

1 General response to Reviewers 1 and 2.
2
3 We thank the reviewers for taking the time to review this manuscript and note their comments have
4 improved the overall quality of the work. The original comments are left in black, the response is given in
5 blue and the updates to the manuscript are red.

6 Reviewer 1

7
8 General point.

9
10 Overall impressions.

11
12 The findings are interesting and potentially valuable given the importance of benzene in the
13 atmosphere. Moreover, the sophisticated instrumentation being used allows data to be obtained,
14 which heretofore has been nearly impossible. The mechanisms of aromatic systems are extremely
15 important for understanding both ozone and particle mass formation. Thus, the paper has great
16 potential in adding to the body of mechanistic knowledge needed to predict these species. The paper
17 is well written and reasonably well organized. However, while the description of the findings in the
18 abstract seems impressive, confidence in them quickly deteriorates upon further reading. For me that
19 occurs at the beginning of Section 2.

20
21 First, for the type of product study being undertaken, a 1.45 m³ reaction vessel is extremely small,
22 which, of course, requires that the system be operated as a CSTR – a requirement more than just a
23 means to homogenise the mixture.

24
25 We do not understand the concerns of the referee. Why is the vessel “extremely” small? And what is
26 wrong about using continuously stirred tank reactors for product studies? We assume there must be a
27 misunderstanding because we did not express the performance as CSTR explicitly enough. From the
28 referee remarks here and later below, it seems that we did not state clearly that we actively stirred the
29 reactor.

30 We will now more clearly state in the manuscript, that

- 31 - JPAC is operated as continuously stirred tank reactor (and not as a simple flow reactor)
- 32 - a Teflon fan provides typical mixing times of less than 2 minutes, which compares to
- 33 residence times of 48 min.
- 34 - the reactor was run in steady state which leads to stable conditions, which are determined by
- 35 the continuous inflow of the reactants, chemical production and destruction of products, wall
- 36 losses, and of course the outflow.
- 37 - we measure the steady state concentrations by measuring in the outflow.

38
39
40 Since it was not stated, the vessel was probably uncoated and the OH wall loss must have been
41 substantial and undoubtedly diffusion limited. This is an infinite sink thus, representing a constant
42 gradient of OH in the system. Now we come to the production of OH. Creating OH from the photolysis
43 of ozone at 254 nm followed by O(1D) + H₂O strikes me as extremely dangerous for interpreting the
44 data. Of course, the radiation is not only available to photolyze ozone but the other organics and the
45 various nitrogen oxides in the chamber. Benzene has a strong absorption at 254 nm and likely being
46 photolysed, depending on the quantum yield.

47
48 We provide the following clarification of the OH budget within JPAC and discussion on benzene
49 absorption at 254 nm. The reactor is operated as CSTR and measurements are taken when the
50 system is in steady state. The chamber is actively mixed within 2 minutes. This leads to a well-mixed
51 core and a boundary layer, which must be penetrated by diffusion before radicals and low volatility
52 compounds are eventually lost to the wall.

53
54 We estimate the typical time for moving by Brownian motion through a layer thickness l :
55

56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103

$$t_{diff} = \frac{l^2}{D}$$

$$l = \sqrt{D \cdot t_{diff}}$$

D is a diffusion coefficient. For a typical HOM molecule $D \approx 0.05 \text{ cm}^2/\text{s}$, HOM lifetime 100 s $\Rightarrow l = 2 \text{ cm}$

\Rightarrow We estimate the “effective” boundary layer thickness is a few mm.

OH background “reactivity” has been determined in collaboration with our LIF group (Broch, thesis, 2011). OH background loss over the years has been pretty stable at 4 s^{-1} , including wall losses.

\Rightarrow Background OH Lifetime 0.25 s.

If we assume a diffusivity of OH = $0.3 \text{ cm}^2/\text{s}$ (larger than water = $0.25 \text{ cm}^2/\text{s}$ but smaller than $\text{H}_2 = 0.6 \text{ cm}^2/\text{s}$) and laminar layer of 5 mm then

$$0.83 = \frac{0.5^2}{0.3} [\text{s}]$$

OH wall loss coefficient = 1.2 s^{-1}

That means OH wall loss contributes about $\frac{1}{4}$ (1.2 s^{-1}) to the OH background loss.

When we do experiments with VOC we have to also to consider the lifetime of OH due to VOC oxidation.

Here, the lifetime of OH with respect to benzene oxidation:

$$k_{\text{OH}+\text{C}_6\text{H}_6} = 1.210^{-12} \text{ cm}^3 \text{ s}^{-1}$$

$$\text{benzene} = 50 \text{ ppb} = 1.2510^{-12} \text{ cm}^{-3}$$

$$\tau_{\text{OH}+\text{C}_6\text{H}_6} = \frac{1}{1.2 \cdot 10^{-12} \cdot 1.25 \cdot 10^{12}}$$

$\Rightarrow \tau_{\text{OH}+\text{C}_6\text{H}_6} = 0.7 \text{ sec}$. This number is likely even shorter due to secondary oxidation of reaction products, so we estimate it to be about half of that, 0.3 s

Thus, the estimation of the total OH loss becomes

$$7.3[\text{s}^{-1}] = \frac{1}{0.25[\text{s}]} + \frac{1}{0.3[\text{s}]}$$

This overall OH loss rate can be rounded up to $10[\text{s}^{-1}]$,

Our claim is that we are able to reach $\text{OH} \approx 10^8 \text{ cm}^{-3}$ under steady state conditions, in other words the destruction of $\text{OH} = 10 \times 10^8 \text{ cm}^{-3} \text{ s}^{-1}$

In steady state:

production = destruction

To keep up $1 \cdot 10^8 \text{ cm}^{-3}$ OH in steady state, the production P_{OH} has to be

$$P_{\text{OH}} = 10 \cdot 1 \cdot 10^8 \text{ cm}^{-3} \text{ s}^{-1}$$

which means that to keep up a steady state concentration of $10^8 \text{ cm}^{-3} \text{ s}^{-1}$ OH, a production of $10^9 \text{ OH cm}^{-3} \text{ s}^{-1}$ is needed.

