RESPONSE to Reviewers

REBUTTAL LETTER

Manuscript Ref. No: **acp-2021-553, Roman et al., Atmos. Chem. Phys. Discuss**

Title: **Investigations on the gas-phase photolysis and OH radical kinetics of nitrocatechols: Implications of intramolecular interactions on their atmospheric behavior**

Special Issue: Simulation chambers as tools in atmospheric research (AMT/ACP/GMD inter-journal SI)

On behalf of all authors of the above-mentioned paper, I want to thank you and to the reviewers for careful and thorough reading of this manuscript and for the thoughtful comments and constructive suggestions. We also greatly appreciate the reviewers for their complimentary comments and advices and we appreciated the recommendations and considered the approach. We find extremely important the completeness and quality of these valuable recommendations. Special thanks to Professor Cornelius Zetzsch for the assessments made on the results of our study. In the attached file, we are pleased to present our response to the detailed review and to discuss the individual points raised by the reviewers. The original comments from the referees are shown in black and our responses are marked in blue. Changes made in the body of the article are marked in red in this document as well as in the revised manuscript and in the supplementary material. Lines indications refer to the positions where the text has been amended in the article body (original manuscript). I would like to draw your attention to the modified paper in response to the extensive and insightful reviewer's comments.

A. Comments by Referee #1

R1: This manuscript represents a considerable progress in the structure – activity relations for reactions of OH with monocyclic aromatic compounds. It deals with a highly relevant class of aromatics for atmospheric chemistry, the hydroxy-nitrated phenols, and I recommend its publication in ACP.

Answer from authors: We have gratefully appreciated the referee for the positive evaluation and the suggestions.

R1: The electron delivering lone-pair substituents (hydroxyl) interact with an electron withdrawing substituent (nitro) via the highly conductive aromatic π system and (even more) directly via H bonds to the nitro group. The H bond appears to increase the electron withdrawing capability of the nitro group enormously, resulting in a lower rate constant of electrophilic addition. A most striking example is the extremely low reactivity of 4-methyl- 5-nitrocatechol, where the effect of the electron-delivering methyl group is completely overrun by this interaction (even increasing the effect) and leads to an even lower reactivity than 4-nitrocatechol. Similar effects of the nitro group have been observed by the authors for the nitrophenols and can be expected for anilines and thiophenes (and possibly heterocyclic and polycyclic and multifunctional compounds), which occur as metabolites and can deliver electrons via the π system and an H atom to form an H bond to the vicinal nitro group.

The same interaction shows up convincingly in the gas-phase IR spectra, where the H bond between the vicinal OH groups appear as broadened peak around 3100 wavenumbers for catechol and shifts to almost 3400 wavenumbers for 4-methyl- 5-nitrocatechol. I would like to suggest that these most interesting IR spectra are added to the title: "Investigations on the gas-phase photolysis, IR spectra and OH radical kinetics of nitrocatechols: Implications of intramolecular interactions on their atmospheric behavior" and that the outcome should appear in the abstract (see below) and be discussed in a little more detail.

Answer from authors: The authors appreciate the reviewer's recommendation and we agree that the IR spectra help explain the results of the present study. However, the synthesis, solid-state characterization made by X-ray diffraction analysis, H-NMR analysis, FTIR-ATR mode spectra interpretation, along with the determination of the gas-phase IR cross-sections of the investigated compounds has been already subject of another scientific article that has been recently published (Roman et al., 2022). In the study published by Roman et al., (2022) the authors discussed the contributions raised up by the hydroxyl and nitro groups and the differences (shifts) between absorption maxima observed in the IR spectra of catechols and their corresponding nitrocatechols, as well as the differences between 3-nitro and 4-nitrocatechols. Also, gas-phase IR cross-sections, both for the absolute absorbance and integrated band intensity, respectively, have been evaluated by Roman et al. (2022). Accordingly, it is not necessarily to refer to “IR spectra” in the title of the present manuscript and anytime is needed to interpret present results with the spectral characterization we could refer to our previous published work.

