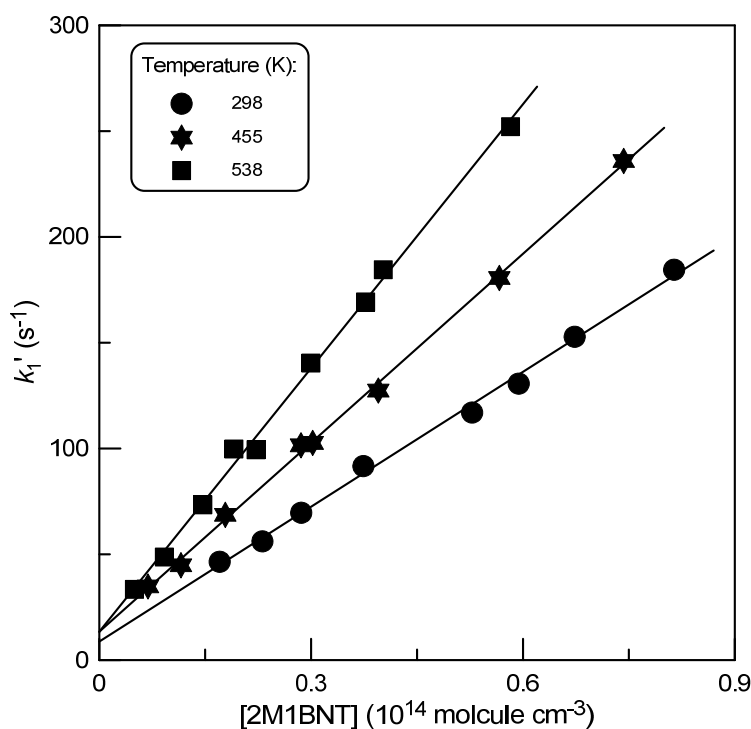


143

144 **Fig. 1.** Examples of the pseudo-first-order decays of OH in reaction with 2-methyl-1-butyl nitrate: T = 455
 145 K. Uncertainty on the measurements of the relative concentrations of OH ($\leq 5\%$) corresponds to the size of
 146 the symbols.

147 Figs. 2 and S2 – S3 (Supplementary Data) show examples of the typical dependencies of
 148 the pseudo-first order rate constant, $k' = k[\text{nitrate}] + k_w$, on concentration of the corresponding
 149 nitrate. k_w represents the rate of OH decay in the absence of nitrate in the reactor and was

150 measured in separate experiments. All the measured values of k' were corrected for axial and
151 radial diffusion of OH (Kaufman, 1984). The diffusion coefficient of OH in He was
152 calculated using the following expression: $D_0 = 640 \times (T/298)^{1.85}$ Torr cm² s⁻¹ (Bedjanian et
153 al., 2010; Ivanov et al., 2007). Corrections on k' were generally less than 10%, however, in a
154 few kinetic runs they were somewhat higher (up to 15%). The slopes of the straight lines in
155 Figs. 2 and S2 – S3 provide the values of the rate constants at respective temperatures. The
156 intercepts were generally in agreement in the range of the experimental uncertainty with the
157 corresponding OH loss rate measured in the absence of nitrates in the reactor: k_w was in the
158 range 7 -25 s⁻¹ depending rather on state of the reactor surface than on temperature.
159



160
161 **Fig. 2.** Pseudo-first-order rate constant (k_1') as a function of the concentration of 2-methyl-1-butyl nitrate at
162 T = 298, 455 and 538 K.

163 In order to check for the possible impact of a secondary chemistry on the results of the
164 measurements, the rates of the OH + nitrate reactions were measured as a function of initial
165 concentration of OH radicals. Fig. S4 (Supplementary Data) shows the results of the
166 measurements of k_1' at a fixed concentration of 2M1BNT and varied initial concentration of

167 OH. Independence of the reaction rate of the concentration of OH for $[\text{OH}]_0 < 10^{12}$ molecule
168 cm^{-3} indicates the negligible contribution of the secondary chemistry to OH loss under
169 experimental conditions of the study ($[\text{OH}]_0 \leq 5 \times 10^{11}$ molecule cm^{-3}). Similar behavior was
170 observed for the reactions of OH with NPTNT and 1HXNT.

171 All the results obtained for the rate constants of reactions (1) – (3) at different
172 temperatures are shown in Table 1. The lowest temperature in the rate constant measurements
173 in both low- and high temperature reactors was limited by impact of the heterogeneous
174 chemistry which was manifested in an anomalous increase of the measured rate constant with
175 decreasing temperature (Morin et al., 2015). Highest temperature of the study (500-540 K)
176 was limited by thermal decomposition of the nitrates (Morin and Bedjanian, 2016, 2017a, b).

