NO$_3$ chemistry of wildfire emissions: a kinetic study of the gas-phase reactions of furans with the NO$_3$ radical

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Abstract. Furans are emitted to the atmosphere during biomass burning from the pyrolysis of cellulose. They are one of the major contributing VOC classes to OH and NO$_3$ reactivity in biomass burning plumes. The major removal process of furans from the atmosphere at night is reaction with the nitrate radical, NO$_3$. Here we report a series of relative rate experiments in the 7300 L indoor simulation chamber at CNRS-ICARE, Orléans, using a number of different reference compounds to determine NO$_3$ reaction rate coefficients for four furans, two furanones, and pyrrole. In the case of the two furanones, this is the first time that NO$_3$ rate coefficients have been reported. The recommended values (cm^3 molecule^{-1} s^{-1}) are: furan $(1.49\pm0.23)\times10^{-12}$, 2-methylfuran $(2.26\pm0.52)\times10^{-11}$, 2,5-dimethylfuran $(1.02\pm0.31)\times10^{-10}$, furfural (furan-2-aldehyde) $(9.07\pm2.3)\times10^{-14}$, α-angelicalactone (5-methyl-2(3H)-furanone) $(3.01\pm0.45)\times10^{-12}$, γ-crotonolactone (2(5H)-furanone) $<1.4\times10^{-16}$, and pyrrole $(6.94\pm1.9)\times10^{-11}$. The furfural + NO$_3$ reaction rate coefficient is found to be an order of magnitude smaller than previously reported. These experiments show that for furan, alkyl substituted furans, α-angelicalactone, and pyrrole, reaction with NO$_3$ will be the dominant removal process at night, and may also contribute during the day. For γ-crotonolactone, reaction with NO$_3$ is not an important atmospheric sink.

1 Introduction

Furans are five membered aromatic cyclic ethers. Furans (and pyrroles – where N replaces O as the heteroatom) are generated during the pyrolysis of cellulose and are a major component of emissions from wildfire burning (Hatch et al., 2015, 2017; Koss et al., 2018; Coggon et al., 2019; Andreae et al., 2019). Such emissions are likely to increase in the future with the spatial extent, number, and severity, of wildfires globally having increased markedly in recent decades (Jolly et al., 2015; Harvey, 2016) and predicted to continue to do so as the climate warms (Krikken et al., 2019; Lohmander, 2020). Furans have also been measured in emissions from residential logwood burning (Hartikainen et al., 2018), and burning of a wide variety of solid-fuels used for domestic heating and cooking (Stewart et al., 2021a). Furans have been shown to account for a significant proportion of the total NO$_3$ (Decker et al., 2019) and OH (Koss et al., 2018; Coggon et al., 2019; Stewart et al., 2021b) reactivity of emissions from burning of typical wildfire and domestic fuels.

Alkyl substituted furans have also been suggested as promising biofuels as they can be derived from lignocellulosic biomass (Roman-Leshkov et al., 2007; Binder et al., 2009; Wang et al., 2014). This would likely lead to fugitive emissions of these compounds during distribution, as well as emissions of unburned and partially oxidised products from vehicle exhaust. The oxidation of certain furan compounds has been shown to have large secondary organic aerosol yields (Hatch et al., 2017; Hartikainen et al., 2018; Joo et al., 2019, Ahern et al., 2019; Akherati et al., 2020), which could adversely impact air quality.

Oxidation of furans in the atmosphere has been shown to produce 2-furanones (mono-unsaturated five-membered cyclic esters) both via OH (notably hydroxy-furan-2-ones, Aschmann et al., 2014) and NO$_3$ (Berndt et al., 1997) reactions. 2-Furanones are

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55 also produced from the OH oxidation of six-membered aromatic compounds (Smith et al., 1998, 1999; Hamilton et al., 2005;
56 Bloss et al., 2005; Wyche et al., 2009; Huang et al., 2015). In both cases, the initial product is thought to be an unsaturated
57 dicarbonyl, with production of the 2-furanone formed via photoisomerisation of the dicarbonyl to a ketene-enol (Newland et al.,
58 2019), followed by ring closure of this molecule. In the case of aromatics, the ketene-enol can also be formed directly via
59 decomposition of the bicyclic peroxy radical intermediate (Wang et al., 2020).

60 Furan type compounds are removed from the atmosphere by reaction with the major oxidants OH, NO_3 and O_3. There have been
61 a number of studies on the rates of reaction of furan type compounds with the dominant daytime oxidant, OH (Lee and Tang,
62 1982; Atkinson et al., 1983; Wine and Thompson, 1984; Bierbach et al., 1992, 1994, 1995; Aschmann et al., 2011; Ausmeel et
63 al., 2017; Whelan et al., 2020). However, there have been fewer studies on the rates of reaction of furan type compounds with
64 the major night-time oxidant, NO_3 (Atkinson et al., 1985; Kind et al., 1996; Cabañas et al., 2004; Colmenar et al., 2012).

65 The nitrate radical, NO_3, is produced in the atmosphere predominantly through the reaction of NO_2 with O_3, and exists in
66 equilibrium with N_2O_5. It has long been known to be an important night-time oxidant (Levy, 1972; Winer et al., 1984). While it
67 is also produced during the daytime, it is rapidly converted back to NO_2 by reaction with NO and by photolysis. However, in
68 environments with low NO, either due to low NOx emissions, or suppression through high O_3 concentrations (e.g. Newland et
69 al., 2021), NO_3 oxidation has been observed to be significant during the day (Hamilton et al., 2021).