104 OH is produced in the chamber by photolyzing O₃ into O¹D, and the fraction of O¹D reacting with
105 water to form 2 OH radicals is in competition with quenching of the O¹D into O³P by N₂ and O₂
106 (=0.07).
107

$$108 \quad P_{OH} = \frac{2 \cdot J_{O^1D} \cdot O_3 \cdot 2.14 \cdot 10^{-10} \cdot H_2O}{3.2 \cdot 10^{-11} \cdot \text{EXP}(67/T) \cdot O_2 + 2.0 \cdot 10^{-11} \cdot \text{EXP}\left(\frac{130}{T}\right) \cdot N_2 + 2 \cdot 10^{-10} \cdot H_2O}$$

109
110 The water concentration at 288K and ≈60%RH = 3x10¹⁷. The J_{O¹D} in the chamber is varied by
111 shielding parts of the quartz lamps with glass tubes.
112

113 In many experiments the J_{O¹D} was 2.610⁻³ s⁻¹ for the whole chamber, but it can be enlarged up to
114 5.210⁻³ s⁻¹. At steady state concentrations of 1x10¹² cm⁻³ (40 ppb) of O₃, we calculate P_{OH} = 4x10⁸ and
115 at J_{O¹D} 5x10⁻³, P_{OH} = 7x10⁸. In addition, we have to consider that when OH is consumed it leads to
116 HO₂ formation, and the recycling of HO₂ to OH will enhance the OH production beyond the primary
117 production, especially in presence of moderate concentrations of (NO).
118

119 Based on the calculation above, we conclude that the observations of OH are expected and
120 consistent with the boundary conditions of the JPAC chamber.
121

122 Independent of that we doubt that coating would make a substantial difference to OH wall loss. Since
123 OH is produced all the time by a local light source amid the chamber, there is always an OH gradient
124 from lamp to wall. Indeed, there is likely a quite complex light and OH field in the chamber. However,
125 as pointed out earlier, the chamber is continuously stirred with a mixing time of less than 2 minutes.
126 This ensures all material with lifetimes >> 2 min in the chamber is homogenised and exposed to a
127 uniform OH dose integrated over the entire OH field.
128

129 The intensity of the TUV lamp is relatively low; it is effective for OH production because O₃ has a
130 cross section of 1.1x10⁻¹⁷ cm² at 254 nm and a quantum yield of 1 for O¹D production. Benzene has
131 absorptions in the spectral range of the TUV lamp, with a narrow maximum cross section at 253 nm of
132 8x10⁻¹⁸. However, this falls quickly off towards 254 nm where it is maximal with 1.4x10⁻¹⁸ at about
133 253.9 nm (Fally et al., 2009). Kamps et al., (1993) report quantum yields of close to zero when
134 shining benzene / inert gas mixtures with 254 nm low pressure HG lamps. This is in accordance with
135 our observation of negligible benzene loss by photolysis when the TUV lamp was switched on.
136 Concentrations were monitored by PTR in dark and photolysis-only conditions (no oxidants). The
137 following sentences have been added to clarify these points in the text.
138

139 “The chamber is operated as a continuously stirred tank reactor with modifications as described in Mentel et al.
140 (2015). A fan made of Teflon provides typical mixing time of less than 2 minutes. The total flow in and out the
141 chamber was 30 L min⁻¹ resulting in an average residence time in the chamber of ~2900 seconds or 48 minutes.”
142

143 “The loss of benzene by photolysis was found to be negligible as measured by Q-PTR during experiments where
144 only benzene was introduced into the chamber, in accordance with observations in the literature (Fally et al.,
145 2009; Kamps et al., 1993).”
146

147 The steady-state concentration of ozone is thus very important. Clearly, ozone does not react with
148 benzene, but once fragmentation occurs, there are plenty of double bonds for ozone to react with,
149 perhaps not as competitively as OH, but that only depends on the concentration of ozone being used.
150 This leads to my first major complaint. Please give the concentrations or concentration ranges being
151 used in the study. Better yet a table of the initial conditions: benzene, ozone, water (ppm), NO, NO₂,
152 chamber residence time is essential. A table of initial conditions should not be relegated to a
153 supplementary section. It is ACP after all; there is no page limitation.
154

155 Table 1 of the main document contains the experimental details. These have been updated as
156 requested. We double checked and recalculated the table input given in the ACPD version and
157 removed erroneous numbers.
158

159 Onto the OH concentration in Table 1. I simply find it implausible that OH concentrations of 10^{10}
160 molecules can be formed in what is basically a smog chamber. (Obviously, high concentrations of OH
161 are generated in flowtubes operated on millisecond timescales. Not here.)

162
163 OH concentrations of up to 10^8 and higher can be produced in the JPAC chamber (e.g. Garmash et
164 al, 2020). This is due to the efficient O₃ photolysis at 254nm as discussed in detail in the previous
165 comments. The average OH values in steady are calculated from the amount of benzene that was
166 consumed, which is simply the difference of the benzene concentration in the inflow and the outflow.
167 The calculation of the OH concentration from benzene consumption was double checked by adding
168 1,8-cineole as a second OH tracer in an extra experiment. Moreover, the calculation of OH by the
169 consumption of hydrocarbons in general was verified in an earlier study by comparison to direct OH
170 measurements by LIF in the chamber (Broch, Thesis 2011). However, the value in the old Table 1
171 was a factor of 2 too large and has been revised.