177 Temperature dependences of the rate constants of the reactions of OH with 2M1BNT,
178 NPTNT and 1HXNT are shown in Figs. 3, 4 and 5, respectively. The combined uncertainty on
179 the measurements of the rate constants was estimated to be nearly 15%, by adding in
180 quadrature the statistical error (within a few percent) and those on the measurements of the
181 flows (5%), pressure (2%), temperature (1%) and the absolute concentrations of the nitrates (~
182 10%). One can note that the temperature dependence of the measured rate constants deviates
183 from a simple Arrhenius behavior as could be expected considering that the overall rate
184 constant is the sum of those for H-atom abstraction channels proceeding through breaking of
185 different C-H bonds. The experimental data were fitted with a three-parameter expression,
186 leading to the following results (solid lines in Figs. 3 – 5):

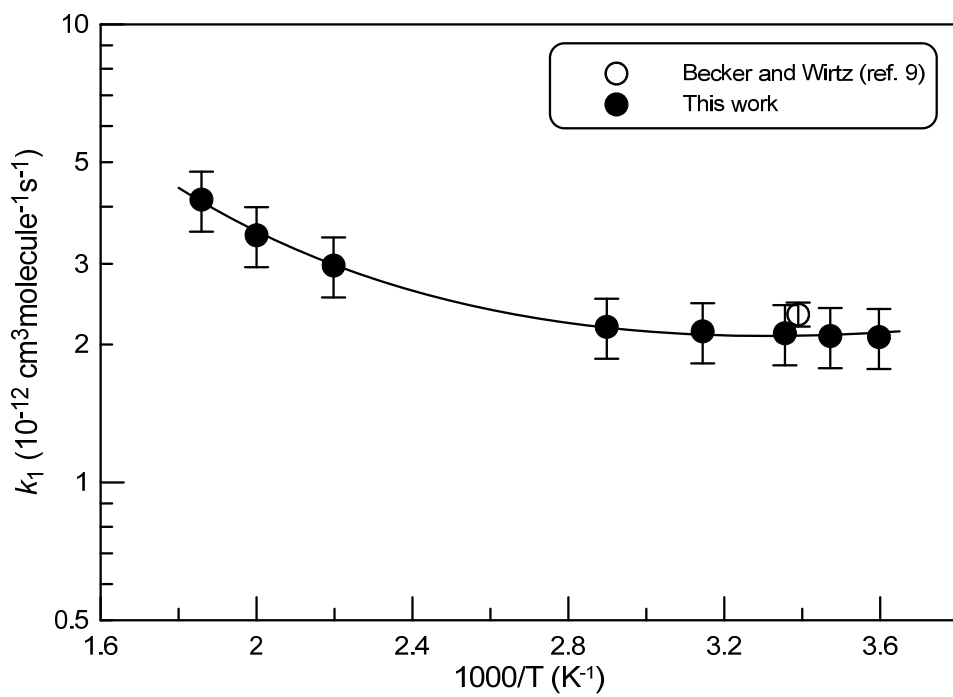
187 $k_1 = 1.54 \times 10^{-14} (T/298)^{4.85} \exp(1463/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 278-538 \text{ K}),$

188 $k_2 = 1.39 \times 10^{-14} (T/298)^{4.89} \exp(1189/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 278-500 \text{ K})$

189 $k_3 = 2.23 \times 10^{-13} (T/298)^{2.83} \exp(853/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 306-538 \text{ K}),$

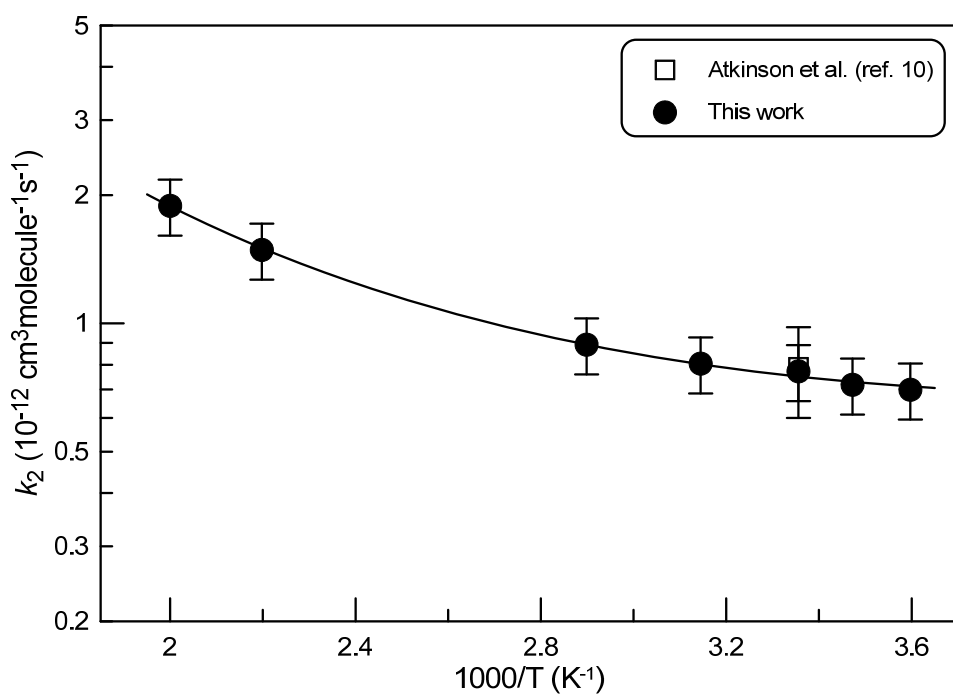
190 with conservative independent of temperature 15% uncertainty on the rate constants.