R1: The determination of the rate constants with two different reference compounds and the photolysis constants for two wavelengths (an illustration of these data is missing) has excellent quality, and the authors might wish to add the values of the wall reactions of figs. 1-4 to the figure captions (or to table 2). The abstract should include the photolysis of all studied compounds by mentioning the photolytic lifetimes and the upper limits of 28 h for the atmosphere instead of the photolysis constants. It is not clear from the heading of the right column in table 2 that the lifetime refers to the atmosphere (do not mention the 365 nm here but explain that this has been calculated on the basis of NO2 photolysis in the chamber). Are UV spectra of the compounds available to give an estimate of quantum yields at the wavelengths of 254 and 365 nm?

Answer from authors: The reviewer suggestions are already partly assimilated in the manuscript. However, additional data acquisition and evaluation were performed and the results are presented in the Supplementary material. Thus, new Figure S1 and Figure S2 representing the photolysis rates of 3NCAT and 5M3NCAT at 365 nm and photolysis rates for 4NCAT and 4M5NCAT at 254 nm, were included in the Supplementary material. Mean values of the wall loss rate constants for nitrocatechols have been added in the text of the manuscript. In the abstract, we included now an upper limit for the photolytic lifetime. Average quantum yields calculated for 350-400 nm range for 3NCAT and 5M3NCAT are included now in the text and in the supplementary material, along with the cross sections measured in the aqueous solution for these two compounds.

Changes in the manuscript/supplementary text:

Changes in the manuscript:

(L18-19) Considering the obtained results, our study suggests that photolysis may be the main degradation process for 3-nitrocatechol and 5-methyl-3-nitrocatechol in the atmosphere, with a photolytic lifetime in the atmosphere up to 2 hours.

(L172) ESC-Q-UAIC reactor ($J_{\text{NO2 - atmosphere}}$/ $J_{\text{NO2 – ESC-Q-UAIC chamber}}$ = 8.5×10^{-3} s^{-1} / 4.3×10^{-3} s^{-1} ≈ 2). The wall loss (k_4) measured for 3NCAT and 5M3NCAT was about $(3.2 \pm 0.4) \times 10^{-4}$ s^{-1}, while for 4NCAT and 4M5NCAT of about $(0.7 \pm 0.3) \times 10^{-4}$ s^{-1}. However, the wall loss was relatively constant over different experiments employed in this study. Average quantum yields calculated for 3NCAT and 5M3NCAT over the 350-400 nm range were obtained using the theoretical approach described by Hofzumahaus et al. (1999), and the evaluated cross-sections of these two compounds in aqueous solutions are presented in Table TS1 in the Supplementary Material (SM). The average quantum yields, calculated for the investigated range ($\phi_{350\text{-}400}$), are: $(7.707 \pm 0.737) \times 10^{-3}$ for 3NCAT and $(4.858 \pm 0.464) \times 10^{-3}$ for 5M3NCAT. The overall errors include contributions from the solution preparation, UV-VIS spectra recording and the photolysis values. A detailed description of the technique, data collection, evaluation and interpretation is presented in the supplementary material.

Added in supplementary material:

The present supplementary material (SM) aims to provide assistance for the obtained results with additional information supporting the reliable conclusions of the research study. The SM provides graphical illustration, details related to recorded data and instrumentation.

Figure S1 and **Figure S2** present the gas-phase photolysis plots for 3-nitrocatechol and 5-methyl-3-nitrocatechol at 365 nm, and gas-phase photolysis plots for 4-nitrocatechol and 4-methyl-5-nitrocatechol at 254 nm. The photolysis rate constants were corrected for the wall loss (k_4), according to the reaction sequence presented in the manuscript.

