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Normal butane oxidation: measurements of autoxidation products in a jet-stirred reactor

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Keywords: n-butane, oxidation, cool flame, jet-stirred reactor, Orbitrap

Highlights:

- 37 stable products of oxidation measured by GC and FTIR
- Hydroperoxides and ketohydroperoxides were detected by Orbitrap
- Products of third O₂ addition on fuel's radicals were detected
- Hydroxyl or hydroperoxyl groups in the products were characterized by H/D exchange

Abstract

The autoxidation of n-butane was studied experimentally in a jet-stirred reactor at 1 atm (560-720 K) and 10 atm (530-1030 K) for an equivalence ratio of 1. Samples of reacting mixtures were analysed in the gas phase by gas chromatography (GC) using several detectors (Flame ionization detector, thermal conductivity detector, quadrupole mass spectrometer), hydrogen peroxide analyser, and Fourier transform infrared spectroscopy. In addition to the fuel and oxygen, 37 products were quantified. Liquid phase samples were obtained by trapping the reacting mixtures in cooled acetonitrile (273 K). The liquid samples were analysed by high resolution mass spectrometry (HRMS Orbitrap Q-Exactive), either after flow injection or separation by high pressure liquid chromatography (HPLC). Besides stable species, several other low-temperature oxidation products, such as hydroperoxides and ketohydroperoxides, were detected. Products of third O₂ addition on fuel's radicals were also detected by high resolution mass spectrometry. To assess the presence of hydroxyl or hydroperoxyl groups in the products of oxidation we performed H/D exchange with D₂O. Qualitative and quantitative results showed the same trends in terms of variation of mole fractions and signal intensities versus reacting temperature. Kinetic modelling was performed using a literature detailed kinetic reaction mechanism already used to simulate previous n-butane oxidation experiments in the cool-flame regime, showing that improvements are needed to better describe the oxidation of n-butane under the present conditions.

34 **1. Introduction**

35 *n*-Butane which has a research octane number of ~ 95 [1] is a minor component of natural gas;
36 it is also present in liquefied gas from petroleum and gasoline [2]. The autoxidation of *n*-butane
37 has already been the topic of many studies in the recent years [3-8]. However, few were devoted
38 to the measurement or detection of elusive intermediate products of cool flames. *n*-Butane
39 autoxidation has been studied in a jet-stirred reactor (JSR) at atmospheric pressure with
40 molecular beam mass spectrometry and synchrotron vacuum UV photoionization [9]. The
41 authors reported the variation of the formation of C₄-ketohydroperoxides (KHP), C₁-, C₂-, and
42 C₄-hydroperoxides. Barhini et al. [5, 6] measured concentration profiles of hydrogen peroxide
43 by cavity ring down spectroscopy (CRDS) in a JSR at atmospheric pressure. Blocquet et al. [8]
44 measured the mole fractions of the hydroperoxyl radical in a JSR at atmospheric pressure using
45 the indirect fluorescence assay by gas expansion technique. Djehiche et al. [4] measured
46 directly the mole fractions of hydrogen peroxide and hydroperoxyl radicals in a JSR at
47 atmospheric pressure. The experiments of Barhini et al. [5] were simulated by Ranzi et al. [10]
48 who considered the Korcek mechanism which transforms γ -ketohydroperoxides into acids and
49 carbonyl products through isomerization and decomposition [10-16]. In the case of *n*-butane,
50 formic acid + acetone and acetic acid + acetaldehyde are expected products. However, none of
51 these previous experimental works investigated the formation of products from a third O₂
52 addition on fuel's radicals, which has been demonstrated to occur several times in the recent
53 literature for a range of fuels including alkanes, aldehydes, esters, and ethers [17-28], and no
54 isomer-resolved data have been reported so far for C₄-KHPs.

55 In the present work, we performed a series of *n*-butane oxidation experiments in a JSR
56 at atmospheric pressure to complement those published earlier by Djehiche et al. [4]. Therefore,
57 we operated under identical conditions of pressure, equivalence ratio, initial fuel mole fraction
58 and residence time. We studied the formation of cool flame products, including products of
59 third oxygen addition on fuel's radicals over a range of temperatures under these conditions.
60 Quantification of chemical products was performed by gas chromatography and Fourier
61 transform infrared spectroscopy. Experiments were also performed at 10 atm in a JSR where
62 hydrogen peroxide and a large set of cool flame products were quantified using a range of
63 analytical techniques. These experiments served to verify the quality of simulated results
64 obtained using a reaction mechanism taken from the literature.

65

66 **2. Experimental**

67 The experiments were performed using a set-up allowing to study the oxidation of *n*-butane
 68 from 1 to 10 atm. A fused silica spherical JSR with a volume of 37 cm³ was used. There, the
 69 stirring is achieved by 4 jets exiting 0.5 mm i.d. injectors nozzles. Details can be found in
 70 previous publications [29-31]. The mean residence time inside the reactor was 1.4 s at 10 atm
 71 and 6 s at 1 atm. These conditions were chosen in order to get enough fuel-conversion and be
 72 able to observe specific cool flame products. Previous work involved CRDS-GC-FTIR
 73 experiments performed at 6 s residence time in a JSR having the same geometry as that used
 74 here [4]. Also, a similar reactor was used earlier where a range of fuels were oxidized at
 75 residence times in the range 2-4 s [17, 32-35]. No mixing issue was noticed in these previous
 76 works. The temperature along the main axis of the reactor was measured by a movable Pt/Pt-
 77 Rh 10% thermocouple (0.1 mm in diameter) located inside a thin-wall fused silica housing.
 78 Temperature gradient was measured to be ~ 2 K.cm⁻¹ (see Supporting Material, Fig. S1).