191



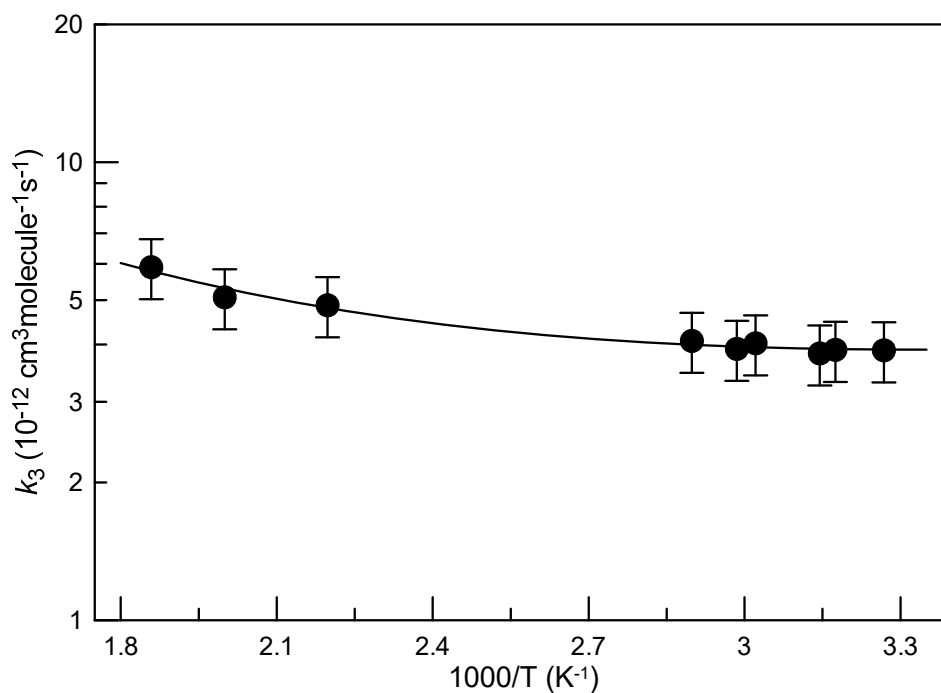
192
193
194
195

Fig. 3. Temperature dependence of the rate constant of the reaction OH + 2-methyl-1-butyl nitrate.



196
197

Fig. 4. Temperature dependence of the rate constant of the reaction OH + neopentyl nitrate.



198

199

Fig. 5. Temperature dependence of the rate constant of the reaction OH + 1-hexyl nitrate.

200

3.2. α -hydrogen atom abstraction channel in reaction (2).

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

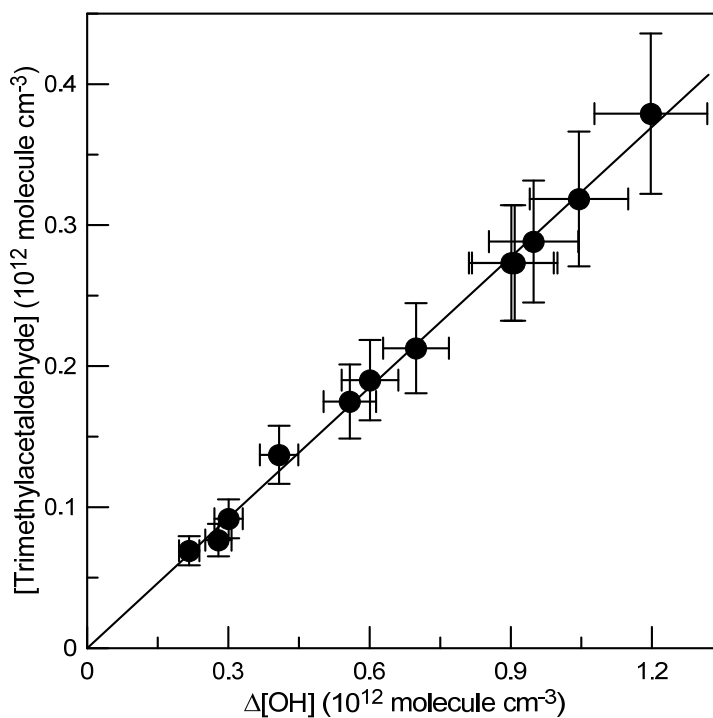


204 These radicals are known to be unstable, dissociating spontaneously without an energetic
 205 barrier to form a carbonyl compound and NO₂ (Vereecken, 2008):



207 In this respect, the measurements of the yield of corresponding carbonyl compound provide
 208 the information on the extent of H-atom abstraction from α carbon. In the present paper, we
 209 have determined at T = 298 K the yield of trimethylacetaldehyde ((CH₃)₃CCHO), resulting
 210 from the abstraction by OH of an α -hydrogen atom in neopentyl nitrate followed by
 211 corresponding α -substituted alkyl radical decomposition. The experiments on the
 212 determination of the yield of trimethylacetaldehyde in reaction 2 consisted in the monitoring
 213 of the consumed [OH] and [(CH₃)₃CCHO] formed at a reaction time of (7 – 28) ms. The

214 concentration of neopentyl nitrate in these experiments was nearly 1.5×10^{14} molecule cm^{-3}
215 and $[\text{OH}]$ was varied in the range $(0.23\text{-}1.27) \times 10^{12}$ molecule cm^{-3} . Concentration of OH
216 consumed in reaction with nitrate was determined as a difference between initial
217 concentration of the radicals (measured in the absence of the nitrate and presence of Br_2 in the
218 main reactor) and concentration of OH recorded in the presence of the nitrate in the reactor
219 (Br_2 being added at the end of the reactor). The relative contribution of the wall loss to
220 consumed $[\text{OH}]$ was $\leq 10\%$ in these experiments and was taken into account. The
221 experimental data are shown in Fig. 6.