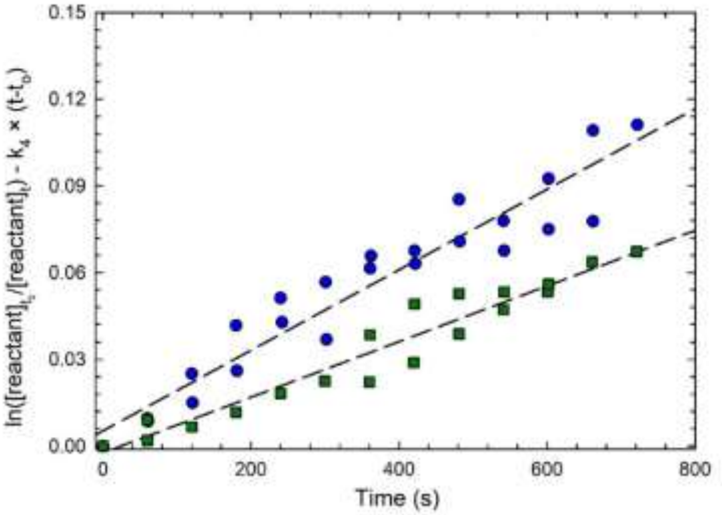

Figure S1: Kinetic plots according to the photolysis of (●) 3NCAT and (■) 5M3NCAT at 365 nm corrected for the wall loss (see details in the manuscript text).

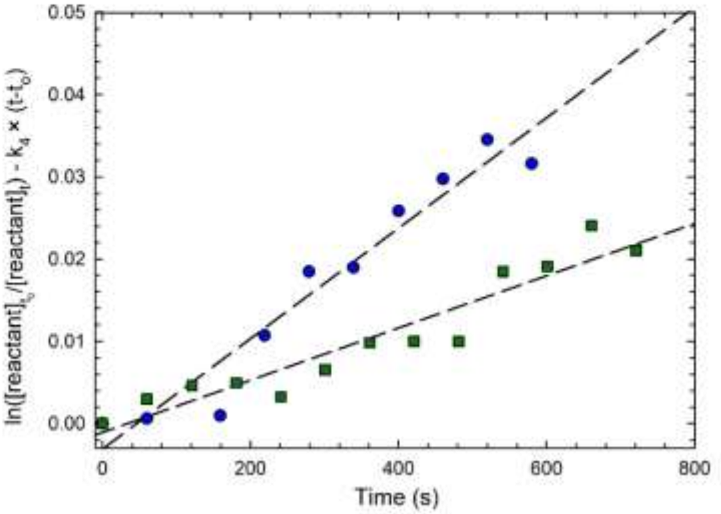

Figure S2: Kinetic plots according to the photolysis at 254 nm of (●) 4NCAT and (■) 4M5NCAT corrected for the wall loss (see details in the manuscript text).

Figure S3 illustrates the UV-VIS spectra for 3-nitrocatechol and 5-methyl-3-nitrocatechol and the calculated UV-VIS cross-sections. For comparison, the insertion represents the emission spectra of the used lamps that emitting light in the range of 310 ÷ 460 nm within maxima at 365 nm, recorded with an LI-COR spectroradiometer at a resolution of 1 nm inside the ESC-Q-UAIC chamber. The UV-VIS spectra for 3-nitrocatechol and 5-methyl-3-nitrocatechol from Figure S3 shows two intense absorption bands (λ< 250 and 260>λ<350) corresponding to a π-π^* transition and one absorption band with a smaller intensity placed from 350 to 450 nm corresponding to n-π^* transition in the 3-nitrocatechol molecule. **Table TS1** shows the values for the absorption cross sections (σ) calculated in the 350-400 nm range (similar with the band intensity range emitted by the 365 nm lamps in the ESC-Q-UAIC reactor).

UV-VIS spectra of 3-nitrocatechol and 5-methyl-3-nitrocatechol, recorded in aqueous solution for the 220 - 500 nm wavelength range, were registered using a SPECORD 210 Plus UV-VIS spectrophotometer from Analytic Jena. Stock solution of 0.950 mg/mL of 3NCAT and 0.568 mg/mL of 5M3NCAT were used to obtain solutions by dilution over a large concentration range from 3.69×10^{15} to 2.95×10^{17} cm^{-3}. The solution with five different concentrations were used to evaluate the absorption cross-sections.