172
173 There are just too many things for OH to do. As mentioned, walls and double-bonds are but two. This
174 is all based on the p.5 equation for benzene loss and the low rate constant for irradiations over a
175 period of minutes results in high calculated OH levels. First, I would call Column 3, benzene loss
176 because that is what is measured.

177
178 Yes, the OH steady state concentration is determined by its source strength ($J_{O_3+H_2O}$) as shown
179 above, and by all losses, including reactions with the reacted benzene and its oxidation products, as
180 well as losses to the wall. The chamber is permanently irradiated over the whole experiment period of
181 several hours and OH is constantly produced. As mentioned above, benzene losses due to photolysis
182 at 254 nm are negligible. The steady state measurements were integrated over several minutes. We
183 have now clarified in the introduction that we are measuring the oxidation of benzene and its oxidation
184 products, which includes unsaturated species and clarified the comments on wall losses.

185
186 Second, the absolute benzene loss is irrelevant. Thus, either the initial benzene concentration in
187 Table 1 caption or percent loss in the table should be given. In my opinion, the observed loss is some
188 combination of reaction with OH and photolysis by 254 nm mercury radiation. This would thus lower
189 the calculated OH concentration.

190
191 The table of initial conditions has been updated. Experiments were conducted to verify the
192 concentration of OH by introduction of 1,8-cineole in addition to benzene. OH concentrations were
193 confirmed to be within 6 – 12% of the original values (Garmash et al., 2020).
194 The loss of benzene by photolysis at 254 nm is negligible, due to a near zero quantum yield. This was
195 further tested and verified in a dark experiment without oxidants, where benzene was introduced into
196 the chamber as in the actual experiments, and after reaching steady state benzene concentration, the
197 254nm lamp was switched on. In this experiment ozone had not been added to the chamber, so no
198 OH was produced; all benzene loss would be due to photolysis of the lamp. This experiment verified
199 the assumption based on literature that the photolysis of benzene at 254nm is negligible.

200
201 The following has been added to the text for clarification.

202
203 **“Verification experiments were done by introducing 1,8-cineole into the chamber, which confirmed the**
204 **calculated OH concentrations to be within 6 - 12% (Garmash et al., 2020).”**

205
206 However, if we take these concentrations seriously recognizing that the products are likely to be
207 considerably more reactive than the parent compound, it is easy to believe that 3-5 generations of
208 products are likely to be present in the chamber with the CIMS measuring all of them, and perhaps
209 with increased oxidation, later generation products are being measured more sensitively than earlier
210 generation products.

211
212 We agree with the referee that benzene is interesting and challenging because its products react
213 faster with OH than benzene itself. We also agree that we obviously observe several generations of
214 products and would claim that autoxidation (H-shifts in peroxy radicals) accelerates formation of
215 multiple generations in a short time (here 45 min).

216
217 Maybe it is important to remark here that we are fully aware that the CIMS sensitivity to the wide
218 range of compounds with different degrees of oxidation will intrinsically “never” be available. We make

219 no attempt to quantify CIMS sensitivity as a function of product generation or claim that the CIMS
220 measures all oxidation products within the system. However, we observe many formula with
221 significant signal strength. We want to address the question of what can be learned from such CIMS
222 mass spectral patterns (measured with two different ionization schemes) for mechanistic
223 understanding. For example, we show that the iodide CIMS is not able to observe all products of
224 benzene oxidation suggested by the MCM, and show the difference in observed product distributions
225 compared to the nitrate ionisation, which is in agreement with other studies referenced in the
226 manuscript.

227
228 Of course, a major issue as noted in the manuscript is a lack of calibrations for products formed. This
229 is unavoidable in these types of experiments. This is even worse when using a CIMS since the
230 sensitivity of seemingly similar compounds can be one or more order-of-magnitude different.
231 Therefore, to compare signal strength, as though implying, they are linearly related to concentration is
232 a rapid path to mis-interpretation. I would recommend that graphics based on signal strength should
233 be treated very carefully and worded conservatively.

234
235 As recognised here by the reviewer we state clearly that a lack of calibration prevents true
236 quantification. We aim at pattern analysis as mentioned in the previous comment. For these reasons
237 we make an honest attempt to present data in alternative yet still useful ways e.g. absolute numbers
238 of species, qualitative descriptions of those identified species, trends, as well as using analytical
239 techniques that do not require calibrated data. Where signal is reported it is of course always within
240 the context of measurements by iodide CIMS and should be interpreted as such. As an aside, we
241 would claim that even if the sensitivity changes by an order of magnitude, the information about
242 hundreds of formula provides valuable information for mechanistic understanding of the system. It is
243 only a first step, though. Whilst it is true that due to the wide range of response factors a direct
244 equivalence cannot be made between iodide CIMS instrument response and concentration, it is
245 possible to infer broad trends for simple and well understood compounds. For example, iodide
246 ionisation has poor sensitivity to low O content species e.g. alcohols or ketones compared to
247 multifunctional and higher O containing functional groups such as carboxylic acids. In this manuscript
248 it is reported that ring retaining compounds containing 1 oxygen atom, i.e. phenol, consist of ~0.4 of
249 the total signal fraction in the low NO_x experiment. Thus, if the sensitivity is low and the signal is high
250 then a broad conclusion can be made that this compound is present in 'large' amounts. Such
251 descriptions are not made in the manuscript because they are not properly quantifiable to any useful
252 degree, but nonetheless may be interpretable to those familiar with the measurement technique. This
253 of course becomes impossible when isomers and larger degrees of freedom are introduced.

254
255 Other iodide CIMS studies of aromatic systems have shown that cross calibrations and signal
256 distributions with other instruments (VOCUS) show that calibration factors for compounds with 1 to 6
257 oxygen atoms do not vary by orders of magnitude (Mehra et al., 2020). Whilst this would be an
258 assumption in this case, it is not an unreasonable inference that for broadly similar compounds,
259 sensitivities are not changing by orders of magnitude, but rather by a factor of <10.