79 High-purity reactants from Air Liquide were oxygen (99.995% pure) and *n*-butane
 80 (>99.5% pure). They were diluted with nitrogen from Air Liquide (<5 ppm H₂, <50 ppm O₂,
 81 <100 ppm H₂O, <1000 ppm Ar) and mixed just before entering the injectors. For the 10 atm
 82 experiments, a cylinder containing 1% of *n*-butane in N₂ (Air Liquide) was used. The *n*-
 83 butane/nitrogen mixture was injected through a capillary and the O₂/N₂ mixture flowed in the
 84 reactor extension tube [31]. Mass flow controllers (Brooks 5850TR) were used for gas delivery.
 85 The gases were preheated before injection in the reactor to minimize temperature gradients
 86 inside the JSR. The experimental conditions are summarized in Table 1.

87

88 **Table 1.** Experimental conditions.

Parameters	1 atm experiments	10 atm experiments
Temperature range (K)	560-720	530-1030
Mean residence time (s)	6	1.4
Equivalence ratio	1	1
Initial mole fraction of <i>n</i> -butane	0.023	0.004
Initial mole fraction of O ₂	0.1495	0.026

89

90 Mole fractions of reactants and stable species formed during the autoxidation of *n*-
 91 butane at 1 and 10 atm were obtained using several instruments (gas chromatography with flame
 92 ionization detection–FID, thermal conductivity detection–TCD, and benchtop mass
 93 spectrometry–MS, online Fourier transform infrared spectroscopy–FTIR, online ATI hydrogen

94 peroxide dual-channel monitor at 10 atm). The gas samples taken with a sonic probe were
95 analysed online by FTIR and stored at 50 mbar in 1 L Pyrex bulbs for off-line gas
96 chromatography analyses. For GC and FTIR analyses, uncertainties on mole fractions were ca.
97 15%. For ATI analyses of H₂O₂, uncertainties on mole fractions were < 20 %.

98 In addition, for the autoxidation experiments at 1 atm, samples were taken by bubbling
99 oxidation samples in 20 mL of cool acetonitrile (0°C) for 75 min. The solution obtained was
100 analysed by flow injection (FIA) - Orbitrap Q-Exactive and liquid chromatography - Orbitrap
101 Q-Exactive. Two ionisation sources were used in positive and negative modes, i.e., atmospheric
102 pressure chemical ionisation (APCI) and heated electrospray ionisation (HESI). A HPLC
103 column (Acentis silica column from Supelco, 5µm, 100 Å, 250x2.1 mm) was used with an
104 acetonitrile-water solvent (82.5% acetonitrile and 17.5% water). This procedure providing
105 qualitative data is described at length in previous publications [18-20, 23, 25-27]. Because
106 Orbitrap Q-Exactive cannot detect ions at $m/z < 50$, M-HCOO⁻ adduct ions were recorded. That
107 way, H₂O₂ and C₁-C₃ products (CH₂O, CH₂O₂, C₂H₄O) were analysed. Ketohydroperoxides,
108 butyl hydroperoxides or diols and diketones were analysed as a function of temperature, and
109 products of third O₂ addition on fuel's radicals were detected. To assess the presence of OOH
110 and/or OH functional groups in the products of oxidation, we performed OH/OD exchange.
111 Here, 300 µL of D₂O (99.98% from Sigma-Aldrich) were introduced into 1 mL of liquid
112 samples. We let H/D exchange to proceed for 20 min before analyses.

113

114 **3. Kinetic modelling**

115 Kinetic modelling was performed using the Chemkin software [36]. We used the semi-detailed
116 chemical kinetic reaction mechanism from Ranzi et al. [10] which takes into account the Korcek
117 mechanism converting γ -ketohydroperoxides into acids and carbonyls. In that mechanism,
118 butyl hydroperoxides, butyl ketohydroperoxides and cyclic ethers are represented by a single
119 specie (C₄H₉OOH, NC₄-OQOOH, C₄H₈O, respectively). The measured temperatures in JSR
120 experiments were used as input in the PSR module for computations.