70 Here, we present results of a series of relative rate experiments for furan, 2-methylfuran, 2,5-dimethylfuran, furfural (furan-2-
71 aldehyde), α-angelicalactone (5-methyl-2(3H)-furanone), γ-crotonolactone (2(5H)-furanone), and pyrrole reaction with the NO_3
72 radical, performed in the 7300 L indoor simulation chamber at CNRS-ICARE, Orléans, France.

2 Experimental

2.1 CSA-Chamber

76 The CNRS-ICARE indoor chamber is a 7300 L indoor simulation chamber used for studying reaction kinetics and mechanisms
77 under atmospheric boundary layer conditions. Further details of the chamber setup and instrumentation are available elsewhere
78 (Zhou et al., 2017). Experiments were performed in the dark at atmospheric pressure (*ca.* 1000 mbar), with the chamber operated
79 at a slight overpressure to compensate for removal of air for sampling, and to prevent ingress of outside air to the chamber. The
80 chamber is in a climate controlled room and the temperature was maintained at 299±2 K.

2.2 Experimental Approach

84 Starting with the chamber filled with clean air, the VOCs of interest (*ca.* 3 ppmv) were added, followed by ~ 1 Torr of the inert
85 gas SF_6 to monitor the chamber dilution rate. The chamber was left for at least thirty minutes prior to the start of the experiment
86 to monitor the dilution rate and losses of the VOCs to the chamber walls. These losses, $(1 - 8) \times 10^{-6} \, s^{-1}$, were always smaller than
87 dilution ($\sim 1.2 \times 10^{-5} \, s^{-1}$). The reaction was then initiated by continuously introducing an N_2O_5 sample, held in a trap at ~ 235 K
88 with air flow of $(2.5 - 5)$ L/min through it, for the duration of the experiment. The chamber was monitored until most of the
89 VOC of interest was consumed, with experiments generally taking $0.5 - 2$ hours. The experiments were performed under dry
90 conditions (RH ≤ 1.5 %).

96 VOC abundance was determined by *in-situ* Fourier Transform Infrared (FTIR) Spectroscopy using a Nicolet 5700 coupled to a
97 White-type multipass cell with a pathlength of 143 m. Each scan was comprised of either 30 or 60 co-additions, taking a total of
98 2 or 4 minutes respectively, depending on the expected rate of loss of the VOCs, with a spectral resolution of 0.25 cm^{-1}.
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2.3 Materials

101

102 The VOCs of interest: furan (>99%, Sigma-Aldrich), 2-methylfuran (>98%, TCI), 2,5-dimethylfuran (>98%, TCI), pyrrole
103 (>99%, TCI), α-angelicalactone (>98%, TCI), furfural (>98%, TCI), and γ-crotonolactone (>93%, TCI); and reference
104 compounds: α-terpinene (90%, Sigma-Aldrich), 2,3-dimethyl-but-2-ene (98%, Sigma-Aldrich), 2-carene (97%, Sigma-Aldrich),
105 camphene (95%, Sigma-Aldrich), α-pinene (98%, Sigma-Aldrich), cyclohexene (≥99%, Sigma-Aldrich), 3-methyl-3-buten-1-ol
106 (97%, Sigma-Aldrich), and cyclohexane (99.5%, Sigma-Aldrich), were used as supplied without further purification.
107 N_2O_5 was synthesised by reacting NO_2 with excess O_3. First, NO and O_3 were mixed to generate NO_2 (Reaction R1). This NO_2 /
108 O_3 mixture was then flushed into a bulb in which NO_3 and subsequently N_2O_5 were generated through Reactions R2-R3.
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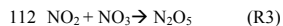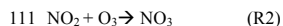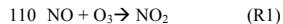
110 $NO + O_3 \rightarrow NO_2$ (R1)
111 $NO_2 + O_3 \rightarrow NO_3$ (R2)
112 $NO_2 + NO_3 \rightarrow N_2O_5$ (R3)
113

114 N_2O_5 crystals were then collected in a cold trap at 190K. The N_2O_5 sample was purified by trap to trap distillation under a flow
115 of O_2 / O_3. The final sample was stored at 190 K and used within a week.
116

2.4 Analysis

118

119 VOC concentrations were monitored by FTIR. The furans generally have a number of major absorption bands in the infrared.
120 The main bands used for analysis are shown in Table 1 (bold), as well as other characteristic bands for each compound. Reference
121 spectra of the major bands for each compound taken in the chamber at a resolution of 0.25 cm^{-1} are provided in the Supplement
122 (Figures S8-S14). The ANIR curve fitting software (Ródenas, 2018), which implements a least squares fitting algorithm was
123 used to generate time profiles for each compound based on their reference spectra. Profiles were checked by doing a number of
124 manual subtractions. Example time profiles from an experiment with α-angelicalactone and furan, with cyclohexene as the
125 reference compound, are shown in Figure 1. Further example plots are provided in the supplement (Figures S1-S7). All of the
126 concentration-time profiles are provided in .txt format at 10.5281/zenodo.5721518, and all the raw FTIR output is provided in
127 .csv format at 10.5281/zenodo.5721518. Relative rate plots for all of the experiments are shown in Figure 2.
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141 **Table 1** Maxima of major absorption bands (of Q branches if present) for the compounds used in this study. Bands used
142 predominantly for analysis are shown in bold.