260
261 The comparison with MCM I find both tricky and the reverse of the experimental-deterministic model
262 paradigm. First, given the complexity of MCM and the scarcity of quantitative data upon which later
263 generation (beyond first) mechanisms are based I would describe the mechanisms at best as being
264 tentative. It would be better to use the data in these experiments to provide some credence for later
265 generation MCM product predictions, of course, not stating anything about predicted yields.
266 Otherwise, it looks like "the blind leading the blind".

267
268 We agree with the reviewer that the mechanistic investigation is tentative and without calibrated data,
269 predicted derived yields should not be attempted and they are not in this instance. We do not attempt
270 to investigate yields or branching ratios. We instead provide product distributions and molecular
271 identification with some discussion to potential formation pathways expected from theoretical
272 mechanisms. We feel it is useful to compare the presence of these ions against those listed in MCM
273 as the MCM provides a comprehensive and often used standard of benzene oxidation chemistry. This
274 also provides insight into the usefulness of iodide-CIMS as an instrument for detecting benzene
275 oxidation products and to compare with other CIMS studies of aromatic systems such as those
276 referenced in the manuscript. At the same time the CIMS data indicate where the MCM concepts may
277 fall short.

278

279 Something needs to be added regarding the possible role of NO₃ radicals in the system, especially
280 given the number of oxidized nitrogen compounds being detected. Given what I expect to be a high
281 ozone concentration (ppm), its reaction with NO₂ is probably occurring to some non-negligible
282 degree.

283
284 Steady state ozone concentrations are measured at a maximum of 60 ppb. This has now been added
285 to table 1. NO₃ cannot be build up under the given conditions, since loss of NO₃ is rapid due to N₂O₅
286 formation and subsequent loss to surfaces due to the 60% humidity. This renders the impact of NO₃
287 radicals negligible.

288
289 I see no evidence provided that autooxidation plays an important role in the system. Perhaps, it does,
290 but not from the data presented. Of course, it may be that the authors have considered and
291 addressed the issues above and similar issues. However, these issues are critical to understanding
292 how the data are interpreted and must be included in the paper, if the study is to have any credibility.

293
294 The reviewer is correct, separating the role of multiple oxidations by OH and autoxidation is not easy
295 in benzene oxidation. This is extensively addressed in our paper by Garmash et al., 2020. Here we do
296 not attempt to describe the relative importance of autoxidation compared to other mechanistic
297 pathways. We describe product distributions and discuss potential autoxidation products and their
298 distribution within the system, under different NO_x conditions. We don't see a need to repeat material
299 published by Garmash et al., but we will give more reference to it.

300
301 Finally, I believe it would be valuable to show how the findings from this paper fit into the
302 understanding of benzene oxidation.

303
304 As discussed previously it is impossible to discuss the finding of this paper in a quantitative way,
305 which leaves qualitative descriptions. Qualitative presentations of product distributions and ion
306 identifications are made and a discussion of the potential origins of those observed ions in terms of
307 widely accepted chemical mechanisms is also made.

308
309 Thus, it is my opinion that this manuscript needs substantial work before it is published.

310
311 We addressed all points by the referee which we think were often based on misunderstandings
312 because of our incomplete description of our setup and boundary conditions. We think that we have
313 addressed these issues in this response. We give more detailed information on the steady state
314 concentrations of major reactants as requested. We believe that with this input it will become clear
315 that the study is within the given limits of quantification. From these points of view we do not believe
316 that this manuscript requires more work, beyond addressing the reviewers' comments and added
317 clarifications to the manuscript. Especially if one considers that much of the requested information
318 was already published previously in refereed journals, like the papers by Mentel et al., ACP (2009,
319 2015) (regarding the chamber performance) or Garmash et al., ACP (2020) regarding benzene
320 oxidation and autoxidation.

321 Regardless of the previously published information, we have tried to make the manuscript more
322 coherent by including more information and reorganisation. Especially we have reorganised the
323 structure of section 3 and we included more illustrative text to better qualify the aims of the study and
324 to improve clarity and to better guide the reader.

325
326 A few line-by-line comments.

327
328 Line 77. Johnson et al. 2005 is a rather poor reference. Dicarbonyl aldehydes were shown to be
329 formed in aromatic systems by the mid-1980's (e.g., Dumdei and O'Brien, Science, 1983; Shepson et
330 al. JPC, 1984; Dumdei et al, EST, 1988.)

331
332 The reference has been updated.

333
334 Line 132. I am not sure what this sentence is saying. Mass closure, if that is ever possible, will require
335 a lot more than complementary instruments. In fact, as these experiments are conducted, each
336 product generation probably gets you further and further away from "mass closure". I would reword
337 the sentence in a more realistic fashion and perhaps with a bit less jargon.

338

339 We believe the use of the word mass here is confusing and unhelpful. The word mass is removed and
340 the sentence is updated to be clearer:

341

342 “However, to observe carbon in a diverse range of forms, e.g. different oxidation states and of different
343 functionalities, multiple ionisation schemes are required as they are sensitivities towards different OVOCs (e.g.
344 Isaacman-VanWertz *et al.*, 2017; Riva *et al.*, 2019). These methods, combined with other measurement
345 techniques, have been demonstrated to enable the complete observation of all the reacted carbon within a system
346 (carbon closure) (Isaacman-Vanwertz *et al.*, 2018).”

347

348 Line 148-49, Table 1. Is it true that the reacted benzene concentrations were identical to three
349 significant figures for the experiments shown? The actual measured data would be more helpful
350 together with the percent benzene loss.

351

352 The table of initial conditions has been updated and revised.

353

354 Line 153. The sentence beginning in this line is a “red herring”. Otherwise, reactions of benzene with
355 ozone in the chamber would lead to product distributions being a complete mess. If benzene and
356 ozone were introduced together, there would probably be less of a mixing issue.