121

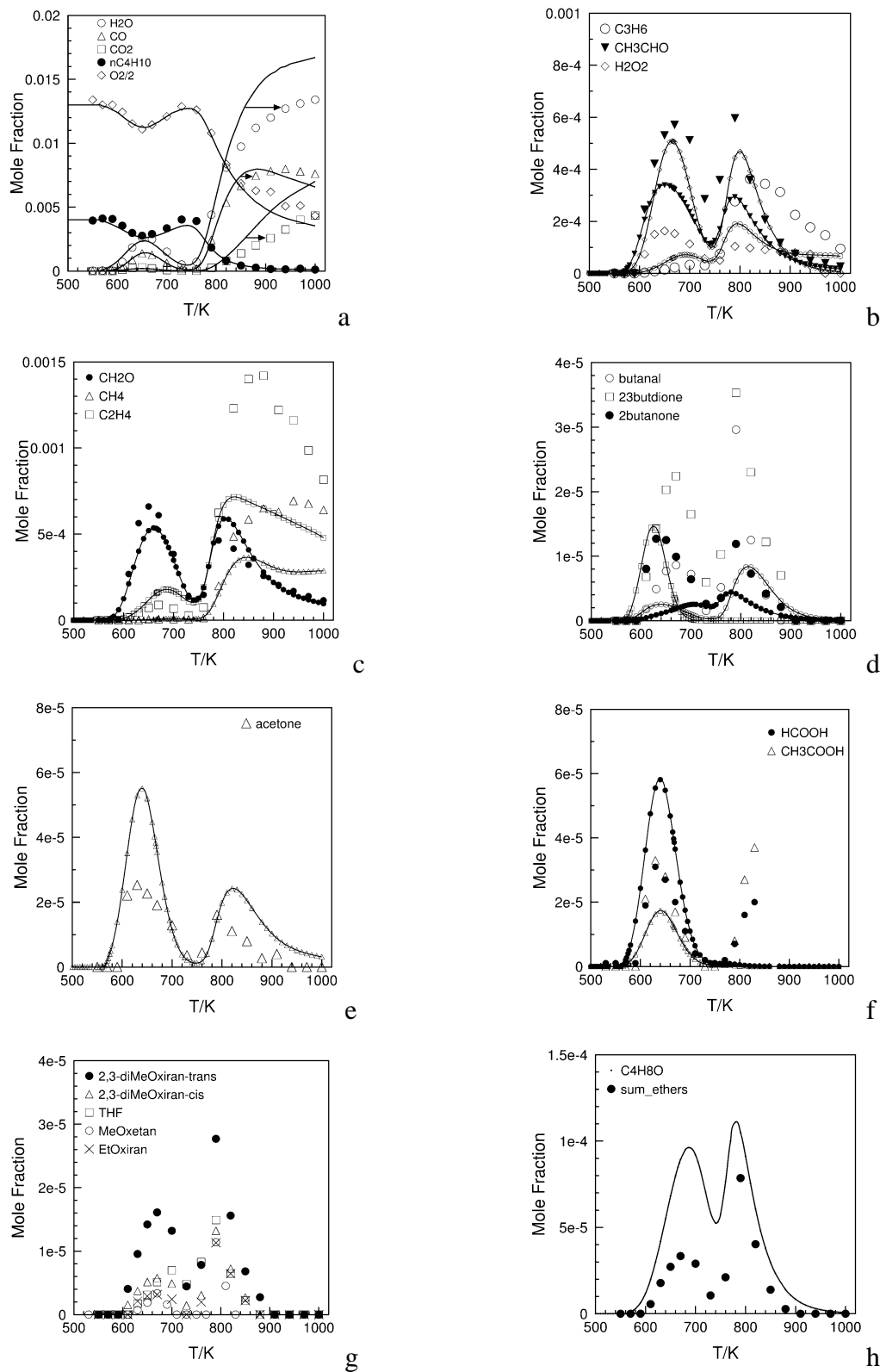
122 **4. Results and discussion**

123 4.1 Oxidation at 10 atm

124 The results obtained under high pressure conditions (Table 1) consisted of mole fractions of the
125 reactants (*n*-butane and oxygen), a large set of stable intermediates, and final products (carbon
126 dioxide and water). Most of the chemical products were measured by FID after capillary column
127 separation (50 m alumina column, 30 m and 3µm DB1 – 25 m and 1.2 µm CP-Sil 5CB, and 60

128 m DB624 capillary columns). A TCD was used to measure oxygen and hydrogen after
129 separation on a 25 m CarboPlot P7 column. FTIR was used to measure CO, CO₂, acids, and
130 CH₂O (temperature-controlled gas cell: 140°C, 10 m pathlength, resolution of 0.5 cm⁻¹, 200
131 mbar of pressure). Calibrations were made by analysing standards. When standards could not
132 be used in FID analyses, carbon-equivalent rules were applied [37]. Gas chromatography-mass
133 spectrometry (GC-MS) was used for products identification (electron impact ionization at 70
134 eV). The quantified chemical species, besides the reactants, were final products and stables
135 intermediates: H₂, H₂O, H₂O₂, CO₂, CO, CH₂O, CH₄, C₂H₂, C₂H₄, C₂H₆, oxirane, C₃H₆, trans
136 2-C₄H₈, cis 2-C₄H₈, 1-C₄H₈, 1,3-C₄H₆, CH₃CHO, methyl oxirane, 2-propenal, propanal,
137 acetone, 2,3-dimethyl oxirane (cis and trans), ethyl oxirane, 2-methyl oxetane, furan, 2,3- and
138 2,5-dihydrofuran, methacrolein, butanal, 2,3-butanedione, 2-butanone, 3-buten-2-ol, methyl
139 vinyl ketone, tetrahydrofuran (THF), formic acid, acetic acid. Figures 1a to 1h illustrate the
140 results and presents a comparison of experimental and simulated mole fraction profiles under
141 stoichiometric conditions.

142 Figure 1a shows that the model [10] slightly overestimates the oxidation rate of the fuel
143 in the negative temperature coefficient regime (NTC). Above ca. 850 K, the predicted formation
144 of carbon dioxide and water is too important. The formation of hydrogen peroxide is too
145 important in the cool flame, due to overproduction of hydroxyl radicals (Fig. 1b). Figures 1b
146 and 1c show that the model also tends to strongly overestimate the rate of oxidation of important
147 intermediates such as ethylene, methane and propene. Acetaldehyde consumption rate above
148 ca. 700 K is also overpredicted. Concerning carbonyl compounds (Figs. 1d and 1e), the model
149 overestimates the production of acetone and underestimates that of 2-butanone and butanal. The
150 formation of 2,3-butanedione is underestimated by a factor of 2 in the cool flame, and not
151 formed in the simulation above 750 K. Although the fuel conversion is well predicted, acetic
152 acid computed mole fractions do not match the data in the cool flame (Fig. 1f). Above ca. 800
153 K, the model does not predict acetic acid formation. Formic acid formation in the cool flame is
154 overpredicted by a factor of ca. 2. No reaction is included in the kinetic model to explain the
155 formation of acids at T > 800 K. Their formation through reactions of the corresponding
156 aldehydes with OH could play a role since formaldehyde and acetaldehyde reach mole fractions
157 of ca. 500 and 600 ppm, respectively. Several C₄-cyclic ethers were measured here (Fig. 1g).
158 In the model, they are represented by a single product, C₄H₈O (Fig. 1h). One can see from
159 Figure 1g that 2,3-dimethyl oxirane is the most important ether formed here. The observed order
160 of importance is: 2,3-dimethyl oxirane (A) >> tetrahydrofuran (B) ≥ 2-methyloxetane (C) ≈
161 ethyloxirane (D).