Compound	Main absorption bands / cm^{-1}
Furan	**995**, 744
2-Methylfuran	**792**, 726, 1151, 2965
2,5-Dimethylfuran	**777**, 2938, 2961
Furfural	**756**, 1720
Pyrrole	**724**, 1017, 3531, 718-722
α-angelicalactone	**731, 939**, 1100, 1834
γ-crotonolactone	**1098**, 805, 866, 1045, 1812, 2885, 2945
2,3-Dimethyl-2-butene	**2878, 2930, 3005**
2-Carene	**2874, 2928, 3009**
α-pinene	**2971, 2998, 3035,** 789, 2847, 2893, 2925, 2931
Camphene	**2967, 2972, 2986**, 882, 2881, 3075
Cyclohexene	**2934,** 744, 919, 1140, 2892, 2943, 3033, 3036
3-Methyl-3-buten-1-ol	**1065,** 896, 903, 2886, 2948, 2981, 3084
Cyclohexane	**2862, 2933**

143

144 Relative rate experiments were performed, whereby a compound (or two) with an unknown reaction rate coefficient (k_{VOC}) with
145 NO$_3$ was added to the chamber with a reference compound with a known NO$_3$ reaction rate coefficient (k_{ref}). A plot of the relative
146 loss of the compound against the reference compound following addition of NO$_3$ (via N$_2$O$_5$ decomposition), accounting for both
147 chamber dilution and wall losses (k_d), gives a gradient of k_{VOC}/k_{ref} (Equation E1).

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149
$$\ln\frac{([VOC]_0)}{([VOC]_t)} - k_d t = \frac{k_{VOC}}{k_{ref}}\ln\frac{[ref]_0}{[ref]_t} - k_d t \qquad (E1)$$

150

151 A number of reference compounds were used for each VOC, chosen so that the reference rate coefficient was roughly within a
152 factor of five of the expected unknown rate coefficient, and with an attempt to use different references that had both larger and
153 smaller NO$_3$ reaction rate coefficients than the VOC. Rate coefficients of the reference compounds (Table 2) are taken from the
154 Database for the Kinetics of the Gas-Phase Atmospheric Reactions of Organic Compounds v2.1.0 (McGillen et al., 2020),
155 available at data.eurochamp.org/data-access/kin/#/home.
156 N$_2$O$_5$ was not present at detectable levels (by FTIR) during most of the experiments. The only experiments in which N$_2$O$_5$
157 concentrations built up in the chamber, were those with the slowest reacting VOCs, i.e. furfural and γ-crotonolactone. NO$_2$
158 concentrations increased throughout all experiments, typically up to 2 – 3 ppmv. The NO$_2$ is initially produced from the
159 decomposition of N$_2$O$_5$, and later potentially by the loss of NO$_2$ from nitrated VOCs / nitrated radicals. HNO$_3$ concentrations
160 increased throughout the experiments, typically up to 3 – 4 ppmv. This could be either due to impurities in the N$_2$O$_5$ sample, or

168 <u>from H abstraction reactions of NO$_3$. It is not thought that this level of HNO$_3$ will cause any interference in the rate coefficient</u>
169 <u>determinations.</u>
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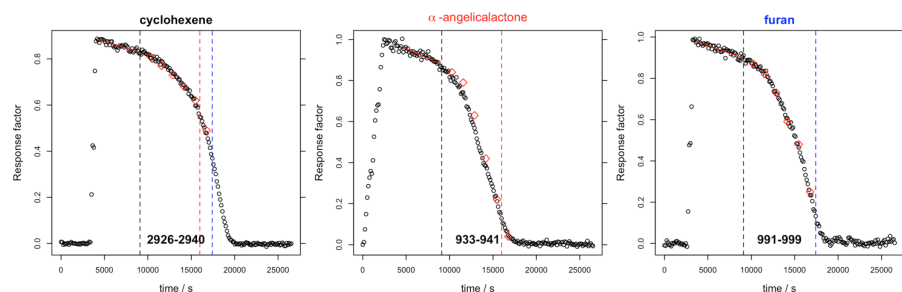
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172 **Figure 1** Concentration-time profiles from experiment with cyclohexene, α-angelicalactone and furan. Black circles are response
173 factors generated by the ANIR curve fitting program relative to the reference spectra. Red diamonds are obtained from manual
174 subtractions. Left black dashed vertical line is the beginning of the region used for the relative rate calculation, the red dashed
175 line is the end of the region used for the calculation of the α-angelicalactone relative rate, the blue line is the end of the region
176 used for the calculation of the furan relative rate. Bold values at the bottom are the absorption bands used for analysis.

177 **Table 2.** Reference compounds used. Recommended rate coefficients and uncertainties from McGillen et al. (2020).