357

358 The words “in order to prevent reactions occurring inline” have been removed.

359

360 Line 204. How about calibrations for the instrument sensitivity for the inorganic nitro-geneous
361 compounds? Were any undertaken?

362

363 We try to monitor one easily calibrated organic compound (here formic acid) during measurements to
364 assess sensitivity changes throughout the experiment as an indicator of instrument performance.
365 Although this information is not used explicitly to calculate any concentrations, it may be useful for
366 others to assess the performance of our instrument during these experiments and so is presented
367 here. We do not deem the quantification of other inorganic nitrogen compounds by CIMS necessary
368 to the work presented here.

369

370 Line 246. I am not sure what the term “time series” means in the context of these experiments. They
371 were all done under steady-state conditions.

372

373 The reviewer states “*Thus, three or four residence times are typically needed to achieve steady*
374 *state*”. Thus, they acknowledge the dynamic nature of the system before steady state is achieved. We
375 take advantage of this and use the information we can gather from before steady state to aid
376 understanding of molecular identification. This is discussed in terms of product type and oxidation.
377 Beyond photostationary steady state the reaction produces semi-volatile and condensable material
378 that deposit and equilibrate with sample line walls. This partitioning between condensed and gas
379 phase is detected here and discussed appropriately within the context of similar literature. We also
380 show the usefulness of clustering time series, similar to other studies referenced in the manuscript,
381 within the context of an experiment with well-defined and different conditions, in this case different
382 NO_x fractions. We have added the following sentence clarifying the analysis:

383

384 “We use hierarchical clustering analysis (HCA) of the time series’ from the iodide ToF-CIMS to explore the
385 effects of different NO_x conditions on the instrument response to different organic nitrogen containing
386 products.”

387

388 Line 275. This would be an excellent place to include a table for the initial conditions. This would also
389 allow us to see how many experiments the data is based on. One of my main questions is how many
390 different residence times were tested. For example, it would have been helpful to have one
391 experiment at $\tau=1450$ s and another at $\tau=5800$ s. (Note: I am not asking for any additional experiments
392 if only one residence time was tested.)

393

394 Updated table 1 contains the details of initial conditions including number of experiments. Only one
395 residence time was tested. Testing different residence times was beyond the scope of this study.

396

397 Line 280. Again, I am not sure what “time-series behavior” means when conducting experiments in a
398 steady-state reactor.

399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458

This point is addressed in an earlier response: we monitor also the transient periods, i.e. the rise time of products, although most data was analysed for steady state conditions

Line 283. The other studies mentioned were probably performed with the experiment(s) being conducted in a batch mode. However, for a CSTR used in reactive systems, a broad spike occurs at the beginning solely from the dynamics of a reacting system reaching steady state. Thus, three or four residence times are typically needed to achieve steady state. Moreover, I suspect the system is not fully homogeneous and certainly not at the beginning of the irradiation. OH is certainly a problem – high concentrations near the lamp and low concentrations near the wall. There is also the question as to whether the radiation is optically thin. I believe there are many factors leading to this “spiking” with gas-aerosol partitioning probably being a minor one.

This spiking behaviour is discussed in Garmash et al., 2020. The manuscript also states

“The early spiking also describes the dynamic nature of oxidation concentrations before the steady state is reached.”

This is in line with the reviewers comment here, and we have re-written the sentence to improve its clarity.

“This early transient maximum has been observed in other studies investigating VOC oxidation using the nitrate ToF-CIMS (e.g. Ehn et al. 2014) and is thought to be a consequence of a mixture of phenomena that could include a latent aerosol sink shifting the equilibrium species from the gas to the aerosol phase as well as the dynamic nature of oxidant concentrations (mainly adaptation of O₃) before the steady state is reached and mixing is totally homogenous.”

Line 381. I find this section a bit too speculative and should be written more conservatively. I again repeat my comments regarding MCM and the CIMS data. Certainly, the CIMS data has no quantitative significance, since the sensitivities are typically all-over-the-map. This section would be a good place to consider what the uncertainties are present in these experiments.

The mechanistic investigation is described in the manuscript as theoretical and within the restrictions of the MCM mechanism with the additional autoxidation mechanism applied; the framework of MCM + autoxidation is clearly defined. We believe this clearly indicates the constraints placed on the investigation in this section. At no point do we attempt to quantify anything other than the number of ions observed and their formulae and discuss them in terms of the mechanism described. We improve the clarity of this section to ensure the reader is aware of the limitations of the investigation.

“This was repeated for phenol and catechol precursors as products of subsequent OH attack (Garmash et al., 2020). To reduce complexity, this subsequent OH attack is only considered at the beginning of the mechanism. This provides a total of 53 individual oxidation products with 21 unique formula.”

Line 421. A consideration of the photolysis of the nitrogenated products at 254 nm might be considered in this section as well.

Unfortunately not much data exist on the absorption cross sections of CHON compounds at 254 nm and almost none of quantum efficiencies in this wavelength range (Keller-Rudek et al., 2013). Robers and Fajer (1989) and Talukdar et al. (1997) report cross section of several organic nitrates of a few times 10⁻²⁰s-10⁻¹⁹. For methyl nitrate quantum yields for NO₂ formation are close to one at 248 nm. Therefore, unlike with benzene, we cannot exclude minor contributions of photolysis of organic nitrates at 254 nm to the product spectrum. However, many aromatic N compounds are known to absorb at higher wavelengths (300 – 400 nm) (Laskin et al., 2015) and so we expect the highest absorption cross section of aromatic N containing compounds to be shifted to these higher wavelengths and not to be impacted by the weak and coherent 254 nm TUV emission so much.