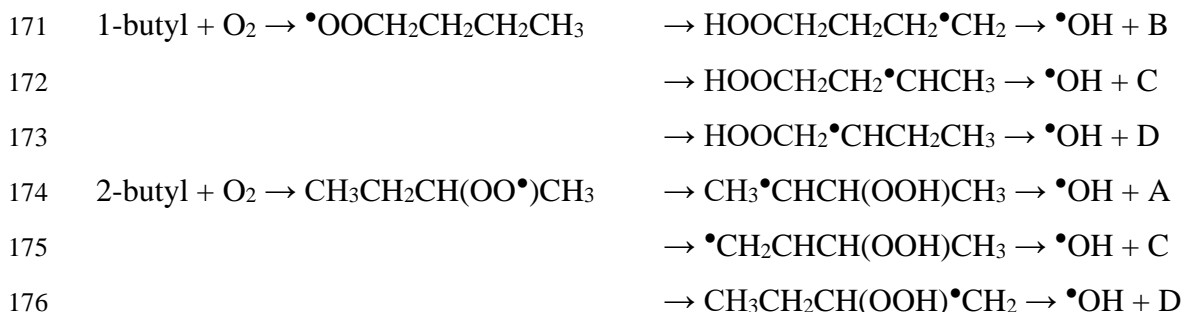


163 **Fig. 1.** Comparison of experimental (symbols) and simulated (lines and small symbols) mole
 164 fractions of selected species measured during the oxidation of *n*-butane in a JSR under
 165 stoichiometric conditions at 10 atm (see Table 1).

166

167 The oxidation of 2-butyl can lead to the formation of all these isomers, except THF,
168 whereas the oxidation of 1-butyl leads to the formation of tetrahydrofuran, 2-methyloxetane,
169 and ethyloxirane:

170



177

178 The sum of the mole fractions of these ethers was compared to the computed C₄H₈O
179 mole fractions (Fig. 1h). Because the model does not predict a NTC as strong as in the
180 experiments, it could not fully represent all the data. Whereas pathways other than the Korcek
181 mechanism could yield acetone, formic acid, acetaldehyde and acetic acid, as noticed at 10 atm
182 in the cool flame, the two acids are produced in nearly equal quantities similar to acetone.
183 Acetaldehyde maximum mole fraction is nearly 12 times higher. Reaction pathway analysis
184 was performed at 640 K, showing that formic acid is produced via nC₄-OQOOH → HCOOH +
185 CH₃COCH₃, acetaldehyde comes mainly from nC₄-OQOOH → CH₃CHO + 0.3 CH₃CO + 0.7
186 CH₂CHO + OH and OH + nC₄-OQOOH → H₂O + CH₂CO + CH₃CHO + OH (half importance),
187 acetic acid is formed via nC₄-OQOOH → CH₃CHO + CH₃COOH, and acetone's
188 overproduction is due to nC₄-OQOOH → HCOOH + CH₃COCH₃.

189 In summary, the model proposed by Ranzi et al.[10] describes only a fraction of the
190 present 10 atm data whereas it was previously shown to represent data obtained at atmospheric
191 pressure. Nevertheless, we further used that mechanism for simulating experiments performed
192 at 1 atm (Section 4.2).

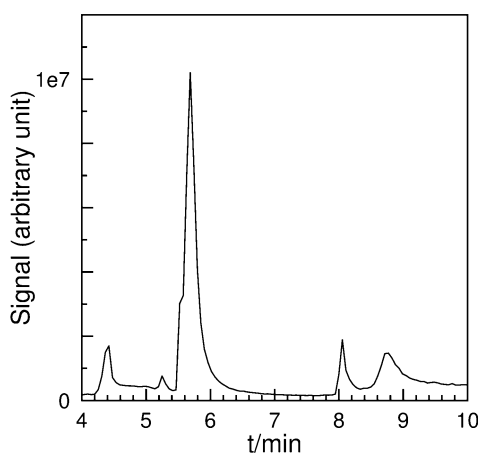
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194 4.2 Oxidation at 1 atm

195 In addition to chromatographic and FTIR analyses (see Section 3.1 for details),
196 qualitative analyses were made by Orbitrap. They consisted of ions signal profiles obtained for
197 samples taken as a function of JSR temperature and constant residence time. FIA and HPLC
198 were used. M-HCOO⁻ adduct ions were recorded (APCI in negative ionisation mode) for low-
199 mass products: H₂O₂, CH₂O, C₂H₄O. Ketohydroperoxides (KHP, C₄H₈O₃) and isomers,