Compound	k / cm^3 molecule^{-1} s^{-1}
2,3-dimethyl-2-butene	$(5.70\pm1.71)\times10^{-11}$
2-carene	$(2.0\pm0.3)\times10^{-11}$
α-pinene	$(6.20\pm1.55)\times10^{-12}$
camphene	$(6.60\pm1.65)\times10^{-13}$
cyclohexene	$(5.60\pm0.84)\times10^{-13}$
3-methyl-3-buten-1-ol	$(2.60\pm0.78)\times10^{-13}$
cyclohexane	$(1.35\pm0.20)\times10^{-16}$

178

179 It is noted that no OH scavenger was used in these experiments (as is the case for most, if not all, NO$_3$ previous relative rate
180 studies to the authors' knowledge). NO$_3$ reaction with alkenes tends to proceed by electrophilic addition to the double bond
181 followed by addition of O$_2$ to the resulting radical, leading to a nitrooxy peroxy radical (β-ONO$_2$-RO$_2$) (Barnes et al., 1989;
182 Hjorth et al., 1990). It has recently been shown (Novelli et al., 2021) that there is the possibility of OH formation through the
183 reactions of β-ONO$_2$-RO$_2$ with HO$_2$. HO$_2$ could be generated in these experiments from the abstraction of an H atom by O$_2$ from
184 a β-ONO$_2$-RO radical with available H atoms. The initial NO$_3$ reaction with furans is not thought to form β-ONO$_2$-RO$_2$ radicals,
185 with NO$_3$ addition to the C2 carbon followed by O$_2$ addition to the C$_5$ carbon (Berndt et al., 1997), analogous to the OH addition
186 reaction (Bierbach et al., 1995; Mousavipour et al., 2009; Yuan et al., 2017; Whelan et al., 2020). However, some of the reference
187 compounds used in the experiments will form such radicals. For example, the reaction of HO$_2$ with the β-ONO$_2$-RO$_2$ radicals
188 formed from α-pinene + NO$_3$ has been reported to have an OH yield of up to 70 % (Kurtén et al., 2017). <u>An additional minor</u>

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191 source of HO_2 during the experiments will be H abstraction reactions by NO_3. These will produce RO_2 that can react to form RO
192 radicals which may yield HO_2 following abstraction of an H atom by O_2. However, the rate coefficient of H abstraction by NO_3
193 is generally expected to be negligible relative to that of the NO_3 addition pathway. A box model run was performed to test the
194 impact of this chemistry in this study. The α-pinene scheme from the MCMv3.3.1 (Jenkin et al., 1997; mcm.york.ac.uk) was
195 incorporated into the box model AtChem (Sommariva et al., 2020), and an OH yield of 0.5 was assigned to the reaction of HO_2
196 with the initial β-ONO_2-RO_2 radicals formed from the α-pinene+NO_3 reaction. The model was initiated with 2-methylfuran and
197 α-pinene concentrations of 3 ppmv, representative of the experiments performed here. NO_3 concentrations were constrained to
198 give a lifetime of ~ 1 hour for the VOCs, typical of the experiments. OH reaction was found to account for less than 1 % of the
199 removal of 2-methylfuran or α-pinene through the model run. Consequently, it can be assumed that OH chemistry is a negligible
200 interference in these experiments.
201 A further potential interference with the current experimental setup, is the reaction of NO_2 with the compounds used. Rate
202 coefficients have been measured for reaction of NO_2 with a number of unsaturated compounds. For conjugated dienes, these
203 values can be large enough (~10^{-18} cm^3 $molecule^{-1}$ s^{-1}) to provide a significant loss under the experimental conditions employed
204 here (Atkinson et al., 1984; Bernard et al., 2013). NO_2 is formed during these experiments from the decomposition of N_2O_5, with
205 the NO_2 mixing ratio typically increasing up to roughly 3 ppmv through the experiment. Separate experiments were performed
206 to look at the potential reaction of NO_2 with furan, 2,5-dimethylfuran and pyrrole. For all three compounds, their loss in the
207 presence of NO_2 (allowing for dilution) was indistinguishable from zero, allowing an upper limit of < 2×10^{-20} cm^3 $molecule^{-1}$ s^{-1}
208 to be placed on their k(NO_2) rate coefficients.
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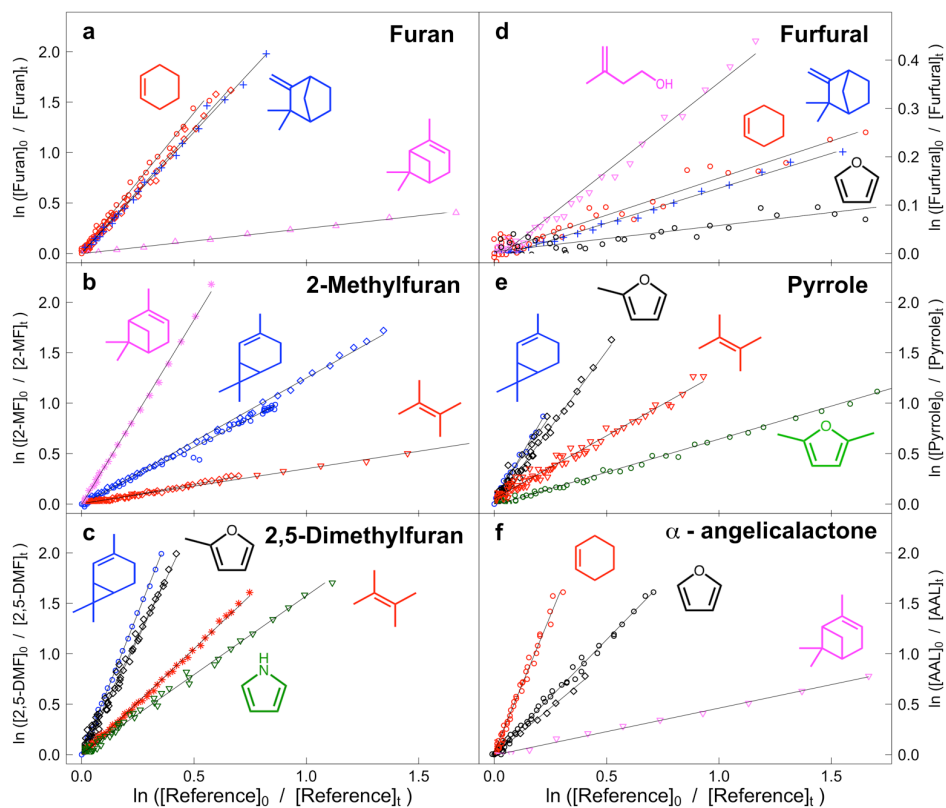
Figure 2. Relative rate plots for: **a.** furan relative to cyclohexene (red), camphene (blue), and α-pinene (pink); **b.** 2-methylfuran relative to 2-carene (blue), 2,3-dimethyl-2-butene (red), and α-pinene (pink); **c.** 2,5-dimethylfuran relative to 2-carene (blue), 2,3-dimethyl-2-butene (red), 2-methylfuran (black), and pyrrole (green); **d.** furfural relative to camphene (blue), cyclohexene (red), furan (black), and 3-methyl-3-buten-1-ol (pink); **e.** pyrrole relative to 2-carene (blue), 2,3-dimethyl-2-butene (red), 2-methylfuran (black), and 2,5-dimethylfuran (green); **f.** α-angelicalactone relative to cyclohexene (red), furan (black), and α-pinene (pink). Different shapes are used for different experiments with the same reference compound.