Line 470. The first sentence of the conclusion is totally unsupported. The sentence reads as though NO_x is decoupled from OH. Experiments having steady-state OH concentrations near 10(+8) molec/cc have at best marginal relevance even with atmospherically plausible levels of NO_x being tested. I would be far more circumspect in making atmospherically relevant statements from this

459 dataset. At minimum, additional qualifying statements need to be provided in this paragraph. I would
460 highly recommend simply leaving out the first paragraph.

461
462 We agree and the qualification “atmospheric relevant” may be overstated in this context. We will
463 remove it from the sentence. However, OH concentrations of up to 10^7 can be observed in the
464 atmosphere. Whilst the OH concentrations in these experiments are 5-10 times higher than typical
465 atmospheric concentrations, integrating the OH concentration over the residence time gives a total
466 dose of OH which can then be equated to an equivalent exposure time at an atmospherically relevant
467 concentration. This has been clarified with the additional statements and added into the initial
468 conditions table:

469
470 “Integrating the OH concentrations over the residence time gives an equivalent OH dosage that may be compared
471 to atmospheric levels. Here OH equivalent doses are equivalent to approximately 5 days of oxidation at a relevant
472 atmospheric OH concentration (10^6 molecules cm^{-3}).”

473 Line 486ff. From this point on, I think the data is being overinterpreted.

474
475 This includes most of the conclusion, including purely descriptive sentences that summarise the same
476 points communicated in the relevant sections of the text. Without any specific comments, this is
477 difficult to address. We underline more clearly the qualitative character and the limit that the sensitivity
478 can also change the relative importance. The following line has been added to improve clarification of
479 interpretation

480
481 “It is stressed that as these values are reported as uncalibrated instrument responses, they cannot be used to
482 directly assess chemical pathways.”

483
484

485 Reviewer 2

486

487 However, the major issue is that the discussions are fragmented. Many interesting observations
488 are presented, but it is a bit blurred how such detailed measurements of nearly 200 ions improve
489 our understanding on the fundamental oxidation mechanism of benzene, besides leaving the
490 impressions that the benzene oxidation generates hundreds of products and the oxidation
491 products are different between low- and high- NO_x conditions. The manuscript can be largely
492 improved if the detailed discussions can be synthesized in a coherent fashion. Overall, I
493 recommend publication after major revision

494 We agree with the reviewer that the structure of the paper can be made more coherent. We have
495 reorganised the structure and included more illustrative text to better qualify the aims of the study and
496 to improve clarity and to better guide the reader.

497
498 In this study, the oxidation of benzene and its oxidation products by OH under high and low NO_x conditions are
499 investigated in the Jülich plant atmosphere chamber (JPAC) (Mentel et al., 2009, 2015) with two time of flight
500 chemical ionisation mass spectrometers (ToF-CIMS) using the iodide and nitrate ionisation schemes. The
501 ionisation schemes are compared to assess the similarities in detected oxidation products in terms of molecular
502 identification and bulk properties. Mechanistic investigations to assess the ability of the iodide CIMS to detect
503 species that currently aren't accounted for i.e. HOM and those described in the MCM are investigated.
504 Additionally high and low NO_x conditions are probed. As sensitivities for the iodide CIMS are lacking, an
505 exploration of product descriptions is made using bulk analysis, as well as broad groupings defined by bulk
506 properties. Finally, the application of hierarchical clustering analysis (HCA) is used to provide the basis of a

507 methodology to assess the time series behaviour of oxidation products that can further aid molecular identification
508 e.g. by inferring potential functionality.

509 Moved mechanistic investigation section to 3.2 and added the text

510 “Nitrate CIMS is routinely used to detect HOM, but iodide CIMS is also able to detect high mass compounds
511 (Mohr et al., 2019). To test the extent to which the iodide CIMS is able to detect HOM that could potentially
512 originate from autoxidative processes, a number of theoretically suggested formulae based on the autoxidation
513 mechanism with propagation and termination steps were devised and then searched for within the spectra.”

514 “HOM and autoxidation are currently not a common inclusion in chemical box models, although some
515 mechanisms are available (e.g. Weber *et al.*, 2020). Due to its usage and optimisation for HOM detection, nitrate
516 CIMS does not typically provide insight into traditional oxidation chemistry, as its sensitivity to low molecular
517 weight species is poor. In order to assess the traditional oxidation chemistry of this system, we describe which
518 oxidation products from the MCM (Jenkin *et al.*, 2003; Bloss *et al.*, 2005) are detectable by iodide CIMS.”

519 Moved MCM products to section to 3.2.1 and added the text

520 “Without calibration, much of the oxidation product descriptions must be either; tentative, when making direct
521 identifications; or broad, and describe bulk organic properties. In the absence of direct calibration, we describe
522 the bulk properties of iodide CIMS detected CHO and CHON compounds and group them according to chemical
523 composition criteria in order to present an overall depiction of all detectable oxidation products.”

524 Moved Iodide CIMS detected CHO and CHON under different NO_x conditions to section 3.3

525 Moved Ring retention and ring breaking products to section to 3.3.1 and added the text

526 “Descriptions of bulk properties and groupings into large families are a useful method to assess broad trends
527 within the system. However, it may be possible to produce less granularity in identified species by looking at
528 specific atomic composition and attempting to infer potential functionality.”

529 Added text to the conclusion.

530 “This methodology used in conjunction with an internal calibration procedure such as voltage scanning (Lopez-
531 Hilfiker et al., 2015) could then be used to quantitatively describe shifts in CHON composition as a function of
532 NO/NO_x and further investigate the relative importance of species isomers and their formation pathways to a mass
533 spectrometric signal.”

534 Comments

535 1. Many products more than 6 carbons (like C8, C9) have been detected. Please discuss the
536 potential formation mechanisms of these compounds.

537
538 The following sentence has been added.

539
540 “Detection of molecules with greater than C₆ that are not C₁₂ dimers are likely formed through peroxy radical
541 cross reactions.”