Assuming similar cross-sections in the gas-phase with those in the aqueous solution, for the 350-400 nm photolytic range, an average quantum yield can be estimated using **equation S_{eq} 1** (Hofzumahaus et al., 1999). Using a boxcar integration method, the overall average quantum yields for this photolytic range ($\phi_{350-400}$) are: (7.707 ± 0.737) × 10^{-3} for 3NCAT and (4.858 ± 0.464) × 10^{-3} for 5M3NCAT. The overall errors include contributions from the solution preparation, UV-VIS spectra recording and the photolysis value. The quantum yields values from the present study should be considered with care since many significant uncertainties are linked to the assumption of the gas-phase and water-solution for the determined cross-section. For example, the bathochromic effect of the solvent at the 350-400 nm band could affect the measurements (Bejan, 2006).

$$-\frac{d[A]}{dt} = [A] \times J = [A] \times \int_{\lambda} \phi(\lambda)\ \sigma(\lambda)\ F(\lambda)\ d\lambda \qquad \mathbf{S_{eq}1}$$

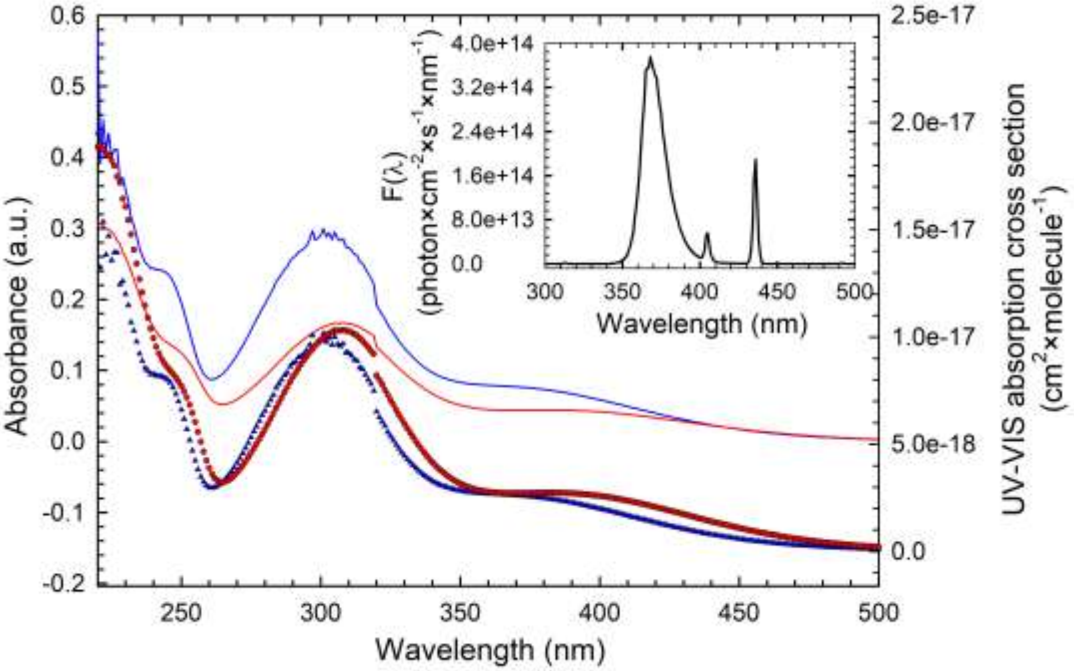

Figure S3: UV-VIS absorbance spectra of (—) 3NCAT and (—) 5M3NCAT in aqueous solution with the corresponding cross sections for (●) 3NCAT and (●) 5M3NCAT in the 220÷500 nm range. Insertion represents the emission spectra in the range of 300÷500 nm of the lamps used for the gas-phase photolysis of nitrocatechols in the ESC-Q-UAIC reactor.

Table TS1: UV-VIS absorption cross section of 3NCAT and 5M3NCAT in aqueous solution in the 350-400 nm spectral range.