3 Results and Discussion

The $k(NO_3)$ rate coefficients determined with each reference compound are given in Table 3 and Figure 3. A recommendation of an updated rate coefficient for α-terpinene+NO_3 is also given in Table 3. Overall recommended values for the rate coefficient for each compound are calculated by taking the mean (weighted by the reported uncertainty of the reference) of the rate

223 coefficient derived from each experiment with each reference compound, including using the recommended values for the other
224 furans presented in Table 3. Uncertainties for the relative rates in Table S1 are assumed to be < 10 % and to be dominated by
225 statistical errors in fitting to the absorption bands. Uncertainties for the rate coefficients reported in Table 3 are dominated by
226 the assumed uncertainties in $k(NO_3)$ of the reference compounds. For most of the references, the uncertainties are 20 – 30 %,
227 taken from the recommendations of McGillen et al. (2020). For 2,3-dimethyl-2-butene, the recommended uncertainty in
228 McGillen et al. (2020) is 150 %, but based on the fact that the rate coefficients derived using 2,3-dimethyl-2-butene for 2-
229 methylfuran, 2,5-dimethylfuran and pyrrole agree very well with those using other references with much smaller uncertainties,
230 a conservative estimate of 30 % is used here. It is noted that for all compounds, the rate coefficients derived with different
231 references agree very well, to within 10%. The experimentally determined $k(NO_3)$ rate coefficients of the furans relative to each
232 other are in good agreement (to within 6%) with those calculated using the weighted means shown in Table 3 (Table S2). This
233 gives further confidence in the $k(NO_3)$ values used for the reference compounds.

234

235 The rate coefficient derived for furan, agrees well with the value previously reported by Atkinson et al. (1985) from a chamber
236 relative rate experiment. However, there is significant differences between the values reported here for furan, 2-methylfuran and
237 2,5-dimethylfuran, and those reported by Kind et al. (1996) from relative rate experiments in a flow reactor. While the value
238 reported for 2-methylfuran agrees within the uncertainties between the two studies, the values for furan and 2,5-dimethylfuran
239 are ~ 50 % and 100 % greater respectively. It is unclear what is behind this observed disparity; the good agreement between the
240 two studies for the 2-methylfuran rate coefficient suggests that there is not a systematic difference between the experimental
241 setups. For pyrrole, the rate coefficient determined here is about 50% faster than the value reported by Atkinson et al. (1985)
242 from a chamber relative rate experiment using N_2O_5 thermal decomposition. Cabañas et al. (2004) reported an upper limit of
243 $<1.8×10^{-10}$ cm^3 molecule^{-1} s^{-1} (298K) using an absolute technique of fast flow discharge.
244 For 2-furanaldehyde (furfural) + NO_3, the rate coefficient recommended here is an order of magnitude slower than the only
245 previously reported values (Colmenar et al., 2012), derived from small chamber relative rate experiments with 2-methyl-2-butene
246 and α-pinene as references. The rate coefficient from Colmenar et al. (2012) is very similar to the reported rate coefficient for
247 furan+NO_3. This is surprising, since the presence of a formyl group attached to a double bond is expected to be strongly
248 deactivating with respect to addition to that bond, due to the electron withdrawing mesomeric effect of the –C(O)H group
249 (Kerdouci et al., 2014). This has also been observed for other electrophilic addition reactions, such as those with OH and O_3
250 (Kwok and Atkinson, 1995; McGillen et al, 2011; Jenkin et al., 2020). And while there is the possibility of H abstraction from
251 the formyl group, which would increase the overall rate coefficient, such reactions are typically of the order of 10^{-14} cm^3s^{-1}
252 (Kerdouci et al., 2014), and hence would not be expected to compensate for the reduction in the contribution to the overall rate
253 coefficient of the addition reaction.
254 For 5-methyl-(3H)-furan-2-one (α-angelica lactone) + NO_3 this is the first reported rate coefficient. For (5H)-furan-2-one (γ-
255 crotonolactone), relative rate experiments with several reference compounds were attempted, with the slowest reacting of these
256 being cyclohexane (k_{NO3} = $1.4×10^{-16}$ cm^3 molecule^{-1} s^{-1}). Roughly 10 % of the cyclohexane was removed in this experiment
257 (accounting for loss by dilution), with no appreciable loss of γ-crotonolactone. We can therefore deduce that k(γ-
258 crotonolactone+NO_3) $<< 1.4×10^{-16}$ cm^3 molecule^{-1} s^{-1}. Again, this is the first time a NO_3 reaction rate coefficient has been
259 measured for this compound. A comparison of the two furanones shows that 5-methyl-(3H)-furan-2-one reacts more than four
260 orders of magnitude faster than (5H)-furan-2-one. This can be explained in part by the presence of a methyl group, which is seen