542
543 2. Some comparisons between measurement and MCM are not conducted in a meaningful way.
544 For example, in Page 10 Line 351, it is claimed that compounds of formulae that match
545 species in MCM compare 7.3% and 6.4% of the low and high NO_x experiments, respectively.

546 There are two issues in this comparison. First, the values depend on the extent of oxidation.
547 For example, it is well-studied that the phenol yield in benzene oxidation~50%. MCM
548 compounds should least comprise 50% of detected compounds when the secondary
549 chemistry is negligible. Second, as the response factors in I-CIMS vary by orders of
550 magnitude, the raw signal in Hz cannot represent the true product distribution.

551
552
553 We agree that the inclusion of precise percentages here, whilst correct, over emphasise the relevance
554 of signal and can be misinterpreted as a true quantification, which is not the intention. We leave the
555 percentages in the results text because they directly describe the figure (9) which has other
556 interesting features as described in the text. However, we reduce the precision of the percentages
557 and present them more approximately and state clearly that these relate to ion signal and not
558 concentration. The percentages are entirely removed from the conclusion and described more
559 qualitatively to prevent misinterpretation.

560
561 Other iodide CIMS studies of aromatic systems have shown that cross calibrations and signal
562 distributions with other instruments (VOCUS) show that calibration factors for compounds with 1 to 6
563 oxygen atoms do not vary by orders of magnitude (Mehra et al., 2020). Whilst this would be an
564 assumption in this case, it is not an unreasonable inference that for broadly similar compounds,
565 sensitivities are not changing by orders of magnitude, rather by a factor of <10. See also the response
566 to reviewer 1 on the broader inferences that can be made when interpreting CIMS signal, i.e. how
567 high signal for low sensitivity species such as C₆H₆O suggests high concentrations.

568
569 Similarly, because of the two issues mentioned above (i.e., uncertainties in instrument
570 sensitivity and extent of oxidation), it is unclear how meaningful the reported distribution of
571 products is. The discussion on Page 10 Line 359 is one example.

572
573 The oxidation is now defined in terms of OH dosage. The distributions are meaningful in terms of the
574 measurement techniques, which are contrasted and discussed. The following clarification on how
575 these numbers and figures can be interpreted has been added to the text.

576
577 “It is stressed that as these values are reported as uncalibrated instrument responses they cannot be used to
578 directly assess chemical pathways. However, they allow for the comparison of product distributions between
579 high and low NO_x conditions in terms of sensitivity to iodide CIMS measurements (Fig 10 and Fig 11).”

580
581 3. Page 11 Line 375. How are these two values calculated?

582
583 These are calculated from the numbers in the paragraph above; of the 85 oxidation products listed in
584 the MCM, 19 and 26 formulae are detected in each NO_x case. The line has been removed and the
585 information incorporated into the previous paragraph.

586
587 ~~“The iodide CIMS is able to observe 25 % and 30 % of the listed MCM compounds in the low and high NO_x
588 conditions respectively (Fig 8).”~~

589
590 “The iodide ToF-CIMS detects 19 (~25 %) and 26 (~30 %) of these oxidation products under low and high NO_x
591 conditions (Fig 8).”

592
593 4. Page 11 Line 396-397. This statement on the potential formation mechanism of C₆H₈O₆, etc is
594 too strong. The HOMs formation mechanism from benzene oxidation is unclear. For example,
595 Garmash et al. 1 showed that the HOMs yield is higher in benzene oxidation than phenol
596 oxidation. It lacks support to state that C₆H₈O₆, etc can only be formed from phenol or
597 catechol.

598
599 The context within which the statement in this section is made is based upon the current mechanism
600 found within the MCM and the defined autoxidation method outlined in the paragraph above. The
601 following sentences have been added to clarify this:

602
603 “This was repeated for phenol and catechol precursors as products of subsequent OH attack (Garmash et al.,
604 2020). To reduce complexity, this subsequent OH attack is only considered at the beginning of the mechanism.”

605

606 “All the suggestions of potential mechanistic routes to formation are speculative and set against the mechanistic
607 paradigm laid out here.”

608
609 We agree this statement lacks support in terms of precursor and have revised the sentence.

610
611 “Here, C₆H₈O₆, C₆H₈O₇, C₆H₈O₈ are potentially formed through the autoxidation mechanism”

612
613 5. Table 1. Please include the initial concentration of benzene. I estimate that roughly 20-40% of
614 initial benzene is oxidized in the experiments. Because benzene oxidation products are much
615 more reactive than benzene, many detected products are likely from multi-generation
616 chemistry. This should be clearly mentioned in the manuscript.

617
618 Table 1 has been updated to include the initial concentrations. The following sentence in the introduction is
619 updated to include benzene oxidation products.

620
621 “In this study, the oxidation of benzene and its oxidation products by OH under high and low NO_x conditions
622 are investigated in the Jülich plant atmosphere chamber (JPAC) with two time of flight chemical ionisation mass
623 spectrometers (ToF-CIMS) using the iodide and nitrate ionisation schemes.”