222

223 **Fig. 6.** Concentration of trimethylacetaldehyde formed in reaction 2 as a function of the consumed
224 concentration of OH.

225

226 Error bars in Figures 6 correspond to 10% and 15% uncertainties on the measurements of the
227 concentrations of OH and trimethylacetaldehyde, respectively. Higher uncertainty on the
228 measurements of the concentrations of trimethylacetaldehyde is due to important contribution
229 to its parent peak at $m/z = 86$ of neopentyl nitrate upon its fragmentation in the ion source of
230 the mass spectrometer which was operated at 25-30 eV energy. The contribution of neopentyl

231 nitrate was directly monitored in the absence of OH in the reactive system (discharge off) and
232 was extracted from the signal at $m/z = 86$ observed in reaction OH + neopentyl nitrate
233 (discharge on). The slope of the straight line in Fig. 6 provides the yield of
234 trimethylacetaldehyde in reaction (2) at $T = 298$ K: 0.31 ± 0.06 . The estimated nearly 20%
235 uncertainty on the determination of the yield arises mainly from the combined errors on the
236 measurements of the concentrations of OH and the reaction product.

237

238 4. Discussion

239 4.1. Comparison with previous studies and atmospheric implications.

240 To our knowledge, this is the first study of the reaction of OH radicals with 1-hexyl
241 nitrate and the first measurement of the temperature dependence of the rate constant of the
242 OH reactions with 2-methyl-1-butyl and neopentyl nitrates. The rate constants of the reactions
243 1 and 2, $k_1 = (2.33 \pm 0.14) \times 10^{-12}$ and $k_2 = (0.79 \pm 0.19) \times 10^{-12}$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ measured by
244 Becker and Wirtz (1989) at $T = 295$ and Atkinson et al. (1984) at $T = 298$ K, respectively,
245 using relative rate method and placed on an absolute basis in (Calvert et al., 2011) using new
246 recommendation for the reference reaction OH+n-butane, agree in the range of the reported
247 experimental uncertainties with the present data (Figs. 3 and 4). The consistency in rate
248 coefficients measured in previous studies at 1 atm total pressure and those from the present
249 study in 1 Torr of helium is expected for a bimolecular reaction proceeding via H-atom
250 abstraction.

251 In this study, we have determined at $T = 298$ K the yield of trimethylacetaldehyde
252 resulting from the decomposition of α -substituted alkyl radicals formed upon initial
253 abstraction by OH of an α -hydrogen atom in neopentyl nitrate. The measured product yield
254 can be considered as the branching ratio for an α -hydrogen atom abstraction pathway:



256 $k_{2a}/k_2 = 0.31 \pm 0.06$

257 The major atmospheric sinks of alkyl nitrates are their UV photolysis and reactions with
 258 OH radicals. The tropospheric lifetimes of 2M1BNT, NPTNT and 1HXNT, with respect to
 259 their loss via reaction with OH, calculated using the measured rate constants (at T = 298 K)
 260 and a 24h average concentration of OH radical of 10^6 molecules cm^{-3} , are 5.5, 15 and 3 days,
 261 respectively. The gas-phase ultraviolet absorption cross-sections of 2M1BNT, NPTNT and
 262 1HXNT are not known. However, under assumption that the tropospheric lifetimes of these
 263 compounds with respect to their photolysis are close to those reported by Clemitshaw et al.
 264 (1997) for several C₂-C₅ alkyl nitrates (between 3 and 13 days for summer conditions,
 265 depending on altitude (0 – 10 km) and latitude (0 – 60°N)), reaction with OH radicals is an
 266 important atmospheric sink for the alkyl nitrates considered in the present study, comparable
 267 with that due to their photolysis.

268

269 *4.2. Reactivity of alkyl nitrates with OH: trends and updated structure-activity relationship*
 270 *(SAR).*

271 In our recent work (including the present study) (Bedjanian et al., 2017; Morin et al.,
 272 2016; Romanias et al., 2015) we have measured temperature dependence of the rate constant
 273 of the reaction of OH radicals with ten alkyl nitrates, for eight of them for the first time. The
 274 rate coefficients for the reactions of the ten alkyl nitrates with OH radicals determined at T =
 275 298 K are shown in Table 2 together with the data for the reaction of OH with other alkyl
 276 nitrates available in the literature.

277

278 **Table 2**

279 Comparison of the Experimental and Calculated (within SAR) Rate Constants for Reactions
 280 of Alkyl Nitrates with OH at T = 298 K.