266 to increase the rate <u>coefficient</u> by roughly an order of magnitude from e.g. furan to 2-methylfuran to 2,5-dimethylfuran. Berndt

267 et al. (1997) derived an NO_3 reaction rate <u>coefficient</u> of 1.76×10^{-13} cm^3 molecule^{-1} s^{-1} for (3H)-furan-2-one. However, the majority

268 of the difference must be explained by the structure of the two compounds, namely the conjugated nature of the C=C and C=O

269 bonds in (5H)-furan-2-one. The carbonyl group removes electron density from the C=C bond greatly reducing the rate

270 coefficient. A similar relationship is seen for analogous acyclic compounds e.g. the NO_3 rate coefficient of the conjugated ester

271 methyl acrylate is almost two orders of magnitude greater than that of the non-conjugated isomer vinyl acetate.

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274 **Table 3.** NO_3 reaction rate coefficients derived for each experiment and recommended value based on the weighted mean.

Compound	Reference (repeats)	$k(NO_3)$ / cm^3 molecule^{-1} s^{-1}	Weighted mean $k(NO_3)$ / cm^3 molecule^{-1} s^{-1}
2,5-dimethylfuran	2-carene (1)	1.12×10^{-10}	$\mathbf{1.02\pm0.31\times10^{-10}}$
	2,3-dimethyl-2-butene (1)	1.21×10^{-10}	
	pyrrole (1)	9.12×10^{-11}	
	2-methylfuran (2)	9.06×10^{-11}	
pyrrole	2-carene (1)	7.68×10^{-11}	$\mathbf{6.94\pm1.9\times10^{-11}}$
	2,3-dimethyl-2-butene (2)	7.07×10^{-11}	
	2,5-dimethylfuran (1)	6.58×10^{-11}	
	2-methylfuran (2)	6.37×10^{-11}	
2-methylfuran	2-carene (3)	2.47×10^{-11}	$\mathbf{2.26\pm0.52\times10^{-11}}$
	2,3-dimethyl-2-butene (2)	2.12×10^{-11}	
	α-pinene (1)	2.27×10^{-11}	
	pyrrole (2)	1.89×10^{-11}	
	2,5-dimethylfuran (2)	2.21×10^{-11}	
α-angelicalactone	α-pinene	2.89×10^{-12}	$\mathbf{3.01\pm0.45\times10^{-12}}$
	cyclohexene	3.03×10^{-12}	
	furan (2)	3.05×10^{-12}	
furan	cyclohexene	1.45×10^{-12}	$\mathbf{1.49\pm0.23\times10^{-12}}$
	α-pinene	1.55×10^{-12}	
	camphene	1.58×10^{-12}	
	α-angelicalactone (2)	1.49×10^{-12}	
furfural	cyclohexene (1)	8.57×10^{-14}	$\mathbf{9.07\pm2.30\times10^{-14}}$
	3-methyl-3-buten-1-ol (1)	9.54×10^{-14}	
	camphene (1)	9.50×10^{-14}	
γ-crotonolactone	cyclohexane	$< 1.4\times10^{-16}$	$\mathbf{< 1.4\times10^{-16}}$

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Figure 3 The reaction rate coefficients derived for the six compounds in this work (excluding γ-crotonolactone). Red triangles
(and red text, left axis) represent the weighted mean of all experiments in this work, blue inverted triangles (and blue text, left
axis) are the recommended values from McGillen et al. (2020). Horizontal lines represent uncertainty in rate coefficient, colours
(shapes if other furans) represent which reference was used.

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305 **Table 4.** Recommended NO$_3$ rate coefficients from this work compared to those reported in the literature.