Wavelength (nm)	$\sigma_{3NCAT} \times 10^{18}$ ($cm^2 \times molecule^{-1}$)	$\sigma_{5M3NCAT} \times 10^{18}$ ($cm^2 \times molecule^{-1}$)	Wavelength (nm)	$\sigma_{3NCAT} \times 10^{18}$ ($cm^2 \times molecule^{-1}$)	$\sigma_{5M3NCAT} \times 10^{18}$ ($cm^2 \times molecule^{-1}$)
350	2.82	3.16	376	2.54	2.74
351	2.80	3.10	377	2.53	2.74
352	2.78	3.04	378	2.51	2.74
353	2.76	3.00	379	2.50	2.74
354	2.74	2.95	380	2.48	2.74
355	2.73	2.91	381	2.46	2.74
356	2.72	2.88	382	2.45	2.74
357	2.71	2.85	383	2.43	2.74

358	2.70	2.82	384	2.41	2.74
359	2.69	2.80	385	2.38	2.74
360	2.68	2.78	386	2.36	2.73
361	2.67	2.77	387	2.34	2.73
362	2.67	2.75	388	2.32	2.73
363	2.66	2.74	389	2.30	2.72
364	2.66	2.73	390	2.27	2.71
365	2.65	2.73	391	2.25	2.71
366	2.64	2.73	392	2.22	2.70
367	2.63	2.72	393	2.19	2.69
368	2.63	2.72	394	2.16	2.68
369	2.62	2.72	395	2.14	2.66
370	2.61	2.72	396	2.11	2.65
371	2.60	2.73	397	2.08	2.64
372	2.59	2.73	398	2.05	2.62
373	2.58	2.73	399	2.02	2.61
374	2.57	2.73	400	1.99	2.59
375	2.56	2.74			

R1: Have any products from the reaction with OH or of photolysis been observed and identified from their IR spectra?

Answer from authors: The aim of the present study was not focused on performing investigations on the products formation from the OH radical initiated photodegradation and photolysis of nitrocatechols. Further experiments are scheduled to evaluate possible products formed from either photolysis or from reaction with OH radicals. However, preliminary analysis of the residual spectra obtained after irradiation of 3NCAT and 5M3NCAT, presented in Figure S4 in the supplementary material, reveals one signal that could be representative for a ketene-type product. This information cannot be certified for the moment but is in line with previous studies on the photolysis of nitroaromatic compounds (Bejan et al., 2020). Preliminary information for gas-phase product formation the reaction of OH radicals with nitrocatechols recorded from kinetic experiments do not clearly highlight gas-phase oxidation products emerging from 3NCAT or 5M3NCAT infrared residual spectra.

Changes in the manuscript/supplement text:

Added in supplementary material:

In an attempt to preliminary evaluate the gas-phase products formed from the photolysis and from the OH radical initiated gas-phase oxidation of nitrocatechols, the infrared spectra for these reactions were evaluated. No ring-retaining or ring-opening products were identified from the photolysis or photooxidation of the investigated nitrocatechols. However, the residual photolysis product spectra illustrated in **Figure S4** show clear absorption features at 2139 cm^{-1} for 3NCAT and 2135 cm^{-1} for 5M3NCAT. The photolysis mechanism of nitroaromatic compounds leading to the formation of a ketene-type product and HONO elimination has been previously proposed (Bejan et al., 2020), similar to the carboxylic acid formation mechanism in aqueous phase proposed by Alif et al. (1991).