281

Nitrate ^a	k_{exp}^b	$k_{\text{calc}}^{b,c}$ (current SAR)	$k_{\text{calc}}/k_{\text{exp}}$ (current SAR)	$k_{\text{calc}}^{b,d}$ (this work)	$k_{\text{calc}}/k_{\text{exp}}$ (this work)
----------------------	--------------------	------------------------------------------	---------------------------------------------------	----------------------------------------	-------------------------------------------------

MNT	0.23 ^e	0.05	0.22	0.19	0.83
ENT	2.01 ^f	0.65	0.32	1.69	0.84
PNT	5.98 ^f	4.00	0.67	5.90	0.99
IPNT	3.02 ^f	1.32	0.44	3.48	1.15
1BNT	16.6 ^f	15.9	0.96	18.0	1.08
IBNT	12.3 ^f	7.69	0.63	10.4	0.85
1PNNT	30.9 ^f	30.0	0.97	32.1	1.04
IPNNT	30.6 ^f	30.0	0.98	32.0	1.05
NPTNT	7.51 ^f	5.48	0.73	6.63	0.88
2M1BNT	20.9 ^f	20.1	0.96	23.1	1.11
1HXNT	39.0 ^f	44.2	1.13	46.2	1.18
2BNT	8.60 ^e	4.77	0.55	8.01	0.93
2PNNT	17.2 ^g	16.7	0.97	20.1	1.17
3PNNT	10.4 ^g	8.26	0.79	12.7	1.22
3M2BNT	17.0 ^g	8.45	0.50	12.5	0.74
2HXNT	29.4 ^g	30.8	1.05	34.2	1.16
3HXNT	25.0 ^g	20.2	0.81	24.8	0.99
2M2PNNT	15.9 ^g	16.0	1.01	17.1	1.08
3M2PNNT	28.0 ^g	20.8	0.74	25.2	0.90
3HPTNT	34.2 ^g	34.3	1.00	38.9	1.14
3OCTNT	36.0 ^g	48.4	1.34	53.0	1.47

282 ^a Chemical names and formula corresponding to the abbreviations are listed in Table S1 (Supplementary Data).
283 ^b Units of 10⁻¹³ cm³molecule⁻¹s⁻¹.
284 ^c Calculated with $F(-\text{ONO}_2) = 0.04$ and $F(-\text{CH}_2\text{ONO}_2) = F(>\text{CHONO}_2) = F(\equiv\text{C}-\text{ONO}_2) = 0.20$ (Kwok and
285 Atkinson, 1995).
286 ^d Calculated with $F(-\text{ONO}_2) = 0.14$ and $F(-\text{CH}_2\text{ONO}_2) = F(>\text{CHONO}_2) = F(\equiv\text{C}-\text{ONO}_2) = 0.28$ (this work).
287 ^e Atkinson et al. (2006).
288 ^f Data from this group ((Bedjanian et al., 2017; Morin et al., 2016; Romanias et al., 2015) and this work)
289 ^g Data from (Atkinson et al., 1982; Atkinson et al., 1984; Becker and Wirtz, 1989) updated by Calvert et al.
290 (2011).
291

292 For six alkyl nitrates, reaction products corresponding to direct recycling of NO₂ (α -hydrogen
293 atom abstraction channel) were observed and their yield measured (Table 3) ((Bedjanian et
294 al., 2017; Morin et al., 2016; Morin et al., 2015) and this study).

295 **Table 3**
296 Comparison of the experimental and calculated (within SAR) branching ratios for H-atom
297 abstraction from α carbon ($k_\alpha/k_{\text{total}}$) in reactions of alkyl nitrates with OH at T = 298 K.
298

nitrate	$k_\alpha/k_{\text{total}}$				
	exp. ^a	calc. ^b (current SAR)	calc./exp. (current SAR)	calc. ^c (this work)	calc./exp. (this work)

ENT	0.77	0.58	0.75	0.77	1.00
PNT	0.22	0.11	0.50	0.27	1.23
IPN	0.82	0.59	0.72	0.78	0.95
1BNT	0.10	0.03	0.30	0.09	0.90
IBNT	0.15	0.06	0.40	0.15	1.00
NPTNT	0.31	0.08	0.26	0.24	0.77

299 ^a Experimental data from (Bedjanian et al., 2017; Morin et al., 2016; Romanias et al., 2015) and present work.

300 ^b Calculated with $F(-\text{ONO}_2) = 0.04$ and $F(-\text{CH}_2\text{ONO}_2) = F(>\text{CHONO}_2) = F(\equiv\text{C}-\text{ONO}_2) = 0.20$ (Kwok and
301 Atkinson, 1995).