624
625 **References**

- 626 Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-
627 Reviejo, M., Rea, G., Wenger, J. C. and Pilling, M. J.: Development of a detailed chemical mechanism
628 (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, *Atmos. Chem. Phys.*, 5(3), 641–664,
629 doi:10.5194/acp-5-641-2005, 2005.
- 630 Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann,
631 R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S.,
632 Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G.,
633 Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D.
634 R., Wildt, J. and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, *Nature*, 506(7489),
635 476–479, doi:10.1038/nature13032, 2014.
- 636 Fally, S., Carleer, M. and Vandaele, A. C.: UV Fourier transform absorption cross sections of benzene, toluene,
637 meta-, ortho-, and para-xylene, *J. Quant. Spectrosc. Radiat. Transf.*, 110(9–10), 766–782,
638 doi:10.1016/j.jqsrt.2008.11.014, 2009.
- 639 Garmash, O., Rissanen, M. P., Pullinen, I., Schmitt, S., Kausiala, O., Tillmann, R., Zhao, D., Percival, C.,
640 Bannan, T. J., Priestley, M., Hallquist, Å. M., Kleist, E., Kiendler-Scharr, A., Hallquist, M., Berndt, T.,
641 McFiggans, G., Wildt, J., Mentel, T. F. and Ehn, M.: Multi-generation OH oxidation as a source for highly
642 oxygenated organic molecules from aromatics, *Atmos. Chem. Phys.*, 20(1), 515–537, doi:10.5194/acp-20-515-
643 2020, 2020.
- 644 Isaacman-VanWertz, G., Massoli, P., O’Brien, R., Lim, C., Franklin, J. P., Moss, J. A., Hunter, J. F., Nowak, J.
645 B., Canagaratna, M. R., Misztal, P. K., Arata, C., Roscioli, J. R., Herndon, S. T., Onasch, T. B., Lambe, A. T.,
646 Jayne, J. T., Su, L., Knopf, D. A., Goldstein, A. H., Worsnop, D. R. and Kroll, J. H.: Chemical evolution of
647 atmospheric organic carbon over multiple generations of oxidation, *Nat. Chem.*, 10(4), 462–468,
648 doi:10.1038/s41557-018-0002-2, 2018.
- 649 Isaacman-VanWertz, G., Massoli, P., O’Brien, R. E., Nowak, J. B., Canagaratna, M. R., Jayne, J. T., Worsnop,
650 D. R., Su, L., Knopf, D. A., Misztal, P. K., Arata, C., Goldstein, A. H. and Kroll, J. H.: Using advanced mass
651 spectrometry techniques to fully characterize atmospheric organic carbon: current capabilities and remaining
652 gaps, *Faraday Discuss.*, 200, 579–598, doi:10.1039/C7FD00021A, 2017.
- 653 Jenkin, M. E., Saunders, S. M., Wagner, V. and Pilling, M. J.: Protocol for the development of the Master
654 Chemical Mechanism, MCM v3 (Part B): Tropospheric degradation of aromatic volatile organic compounds,
655 *Atmos. Chem. Phys.*, 3(1), 181–193, doi:10.5194/acp-3-181-2003, 2003.
- 656 Kamps, R., Müller, H., Schmitt, M., Sommer, S., Wang, Z. and Kleinermanns, K.: Photooxidation of exhaust
657 pollutants. I. Degradation efficiencies, quantum yields and products of benzene photooxidation, *Chemosphere*,
658 27(11), 2127–2142, doi:10.1016/0045-6535(93)90125-O, 1993.
- 659 Keller-Rudek, H., Moortgat, G. K., Sander, R. and Sörensen, R.: The MPI-Mainz UV/VIS spectral atlas of
660 gaseous molecules of atmospheric interest, *Earth Syst. Sci. Data*, 5(2), 365–373, doi:10.5194/essd-5-365-2013,
661 2013.
- 662 Laskin, A., Laskin, J. and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, ,
663 doi:10.1021/cr5006167, 2015.
- 664 Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., D’Ambro, E. L., Kurtén, T. and Thornton, J. A.:
665 Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic

666 molecules using the collision limit and thermodynamic stability of iodide ion adducts, *Atmos. Meas. Tech.*
667 *Discuss.*, 8(10), 10875–10896, doi:10.5194/amtd-8-10875-2015, 2015.

668 Mehra, A., Wang, Y., Krechmer, J., Lambe, A., Majluf, F., Morris, M., Priestley, M., Bannan, T., Bryant, D.,
669 Pereira, K., Hamilton, J., Rickard, A., Newland, M., Stark, H., Croteau, P., Jayne, J., Worsnop, D., Canagaratna,
670 M., Wang, L. and Coe, H.: Evaluation of the Chemical Composition of Gas and Particle Phase Products of
671 Aromatic Oxidation, *Atmos. Chem. Phys.*, (March), 1–24, doi:10.5194/acp-2020-161, 2020.

672 Mentel, T. F., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Dal Maso, M., Fisseha, R., Hohaus, T.,
673 Spahn, H., Uerlings, R., Wegener, R., Griffiths, P. T., Dinar, E., Rudich, Y. and Wahner, A.: Photochemical
674 production of aerosols from real plant emissions, *Atmos. Chem. Phys.*, 9(13), 4387–4406, doi:10.5194/acp-9-
675 4387-2009, 2009.

676 Mentel, T. F., Springer, M., Ehn, M., Kleist, E., Pullinen, I., Kurtén, T., Rissanen, M., Wahner, A. and Wildt, J.:
677 Formation of highly oxidized multifunctional compounds: autoxidation of peroxy radicals formed in the
678 ozonolysis of alkenes – deduced from structure–product relationships, *Atmos. Chem. Phys.*, 15(12), 6745–6765,
679 doi:10.5194/acp-15-6745-2015, 2015.

680 Mohr, C., Thornton, J. A., Heitto, A., Lopez-Hilfiker, F. D., Lutz, A., Riipinen, I., Hong, J., Donahue, N. M.,
681 Hallquist, M., Petäjä, T., Kulmala, M. and Yli-Juuti, T.: Molecular identification of organic vapors driving
682 atmospheric nanoparticle growth, *Nat. Commun.*, 10(1), 1–7, doi:10.1038/s41467-019-12473-2, 2019.

683 Riva, M., Rantala, P., Krechmer, E. J., Peräkylä, O., Zhang, Y., Heikkinen, L., Garmash, O., Yan, C., Kulmala,
684 M., Worsnop, D. and Ehn, M.: Evaluating the performance of five different chemical ionization techniques for
685 detecting gaseous oxygenated organic species, *Atmos. Meas. Tech.*, 12(4), 2403–2421, doi:10.5194/amt-12-
686 2403-2019, 2019.

687