200 butylhydroperoxides ($C_4H_{10}O_2$) and isomers, cyclic ethers and isomers (C_4H_8O) and
 201 butanediones ($C_4H_6O_2$) resulting from ketohydroperoxides decomposition were measured, as
 202 well as $C_4H_8O_5$, produced via third O_2 addition on fuel's radicals (Table 2). That last product
 203 was too low in concentration to present data as a function of JSR temperature. The formation
 204 of ketohydroperoxides occurs via the addition of two molecules of oxygen on the fuel's radicals:
 205 $C_4H_9\bullet + O_2 \rightarrow C_4H_9OO\bullet$ followed by H-atom transfer yielding $\bullet C_4H_8OOH$ which reacts with
 206 oxygen and, after H-atom transfer, decomposes to form a KHP, i.e., $\bullet C_4H_8OOH + O_2 \rightarrow$
 207 $\bullet OOC_4H_8OOH \rightarrow \bullet C_4H_7(OOH)_2 \rightarrow C_4H_8O_3 + \bullet OH$. Six different KHPs can be produced during
 208 the oxidation of *n*-butane. Our HPLC-Orbitrap APCI (-) analyses demonstrated the presence
 209 of a major chromatographic peak and of four other lower intensity peaks (Fig. 2). Coelution of
 210 the main chromatographic peak could not be avoided. It could be due to KHPs arising from the
 211 peroxidation of 1-butyl and 2-butyl radicals, i.e., $CH_3(C=O)CH_2CH_2OOH$ and
 212 $CH_3CH(OOH)CH_2CH(=O)$, respectively. The isomers could not be identified due to the
 213 formation of too similar fragments (fragmentation energy of 10 eV). However, kinetic
 214 modelling using an in-house detailed scheme [38] predicted the above mentioned KHPs being
 215 dominant ($CH_3(C=O)CH_2CH_2OOH > CH_3CH(OOH)CH_2CH(=O)$).

216



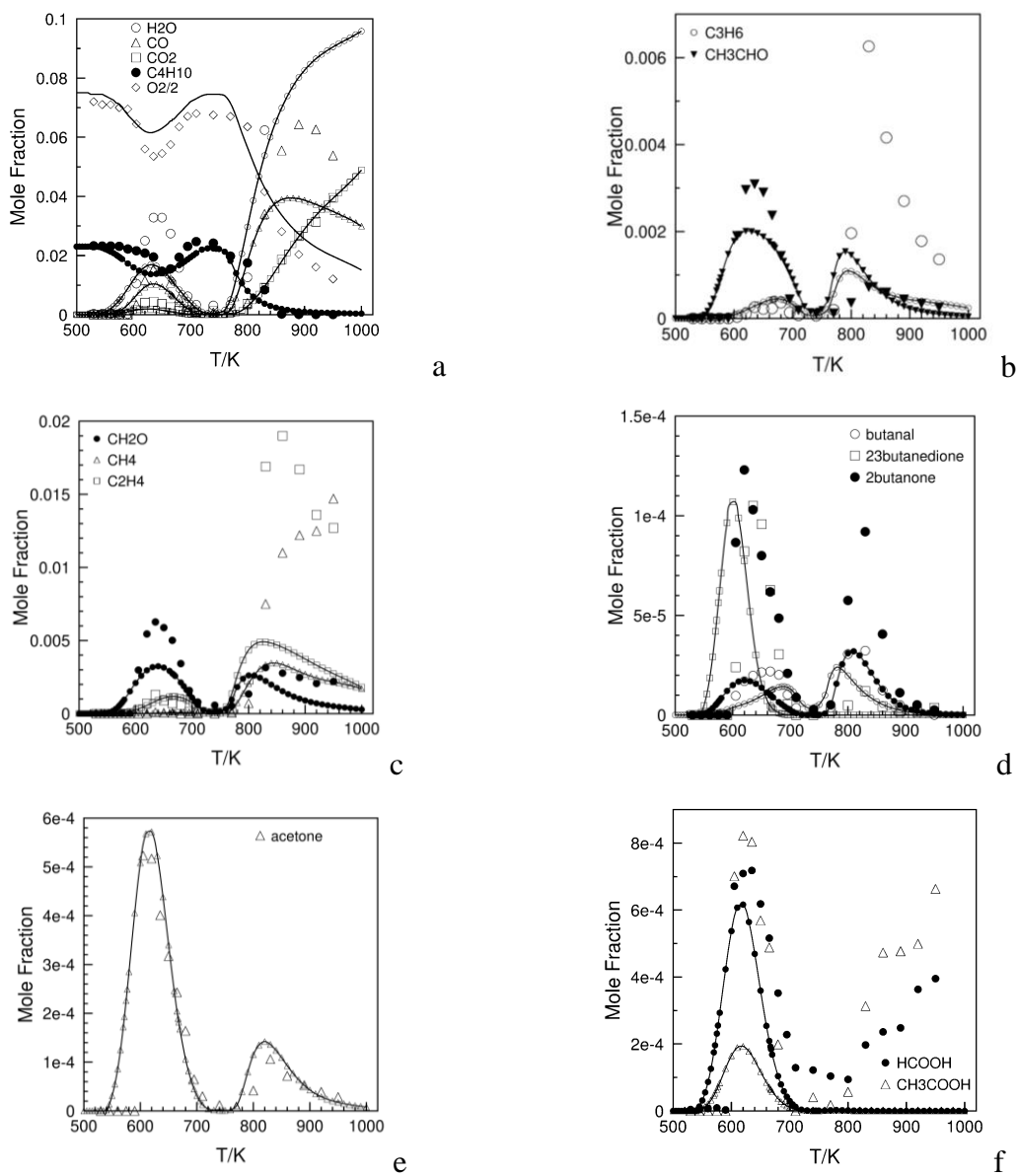
217

218 **Fig. 2.** Separation of ketohydroperoxides by liquid chromatography and detection by Orbitrap.
 219 Sample taken at 1 atm, 600 K. APCI (-) was used; ionic signal at m/z 103.03880. is plotted.