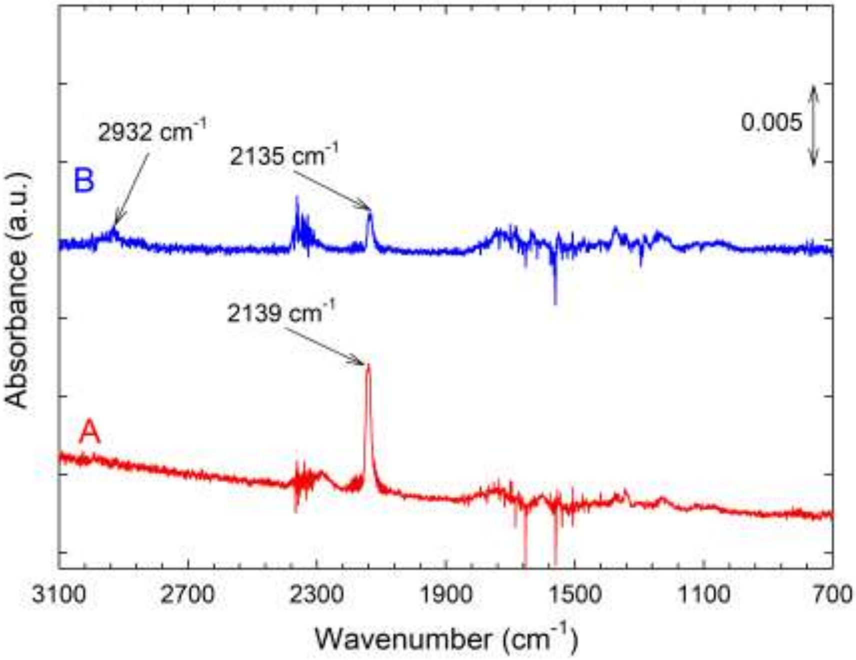

Figure S4: Residual spectra from the gas-phase photolysis of (A) 3NCAT and (B) 5M3NCAT at 365 nm.

R1: Considering fig. 5, additional figures of the gas-phase IR spectra of the nitrophenols of table 3 (and possibly the triols) are desirable to demonstrate if the H bonds show up and obey similar systematics (and if available). Surprisingly, you do not discuss the H bond and its shift to higher wavenumbers in the nitrated catechols, where you might indicate the shifts by arrows from the relevant peaks of 4MCAT via 5M3NCAT to 4M5NCAT and from CAT via 3NCAT to 4NCAT.

Answer from authors: As previously mentioned, there is a recently published article from our group which describes in detail the interactions in the nitrocatechol molecules and how these interactions are identified in the infrared spectrum (Roman et al., 2022). For the present manuscript, Figure 5 was split in two figures corresponding to (A) catechol and nitrocatechols, and (B) 4-methylcatechol and methylated nitrocatechols, where we marked the vibrations corresponding to each ν(OH). However, to support the new results, Figure S5 was included in the SM. Figure S5 show examples of 2-nitrophenols spectra reflecting similar intramolecular interactions as well as spectra from other nitrophenols where the H-bond could not be formed due to the position of the substituents on the aromatic ring as a consequence of the distances between the H-donor and the H-acceptor groups.

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(L193) Figure 5A presents the gas-phase infrared spectra of catechol (CAT), 3NCAT and 4NCAT and Figure 5B the gas-phase infrared spectra of 4-methylcatechol (4MCAT), 5M3NCAT and 4M5NCAT.

Infrared spectra clearly show the presence of the H-bonds between OH (vibrations being marked with * and **) and NO_2 groups substituents attached to the aromatic ring in the nitrocatechols as follows….

(L205) As shown in the spectra from Figure 5A and Figure 5B, the structure…..

Line 233 This bond can be observed also in the IR spectra of 2- nitrophenols (Figure S5 from the SM)….