Compound	Rate coefficient / cm^3 molecule^{-1} s^{-1}	Reference	Technique	NO$_3$ source
2,5-dimethylfuran	**(1.02±0.31)×10^{-10}**	**This work**		
	(5.78±0.34)×10^{-11}	Kind et al. (1996)	Flow reactor: relative (*trans*-2-butene)	N$_2$O$_5$
pyrrole	**(6.94±1.9)×10^{-11}**	**This work**		
	(4.6±1.1)×10^{-11}	Atkinson et al. (1985)	Chamber: relative (2-methyl-2-butene)	N$_2$O$_5$
	< 1×10^{-10}	Cabañas et al. (2004)	Flow reactor: absolute (LIF detection of NO$_3$)	HNO$_3$+F
2-methylfuran	**(2.26±0.52)×10^{-11}**	**This work**		
	(2.57±0.17)×10^{-11}	Kind et al. (1996)	Flow reactor: relative (*trans*-2-butene)	N$_2$O$_5$
α-angelicalactone	**(3.01±0.45)×10^{-12}**	**This work**		
furan	**(1.49±0.23)×10^{-12}**	**This work**		
	(1.5±0.2)×10^{-12} [b]	Atkinson et al. (1985)	Chamber: relative (*trans*-2-butene)	N$_2$O$_5$
	(0.998±0.062)×10^{-12}	Kind et al. (1996)	Flow reactor: relative (*trans*-2-butene)	N$_2$O$_5$
	(1.36±0.8)×10^{-12}	Cabañas et al. (2004)	Flow reactor: absolute (LIF detection of NO$_3$)	HNO$_3$+F

furfural	$(9.07\pm2.30)\times10^{-14}$	This work		
	$(1.17\pm0.15)\times10^{-12}$	Colmenar et al. (2012)	Small chamber: relative (2-methyl-2-butene)	N_2O_5
	$(1.36\pm0.38)\times10^{-12}$	Colmenar et al. (2012)	Small chamber: relative (α-pinene)	N_2O_5
γ-crotonolactone	$< 1.4\times10^{-16}$	This work		

[a] corrected for change to recommended rate for reference (2,3-dimethyl-2-butene); [b] corrected for change to recommended rate for reference (trans-2-butene)

4 Atmospheric implications

The atmospheric lifetimes of the compounds, based on the rate coefficients reported herein, are given in Table 5. These assume concentrations of OH = 5×10^6 molecules cm^{-3} (typical daily peak summertime concentrations 1.5×10^6 – 1.5×10^7 molecules cm^{-3} (Stone et al., 2012)), night-time NO_3 = 2×10^8 molecules cm^{-3} (typical night-time concentrations 1×10^8 – $>1\times10^9$ cm^{-3} (Brown and Stutz (2012)) daytime NO_3 = 1×10^7 molecules cm^{-3} (limited daytime measurements suggest concentrations ~ 0.5 – >1 pptv (2.5×10^7 molecules cm^{-3}) (Brown and Stutz (2012)), and O_3 = 40 ppbv (background O_3 concentration ~ 40 ppb (Parrish et al., 2014)). From these values it is clear that the alkyl substituted furans and pyrrole have very short lifetimes both during the day, when the dominant daytime sink is likely to be reaction with OH, and at night, when the dominant sink will be reaction with NO_3. O_3 may contribute somewhat to the removal of these compounds both during the day and night, particularly for 2,5-dimethylfuran. As $k(NO_3)$ approaches the same order of magnitude as $k(OH)$, e.g. for 2-methylfuran, 2,5-dimethylfuran and pyrrole, the NO_3 reaction is likely to be competitive with the OH reaction even during the day in low NOx environments, with daytime NO_3 concentrations reported to be ~ 1 ppt (2.5×10^7 molecules cm^{-3}) (Brown and Stutz, 2012). The relatively large rate coefficient reported here for α-angelicalactone, suggests that NO_3 reaction will be an important sink for unsaturated non-conjugated cyclic esters. On the other hand, the very small rate coefficient for the γ-crotonolactone +NO_3 reaction suggests that this will not be an important atmospheric sink. γ-crotonolactone has also been shown to have a very slow reaction with O_3 (lifetime > 100 years, Ausmeel et al., 2017), whereas for reaction with OH, the lifetime is much shorter, and this will be the predominant gas-phase sink for γ-crotonolactone. Such a slow NO_3 reaction might be expected to extend to all 2-furanones with a conjugated structure, e.g. hydroxyfuranones – major products of OH oxidation of methyl substituted furans (Aschmann et al., 2014), such that the nitrate reaction may be unimportant in the atmosphere for these structures. Although substitution at the double bond is likely to increase the rate coefficient somewhat, as observed for OH and O_3 reactions with the methyl-substituted form of γ-crotonolactone (Ausmeel et al., 2017).

One of the major sources of furan type compounds to the atmosphere is wildfires. Wildfire plumes can be regions of high NO_3 even during the day due to suppressed photolysis rates in optically thick plumes (Decker et al, 2021). NO_3 oxidation of furans may be even more important in such plumes than in the background atmosphere. Such plumes can extend over hundreds of kilometres and hence affect air quality on a local and regional scale (e.g. Andreae et al., 1988; Brocchi et al., 2018; Johnson et al., 2021). Domestic wood burning is an increasing trend in northern European cities (Chafe et al., 2015). Burning will generally be in the winter during which, with short daylight hours and peak daytime OH often an order of magnitude lower than during the summer, the reaction with NO_3 is likely to be the dominant fate of furan type compounds in such emissions, contributing significantly to organic aerosol in urban areas (Kodros et al., 2020).