220

221 Figures 3 and 4 present the experimental results obtained here. When possible, the
 222 present data are compared to (i) our previous data obtained by CRDS and (ii) modelling results.
 223 Figure 3a shows that the model overestimates the fuel oxidation rate below 700 K although the
 224 formation of water is underestimated in the cool flame. The production of CO and CO_2 is also
 225 underestimated by the model in the cool flame. Above 800 K, the model better represents the

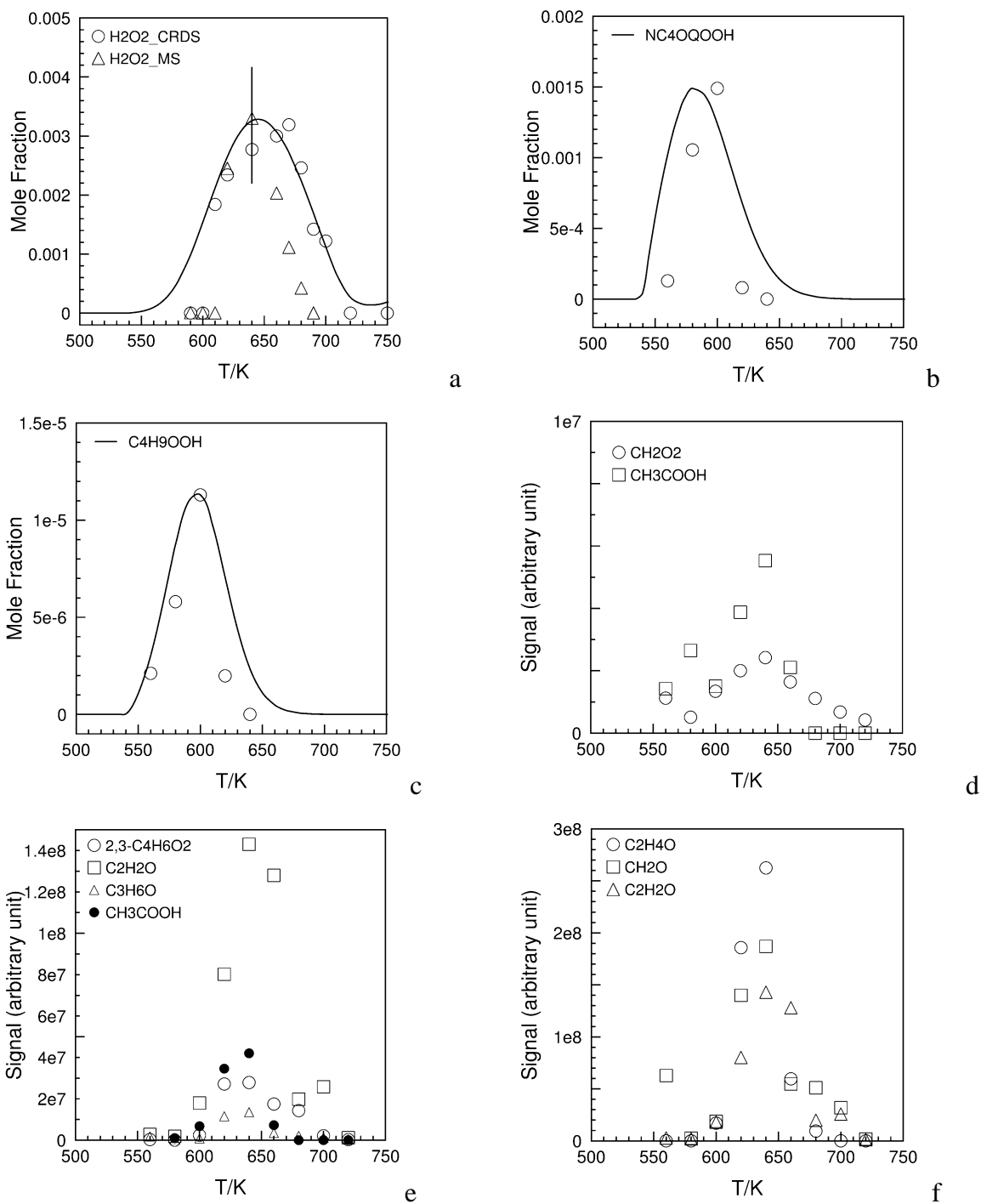
226 data. Figures 3b and 3c show that formation of formaldehyde and that of acetaldehyde are
227 underestimated by the model in the cool flame.
228



229 **Fig. 3** Comparison of experimental (symbols) and simulated (lines and small symbols) mole
230 fractions of selected species measured during the oxidation of *n*-butane in a JSR under
231 stoichiometric conditions at 1 atm (see Table 1).

232

233



234 **Fig. 4.** Comparison of experimental data (symbols) and simulated mole fractions (lines) of
 235 selected species measured during the oxidation of *n*-butane in a JSR under stoichiometric
 236 conditions at 1 atm (see Table 1). Only CRDS data are quantitative in Fig. 4a. MS data were
 237 scaled to the maximum computed mole fraction.