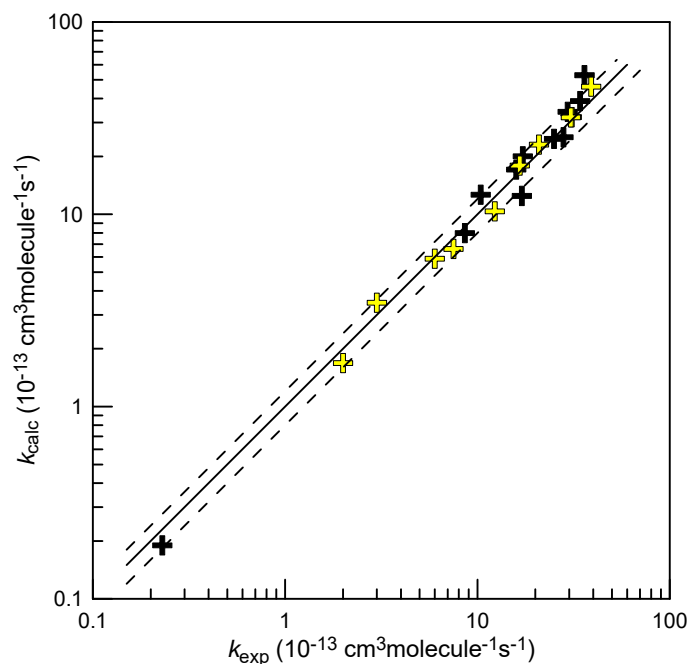
302 ^c Calculated with $F(-\text{ONO}_2) = 0.14$ and $F(-\text{CH}_2\text{ONO}_2) = F(>\text{CHONO}_2) = F(\equiv\text{C}-\text{ONO}_2) = 0.28$ (this work).

303

304 The results of kinetic and mechanistic studies from our group support the previous
305 conclusions (Calvert et al., 2011) on the trends in the reactivity of alkyl nitrates toward OH
306 radicals: (i) reactions proceed through H-atom abstraction channel; (ii) the reactivity increases
307 with the length of alkyl chain, as one could expect, due to increasing number of CH₂ groups
308 and their distance from the deactivating nitrate group; (iii) *n*-alkyl nitrates are more reactive
309 than corresponding *iso*-alkyl nitrates, as one could expect considering increase in reactivity
310 from CH₃ to CH₂ and to CH group; (iv) curved temperature dependencies of the rate constants
311 observed in our studies at elevated temperatures seem to reflect simultaneous occurrence of
312 primary, secondary and tertiary H-atom abstraction pathways.

313 Based on the rate constants measured in our group and those available in the literature
314 (Table 2) we attempted an update of structure-activity relationship for reactions of alkyl
315 nitrates with OH at T = 298 K. The employed procedure was similar to that of Kwok and
316 Atkinson (1995). A nonlinear least-squares analysis of the rate constant data was performed
317 with two variable parameters, substituent factors $F(-\text{ONO}_2)$ and $F(-\text{CH}_2\text{ONO}_2) =$
318 $F(>\text{CHONO}_2) = F(\equiv\text{C}-\text{ONO}_2)$, minimizing $((k_{\text{exp}} - k_{\text{calc}})/k_{\text{exp}})^2$, where k_{exp} and k_{calc} are the
319 experimental and calculated (within SAR) rate constants, respectively. In the analysis, the
320 branching ratios for H-atom abstraction from α carbon measured in this group ($(k_{\alpha}/k_{\text{total}})$ in
321 Table 3) were also included. The used group rate constants for abstraction of primary,

322 secondary, and tertiary H-atoms and other substituent factors were those from Kwok and
323 Atkinson (1995): $k(-\text{CH}_3) = 0.136$, $k(-\text{CH}_2-) = 0.934$ and $k(>\text{CH-}) = 1.94 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$
324 s^{-1} ; $F(-\text{CH}_3) = 1$, $F(-\text{CH}_2-) = F(>\text{CH-}) = F(>\text{C}<) = 0.23$. The best agreement between
325 measured and calculated rate constants was achieved with the following substituent factors:
326 $F(-\text{ONO}_2) = 0.14$ and $F(-\text{CH}_2\text{ONO}_2) = F(>\text{CHONO}_2) = F(\equiv\text{C-ONO}_2) = 0.28$. One can state an
327 excellent agreement (within a factor of nearly 1.2, which is equivalent to the precision of
328 experimental measurements) between the calculated (using these substituents factors) and
329 experimentally measured rate constants (Table 2 and Fig. 7), for all the experimental data
330 available except two compounds (3M2BNT and 3OCTNT). The calculated branching ratios
331 for the H-atom abstraction from α carbon are also in good agreement with the experimental
332 data (Table 3). The rate constants calculated with substituent factors derived previously
333 (Kwok and Atkinson, 1995) significantly deviate from the experimental values, particularly
334 for small nitrates (Table 2), and reproduce very poorly the branching ratio data (Table 3).
335 Difficulties arising for the prediction of the rate constants of OH reactions with organic
336 nitrates were also highlighted in a more recent development of SAR (Neeb, 2000).
337 Considering an excellent agreement between experimental data and those calculated within
338 SAR updated in the present work, the improved SAR can be, potentially, employed for
339 calculations of the total rate constants and primary products of the reactions of OH with alkyl
340 nitrates that have not yet been studied experimentally, and to predict, in this way, the
341 atmospheric lifetime and first steps of the oxidation mechanism of these important
342 atmospheric compounds.



343

344 **Fig. 7.** Comparison of measured with calculated rate constants for reactions of alkyl nitrates with
 345 OH radicals at $T = 298$ K. The solid and dashed lines represent 1:1 and (1 ± 0.2) :1 correlations,
 346 respectively. Yellow symbols represent experimental data from this group.