367 Berndt et al. (1997) identified the major first generation products of furan+NO₃ to be the unsaturated dicarbonyl, butenedial, and

368 2(3H)-furanone, with the NO₃ recycled back to NO₂. However, Tapia et al. (2011), and Joo et al. (2019) found that the major

369 products of the 3-methylfuran+NO₃ reaction predominantly retain the NO₃ functionality. In this case, furan+NO₃ oxidation

370 chemistry may be a significant sink for NOx, sequestering it in nitrate species, which might release it far from source on further

371 gas-phase oxidation, or, due to their low volatility, be taken up into aerosol (Joo et al. 2019).

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383 **Table 5.** Atmospheric gas-phase lifetimes of the compounds reported herein based on typical mid-day OH concentrations of

384 5×10^6 molecules cm^{-3}, night-time NO₃ concentrations of 2×10^8 molecules cm^{-3}, day-time NO₃ concentrations of 1×10^7 molecules

385 cm^{-3}, and background O₃ concentrations of 40 ppbv (1×10^{12} molecules cm^{-3}).

Compound	$\tau_{NO3\ (night)}$	$\tau_{NO3\ (day)}$	$\tau_{OH\ (day)}$	τ_{O3}	$\tau_{total\ (day)}$
2,5-dimethylfuran	0.82 min	16 min	26 min [a]	40 min [b]	8 min
2-methylfuran	3.7 min	74 min	48 min [a]	-	28 min
furan	56 min	19 hours	83 min [a]	116 hours [c]	77 min
pyrrole	1.2 min	24 min	28 min [d]	18 hours [d]	13 mins
furfural	15 hours	13 days	95 min [e]	-	94 min
α-angelicalactone	28 min	9.3 hours	48 min [f]	3.5 hours [g]	37 mins
γ-crotonolactone	> 1.1 year	> 22 years	14 hours [h]	173 years	14 hours

386 [a] Matsumoto (2011); [b] Dillon et al. (2012); [c] Atkinson et al. (1983); [d] Atkinson et al. (1984); [e] Bierbach et al. (1995); [f] Bierbach

387 et al. (1994); [g] estimated (Bierbach et al., 1994); [h] Ausmeel et al. (2017)

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389 **5 Conclusions**

390 Rate coefficients are recommended for reaction of seven furan type VOCs with NO₃ at 298 K and 760 Torr, based on a series of

391 relative rate experiments. These new recommendations highlight the importance of NO₃ chemistry to the removal of furans, and

392 other similar VOCs, under atmospheric conditions. The measured rate coefficients suggest that for the three furans reported here,

393 as well as for pyrrole and α-angelicalactone reaction with NO₃ is likely to be their dominant night-time sink. For the alkyl furans

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406 and pyrrole, reaction with NO_3 may also be a significant sink during the daytime. This work also extends the existing database

407 of VOC+NO_3 reactions, providing valuable reference values for future work.

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410 *Data availability.* Further example plots and experiment information are provided in the supplement. All of the response-time

411 profiles from the FTIR are provided in .txt format at 10.5281/zenodo.5724967, and all of the raw FTIR output is provided in .csv

412 format at 10.5281/zenodo.5721518.

413

414 *Author contributions.* MJN performed the experiments with the technical support of YR and MRM and performed the data

415 treatment and interpretation. MJN wrote the paper. All co-authors revised the content of the original manuscript and approved

416 the final version of the paper.

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418 *Competing interests.*

419 The authors declare that they have no conflict of interest.

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421 *Special issue statement.* This article is part of the special issue "Simulation chambers as tools in atmospheric research

422 (AMT/ACP/GMD inter-journal SI)". It is not associated with a conference.

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α-terpinene was used as a reference compound in two experiments. However, the rate coefficients derived for 2,5-dimethylfuran and pyrrole are significantly smaller using α-terpinene compared to other reference compounds. In addition, its reaction rate relative to 2,3-dimethyl-2-butene is larger than expected based on the recommended rate coefficient of $(1.80\pm1.44)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (McGillen et al., 2020). The reaction with α-terpinene is one of the largest known VOC+NO$_3$ rate coefficients, and hence it is a useful reference and important to know the rate with a good degree of certainty. We derive a rate coefficient relative to 2,5-dimethylfuran of 2.68, to pyrrole of 3.79 and to 2,3-dimethyl-2-butene of 4.39. Using the recommended values given in Table 3 for 2,5-dimethylfuran and pyrrole, and the recommended value for 2,3-dimethyl-2-butene in Table 2, gives an average NO$_3$ reaction rate for α-terpinene of $(2.70\pm0.81)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}. This is considerably faster than a recent absolute rate measurement of $(1.2\pm0.3)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (Fouqueau et al., 2020), and previous relative rate determinations of $(1.6\pm0.6)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 1985) and $(0.9\pm0.4)\times10^{-10}$ (Berndt et al., 1996) using TME as a reference.

α-terpinene	**$(2.74\pm0.81)\times10^{-10}$**	**This work**	
	$(1.6\pm0.6)\times10^{-10}$	Atkinson et al. (1985)	Relative (2,3-dimethyl-2-butene)
	$(0.9\pm0.4)\times10^{-10}$	Berndt et al. (1996)	Relative (2,3-dimethyl-2-butene)
	$(1.2\pm0.3)\times10^{-10}$	Fouqueau et al. (2020)	