238
 239 Above 800 K, discrepancies between data and simulated mole fraction are observed for
 240 all the intermediate products. Figure 3e presents the results obtained for acetone and Fig. 3d
 241 presents those for C₄-carbonyls. One can see that acetone formation is well predicted over the

242 entire temperature range of this study. The production of 2,3-butanedione and that of butanal
243 are predicted well, but the model fails to predict the formation of 2-butanone (17.5 ppm
244 predicted at 620 K vs. 123 ppm measured at 620 K). On Figure 3f, products of the Korcek
245 mechanism are plotted. Whereas other routes than the Korcek mechanism can yield acetone,
246 formic acid, acetaldehyde and acetic acid, it is interesting to note that in the cool flame, the two
247 acids are produced in nearly equal quantities, also very close to that of acetone. Acetaldehyde
248 maximum mole fraction is c.a. 4 times higher. In the cool flame, the formation of formic acid
249 is well predicted whereas that of acetic acid is underestimated by a factor of ca. 4. At 600 K, a
250 rate of production analysis was performed. It indicated that formic acid comes from the
251 decomposition of C₄ KHPs: $n\text{C}_4\text{-OQOOH} \rightarrow \text{HCOOH} + \text{CH}_3\text{COCH}_3$ (Korcek mechanism). In
252 the model, acetaldehyde is mainly formed by two reactions of equal importance: $n\text{C}_4\text{-OQOOH}$
253 $\rightarrow \text{CH}_3\text{CHO} + 0.3 \text{CH}_3\text{CO} + 0.7 \text{CH}_2\text{CHO} + \text{OH}$ and $n\text{C}_4\text{-OQOOH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CO} +$
254 $\text{CH}_3\text{CHO} + \text{OH}$. In the computations, acetic acid is formed through the decomposition of C₄-
255 KHPs: $n\text{C}_4\text{-OQOOH} \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{COOH}$ (Korcek mechanism). In the simulations,
256 acetone is essentially formed through the decomposition of C₄-KHPs: $n\text{C}_4\text{-OQOOH} \rightarrow$
257 $\text{HCOOH} + \text{CH}_3\text{COCH}_3$ (Korcek mechanism).

258 Figure 4 presents the HRMS data compared to simulations for selected products. In Fig.
259 4a, HRMS data were scaled to CRDS data at 640 K; analyses were performed using HPLC-
260 HRMS APCI (-); the signal corresponds to m/z 79.0022 for H₂O₂ with HCOO⁻ adduct. In Fig.
261 4b, HRMS data were scaled to simulated maximum mole fraction. Analyses were carried out
262 by FIA- APCI (+); the signal at m/z 105.05484 is plotted. In Fig. 4c, HRMS data were scaled
263 to simulations. Analyses were performed by FIA-APCI (+); the signal at m/z 91.07576 is
264 plotted. In Fig. 4d to 4f, raw ionic signals are presented. In Fig. 4d, CH₂O₂ is detected with a
265 HCOO⁻ adducts. Analyses of CH₂O₂ were performed using HPLC-HRMS APCI (-); the signal
266 at m/z 91.0021 is plotted. For CH₃COOH analysis, we used HESI (-) HPLC-HRMS; the signal
267 at m/z 59.0124 is presented. In Fig. 4e C₂H₂O and CH₃COOH are detected with HCOO⁻
268 adducts. The analyses of C₂H₂O were carried out using APCI (-) HPLC-HRMS (signal at m/z
269 87.0072). The analyses of C₄H₆O₂ and C₃H₆O were performed using APCI (+) HPLC-HRMS
270 (signal at m/z 87.0447 and m/z 59.0500, respectively). The analysis of CH₃COOH was
271 performed by HESI (-) HPLC-HRMS (signal at m/z 105.0176).

272 In Fig. 4f, C₂H₄O, CH₂O, and C₂H₂O were detected with HCOO⁻ adducts using APCI
273 (-) HPLC-HRMS (signal at m/z 89.0228, m/z 75.0072, and m/z 87.0072, respectively). Figure
274 4a shows a comparison of quantitative measurements of hydrogen peroxide by CRDS [4],
275 qualitative HRMS measurement, and computed mole fractions using the model of Ranzi et al.

276 The HRMS data were scaled to the CRDS data at 640 K. One can see good agreement between
277 all the mole fraction profiles. Figure 4b shows the simulated KHP mole fractions compare to
278 HRMS data scaled to the maximum computed mole fraction. From that figure, one can observe
279 a good match between data and modelling. This is also the case for $C_4H_{10}O_2$
280 (butylhydroperoxides and diols) when HRMS data are scaled to the maximum computed mole
281 C_4H_9OOH fraction. APCI and HESI were used to track a set of other species. The present results
282 are presented in Figures 4d, e, f. From these figures, one can see that all the products present a
283 maximum signal intensity at 640 K, as observed in corresponding GC analyses of most of the
284 intermediate cool flame products. Molecular formulae can correspond to several isomers, e.g.,
285 C_2H_4O . However, one can estimate that CH_2O_2 represents formic acid, CH_2O represents
286 formaldehyde, C_2H_2O represents ketene, $C_2H_4O_2$ represents acetic acid, C_3H_6O represents
287 mostly acetone, and C_2H_4O represents mainly acetaldehyde (~64% acetaldehyde and ~36%
288 oxirane as determined by GC analyses). The profile for 2,3- $C_4H_6O_2$ was obtained by HPLC-
289 HRMS after identification using a 2,3-butanedione standard.

290 In order to further characterise the cool flame products, we performed H/D exchange
291 with D_2O to assess the presence of hydroxyl or hydroperoxyl groups in the products (Table 2).
292 Analyses were performed in FIA/APCI (+/-) modes. For KHPs ($C_4H_8O_3$) a strong H/D
293 exchange was observed as shown in Table 2. Indeed, after addition of D_2O , one measured
294 signals with intensities of $7.32E+6$, $1.16E+7$, and $7.14E+6$ for D_0 , D_1 , and D_2 products,
295 respectively. The D_2 exchange should indicate the presence of ketodiols.