347

348 It should be emphasized that the updated estimation method is applicable only to alkyl
 349 nitrates and does not adequately describe the rate constants of OH reactions with
 350 multifunctional organic nitrates. Multifunctional organic nitrates are low-volatile and highly
 351 soluble and thus can be partitioned to the atmospheric condensed phases (droplets, aerosols)
 352 (Nah et al., 2016). Recent field observations have shown that organic nitrates can represent a
 353 large fraction of ambient submicron organic aerosols (Lee et al., 2016; Xu et al., 2015).
 354 Assessment of the atmospheric fate of multifunctional organic nitrates and their impact on
 355 aerosols composition and properties requires a good knowledge of their reactivity in gas and
 356 condensed phases. In this respect, future detailed studies of the reactivity of functionalized
 357 organic nitrates towards OH radicals would be of great interest to atmospheric science.

358 5. Conclusion

359 In this work, temperature dependencies of the rate constants of the atmospheric
 360 reactions of OH radicals with three alkyl nitrates, 2-methyl-1-butyl, neopentyl and 1-

361 hexyl, were measured for the first time. The yield of trimethylacetaldehyde
362 ((CH₃)₃CCHO), resulting from the abstraction by OH of an α -hydrogen atom in
363 neopentyl nitrate, followed by α -substituted alkyl radical decomposition, was
364 determined as 0.31 ± 0.06 at T = 298 K. Tropospheric lifetimes of the three nitrates,
365 calculated using the measured rate constants, indicate that reaction of these nitrates
366 with OH represents an important sink of these compounds in the atmosphere. Using
367 kinetic data from this study and those available in the literature, we have updated the
368 structure-activity relationship (SAR) for reactions of alkyl nitrates with OH at T = 298
369 K. The updated SAR allows to reproduce the experimental rate constants of the
370 reactions of OH with alkyl nitrates with rather high precision, and can be used to
371 predict the total rate constants and products of the reactions of OH with alkyl nitrates,
372 i.e. to estimate the atmospheric lifetime and anticipate the first steps of the oxidation
373 mechanism of these important atmospheric species.

374

375 **Acknowledgement**

376 This work was supported by French National Research Agency (ANR) through project
377 ONCEM (ANR-12-BS06-0017-02). J. M. is very grateful for his PhD grant from
378 CAPRYSES project (ANR-11-LABX-006-01) funded by ANR through the PIA (Programme
379 d'Investissement d'Avenir).

380 **Appendix A. Supplementary data**

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

382

383

384 **References**

- 385 Atkinson R., Aschmann S.M., Carter W.P.L., Winer A.M., 1982. Kinetics of the gas-phase
386 reactions of OH radicals with alkyl nitrates at 299 ± 2 K. *Int. J. Chem. Kinet.* 14, 919-
387 926.
- 388 Atkinson R., Aschmann S.M., Carter W.P.L., Winer A.M., Pitts J.N., 1984. Formation of
389 alkyl nitrates from the reaction of branched and cyclic alkyl peroxy radicals with NO.
390 *Int. J. Chem. Kinet.* 16, 1085-1101.
- 391 Atkinson R., Baulch D.L., Cox R.A., Crowley J.N., Hampson R.F., Hynes R.G., Jenkin M.E.,
392 Rossi M.J., Troe J., 2006. Evaluated kinetic and photochemical data for atmospheric
393 chemistry: Volume II - gas phase reactions of organic species. *Atmos. Chem. Phys.* 6,
394 3625-4055.
- 395 Becker K.H., Wirtz K., 1989. Gas phase reactions of alkyl nitrates with hydroxyl radicals
396 under tropospheric conditions in comparison with photolysis. *J. Atmos. Chem.* 9, 419-
397 433.
- 398 Bedjanian Y., Le Bras G., Poulet G., 1999a. Kinetic Study of OH + OH and OD + OD
399 Reactions. *J. Phys. Chem. A* 103, 7017-7025.
- 400 Bedjanian Y., Le Bras G., Poulet G., 1999b. Kinetic Study of the Reactions of Br₂ with OH
401 and OD. *Int. J. Chem. Kinet.* 31, 698-704.
- 402 Bedjanian Y., Morin J., Romanias M.N., 2017. Kinetics of the reactions of OH radicals with
403 n-butyl, isobutyl, n-pentyl and 3-methyl-1-butyl nitrates. *Atmos. Environ.* 155, 29-34.
- 404 Bedjanian Y., Nguyen M.L., Le Bras G., 2010. Kinetics of the Reactions of Soot Surface-
405 Bound Polycyclic Aromatic Hydrocarbons with the OH Radicals. *Atmos. Environ.* 44,
406 1754-1760.
- 407 Boschan R., Merrow R.T., van Dolah R.W., 1955. The Chemistry of Nitrate Esters. *Chem.*
408 *Rev.* 55, 485-510.
- 409 Calvert J., Mellouki A., Orlando J., Pilling M., Wallington T., 2011. Mechanisms of
410 Atmospheric Oxidation of the Oxygenates. Oxford University Press, New York.
- 411 Clemitshaw K.C., Williams J., Rattigan O.V., Shallcross D.E., Law K.S., Anthony Cox R.,
412 1997. Gas-phase ultraviolet absorption cross-sections and atmospheric lifetimes of
413 several C₂-C₅ alkyl nitrates. *J. Photochem. Photobio. A* 102, 117-126.
- 414 Finlayson-Pitts B.J., Pitts J.N.J., 2000. Chemistry of the Upper and Lower Atmosphere:
415 Theory, Experiments and Applications. Academic Press, San Diego, 969 pp.

416 Ivanov A.V., Trakhtenberg S., Bertram A.K., Gershenzon Y.M., Molina M.J., 2007. OH,
417 HO₂, and Ozone Gaseous Diffusion Coefficients. *J. Phys. Chem. A* 111, 1632-1637.
418 Kaufman F., 1984. Kinetics of Elementary Radical Reactions in the Gas Phase. *J. Phys.*
419 *Chem.* 88, 4909-4917.
420 Kwok E.S.C., Atkinson R., 1995. Estimation of Hydroxyl Radical Reaction Rate Constants
421 for Gas-Phase Organic Compounds Using a Structure- Reactivity Relationship: an
422 Update. *Atmos. Environ.* 29, 1685-1695.
423 Lee B.H. et al., 2016. Highly functionalized organic nitrates in the southeast United States:
424 Contribution to secondary organic aerosol and reactive nitrogen budgets. *Proceedings*
425 *of the National Academy of Sciences* 113, 1516-1521.
426 Morin J., Bedjanian Y., 2016. Thermal Decomposition of Isopropyl Nitrate: Kinetics and
427 Products. *J. Phys. Chem. A* 120, 8037-8043.
428 Morin J., Bedjanian Y., 2017a. Kinetic and Mechanistic Study of the Thermal Decomposition
429 of Ethyl Nitrate. *Int. J. Chem. Kinet.* 49, 354-362.
430 Morin J., Bedjanian Y., 2017b. Thermal decomposition of n-propyl and n-butyl nitrates:
431 Kinetics and products. *J. Anal. Appl. Pyrolysis* 124, 576-583.
432 Morin J., Bedjanian Y., Romanias M.N., 2016. Kinetics and Products of the Reactions of
433 Ethyl and n-Propyl Nitrates with OH Radicals. *Int. J. Chem. Kinet.* 48, 822-829.
434 Morin J., Romanias M.N., Bedjanian Y., 2015. Experimental Study of the Reactions of OH
435 Radicals with Propane, n-Pentane, and n-Heptane over a Wide Temperature Range.
436 *Int. J. Chem. Kinet.* 47, 629-637.
437 Nah T., Sanchez J., Boyd C.M., Ng N.L., 2016. Photochemical Aging of α -pinene and β -
438 pinene Secondary Organic Aerosol formed from Nitrate Radical Oxidation. *Env. Scie.*
439 *Tech.* 50, 222-231.
440 Neeb P., 2000. Structure-Reactivity Based Estimation of the Rate Constants for Hydroxyl
441 Radical Reactions with Hydrocarbons. *J. Atmos. Chem.* 35, 295-315.
442 Romanias M.N., Morin J., Bedjanian Y., 2015. Experimental Study of the Reaction of
443 Isopropyl Nitrate with OH Radicals: Kinetics and Products. *Int. J. Chem. Kinet.* 47,
444 42-49.
445 Talukdar R.K., Burkholder J.B., Hunter M., Gilles M.K., Roberts J.M., Ravishankara A.R.,
446 1997a. Atmospheric Fate of Several Alkyl Nitrates. Part 2 - UV Absorption Cross-
447 Sections and Photodissociation Quantum Yields. *J. Chem. Soc., Faraday Trans.* 93,
448 2797-2805.

449 Talukdar R.K., Herndon S.C., Burkholder J.B., Roberts J.M., Ravishankara A.R., 1997b.
450 Atmospheric fate of several alkyl nitrates. Part 1 - Rate coefficients of the reactions of
451 alkyl nitrates with isotopically labelled hydroxyl radicals. J. Chem. Soc., Faraday
452 Trans. 93, 2787-2796.

453 Vereecken L., 2008. Computational study of the stability of α -nitroxy-substituted alkyl
454 radicals. Chem. Phys. Lett. 466, 127-130.

455 Xu L., Suresh S., Guo H., Weber R.J., Ng N.L., 2015. Aerosol characterization over the
456 southeastern United States using high-resolution aerosol mass spectrometry: spatial
457 and seasonal variation of aerosol composition and sources with a focus on organic
458 nitrates. Atmos. Chem. Phys. 15, 7307-7336.

459
460
461

462 **Reactions of OH Radicals with 2-Methyl-1-Butyl, Neopentyl and 1-Hexyl**
463 **Nitrates. Structure-Activity Relationship for Gas-Phase Reactions of OH**
464 **with Alkyl Nitrates: an Update**

465

466 **Yuri Bedjanian, Julien Morin, Manolis N. Romanias**

467

468 Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS and Université
469 d'Orléans, 45071 Orléans Cedex 2, France
470

471

472

473

474 **Highlights**

475

- 476 • Rate constants of OH reactions with three alkyl nitrates are measured as a function of
477 temperature
- 478 • Branching ratios for an α -hydrogen atom abstraction in neopentyl nitrate is measured
- 479 • Tropospheric lifetimes of the nitrates with respect to their reaction with OH are
480 determined
- 481 • An updated structure-activity relationship (SAR) for reactions of alkyl nitrates with OH is
482 proposed

483