296 $C_4H_6O_2$ corresponds to several isomers. Butanediones were identified by GC-MS.
297 Because two H/D exchanges were observed here, unsaturated diols are likely present in the
298 analysed sample. Many isomers can correspond to C_4H_8O . In this work, cyclic ethers, ketones,
299 aldehydes, and unsaturated alcohols have been identified by GC-MS. Among this species, only
300 unsaturated alcohols could form deuterated products in presence of D_2O . Here, the observation
301 of $C_4H_7D_1O$ indicates their likely presence in the oxidation products. $C_4H_8O_2$ could represent
302 butyric acid and unsaturated hydroperoxides. Because $C_4H_7D_1O_2$ was observed, the presence
303 of unsaturated ROOH in the analysed sample is likely since the butyric acid isomeric form
304 shows no H/D exchange in presence of D_2O [18]. $C_4H_{10}O_2$ can represent diols and ROOH. The
305 strong signal observed for $C_4H_8D_2O_2^+$ indicates the likely presence of diols in the sample.
306 Indeed, after addition of D_2O , one measured signals with intensities of $9.45E+6$, $1.06E+7$, and
307 $3.25E+6$ for D_0 , D_1 , and D_2 products, respectively. The major H/D exchange yields D_1 products
308 whereas the D_2 exchange represents 1/3 of D_0 or D_1 signals which should indicate the presence
309 of two OH groups in $C_4H_{10}O_2$.

310

311

312 **Table 2.** H/D exchange results for products of *n*-butane oxidation in a JSR at 640K and 1 atm.

M (g/mol)	Species		APCI (+)		APCI (-)	
	Formula	Possible isomers	<i>m/z</i> (M+H) ⁺	Signal (a.u)	<i>m/z</i> (M-H) ⁻	Signal (a.u)
72	C ₄ H ₈ O	cyclic ether ketones aldehydes unsaturated alcohol	73.06538	1.02E8	71.04977	2.87E5
73	C ₄ H ₇ D ₁ O	unsaturated alcohol	74.07173	8.90E7	72.05535	4.11E4
86	C ₄ H ₆ O ₂	dione or unsaturated diols	87.04385	2.93E8	85.02824	5.59E6
87	C ₄ H ₅ D ₁ O ₂	unsaturated diols	88.05024	4.32E7	86.03459	5.18E6
88	C ₄ H ₄ D ₂ O ₂	unsaturated diols	89.05715	1.80E7	87.04084	8.90E4
88	C ₄ H ₈ O ₂	butyric acid or unsaturated ROOH	89.06010	2.38E7	87.04451	3.34E5
89	C ₄ H ₇ D ₁ O ₂	<i>idem</i>	90.06646	2.30E7	88.05024	3.60E5
90	C ₄ H ₆ D ₂ O ₂	<i>idem</i>	91.07281	2.46E6	89.05647	2.51E5
90	C ₄ H ₁₀ O ₂	ROOH or diols	91.07575	9.45E6	89.05959	1.95E5
91	C ₄ H ₉ D ₁ O ₂	<i>idem</i>	92.08211	1.06E7	-	-
92	C ₄ H ₈ D ₂ O ₂	diols	93.08837	3.25E6	-	-
104	C ₄ H ₈ O ₃	KHPs or keto-diols	105.05444	7.32E6	103.03880	7.67E7
105	C ₄ H ₇ D ₁ O ₃	KHPs or keto-diols	106.06120	1.16E7	104.04517	7.77E7
106	C ₄ H ₆ D ₂ O ₃	keto-diols	107.0674	7.14E6	105.05139	5.40E4
136	C ₄ H ₈ O ₅	keto-dihydroperoxide	137.04578	1.54E4	135.02859	2.01E5
137	C ₄ H ₇ D ₁ O ₅	<i>idem</i>	-	-	136.03522	9.41E5
138	C ₄ H ₆ D ₂ O ₅	<i>idem</i>	-	-	137.04152	9.84E5

313
 314 If the second H-atom transfer in a peroxy-alkylhydroperoxide radical does not occur on
 315 the C-atom bonded to the OOH group, a third O₂ addition can occur and yield a keto-alkyl-
 316 dihydroperoxide:



319 Only a small signal of the corresponding ion $C_4H_9O_5^+([M+H]^+)$ was observed under the
320 present conditions with positive APCI ionisation. We performed H/D exchange with D_2O to
321 verify the presence of two hydroperoxyl groups in $C_4H_8O_5$. As can be seen from Table 2,
322 $C_4H_5D_2O_5^-([M-H]^-)$ could be observed, confirming the formation of a keto-alkyl-
323 dihydroperoxide.

324

325 **5. Conclusion**

326 New experimental results were obtained in a JSR at 1 and 10 atm, using a range of analytical
327 techniques: gas chromatography with flame ionization detector, thermal conductivity detector,
328 quadrupole mass spectrometry, hydrogen peroxide analyser, Fourier transform infrared
329 spectrometry, liquid chromatography and high-resolution mass spectrometry (Orbitrap Q-
330 Exactive). H/D exchange with D_2O was used to assess the presence of hydroxyl or hydroperoxyl
331 groups in the products. The large set of qualitative and quantitative data obtained here was
332 combined with published results obtained under the same experimental conditions at 1 atm, and
333 simulated. A kinetic reaction mechanism which takes into account the Korcek mechanism was
334 taken from the literature and used to simulate the present experiments. Reaction pathway
335 analyses revealed that in the model the reactions of the Korcek mechanism are mostly
336 contributing to the formation of formic acid, acetic acid, and acetone at 1 and 10 atm, but not
337 acetaldehyde. This study showed that the selected kinetic model only partially represents the
338 data and should be improved, both under cool flame and high temperature conditions. For future
339 kinetic modelling, one should quantify the highly oxidized products detected by FIA/UHPLC-
340 Orbitrap. This is a very challenging task since such products needed to calibrate the instruments
341 are not commercially available and their synthesis is difficult.

342

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