(L583-587) Figure 5

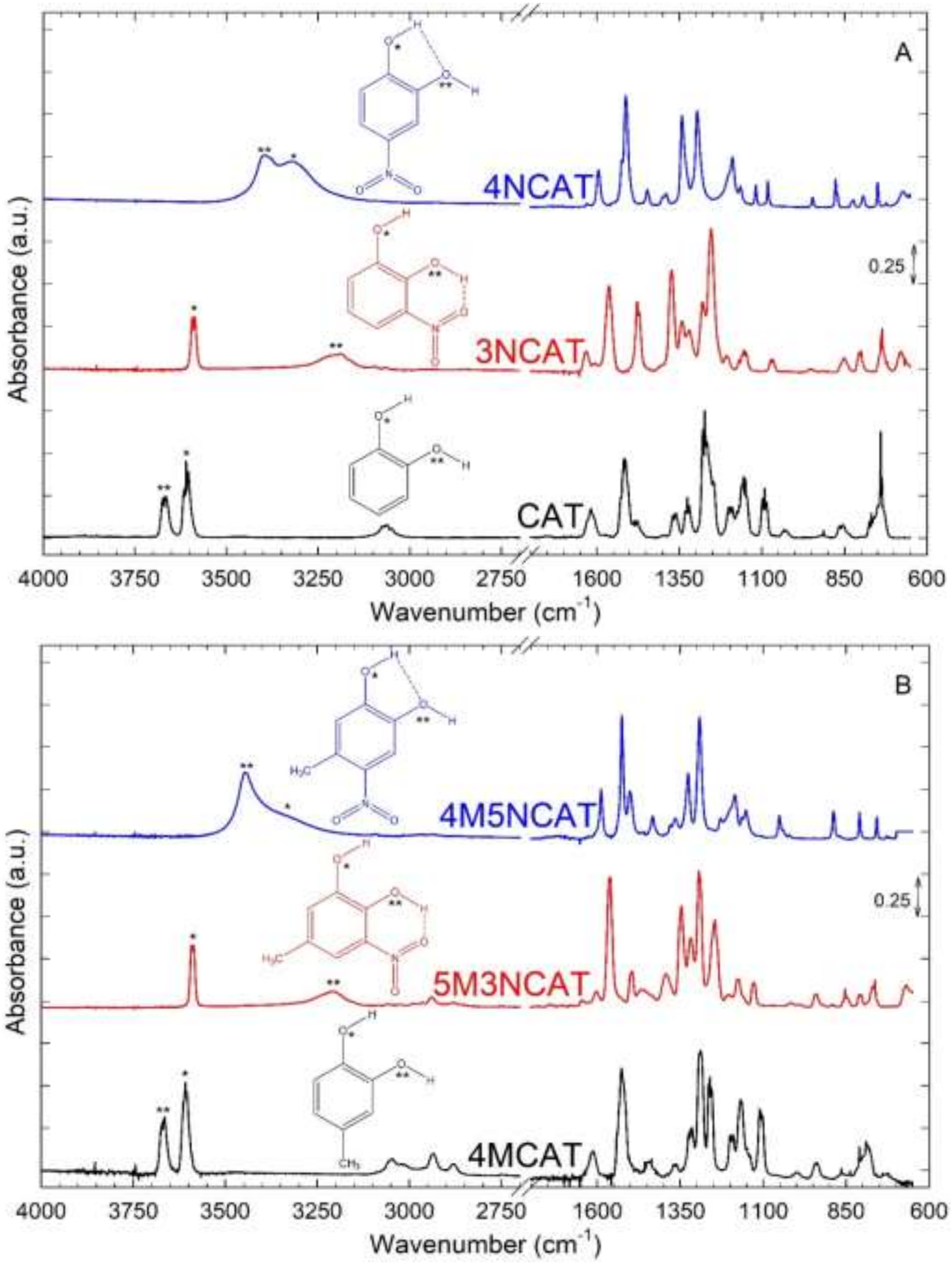

Figure 5: A - Gas-phase IR spectra of catechol (CAT), 3NCAT, 4NCAT;

B- Gas-phase IR spectra of 4-methylcatechol (4MCAT), 5M3NCAT and 4M5NCAT.

Evidence for the intramolecular H-bond occurrence between the substituents marked with */**: catechol and 4MCAT– both free OH present in the spectra; 3NCAT and 5M3NCAT – only one free OH; 4NCAT and 4M5NCAT – both OH involved in H-bond.

Added in supplementary material:

Additionally, the intramolecular H-bond formed between the phenolic H and O-atom from the nitro group can be observed by investigating the gas-phase IR spectra of 2-, 3-, and 4-nitrophenols presented in **Figure S5**. Bejan (2006) has presented similar findings for 2-nitrophenol in comparison with 3- and 4-nitrophenol isomers. Figure S5 adds even more spectral evidence with the main aim to highlight the differences between the OH band position in the gas-phase IR spectra of phenol, 2-methyl-3-nitrophenol and 4-nitrophenol with those from 2-nitrophenols. Spectral shifts up to 350 cm^{-1} were observed between the OH band positions.

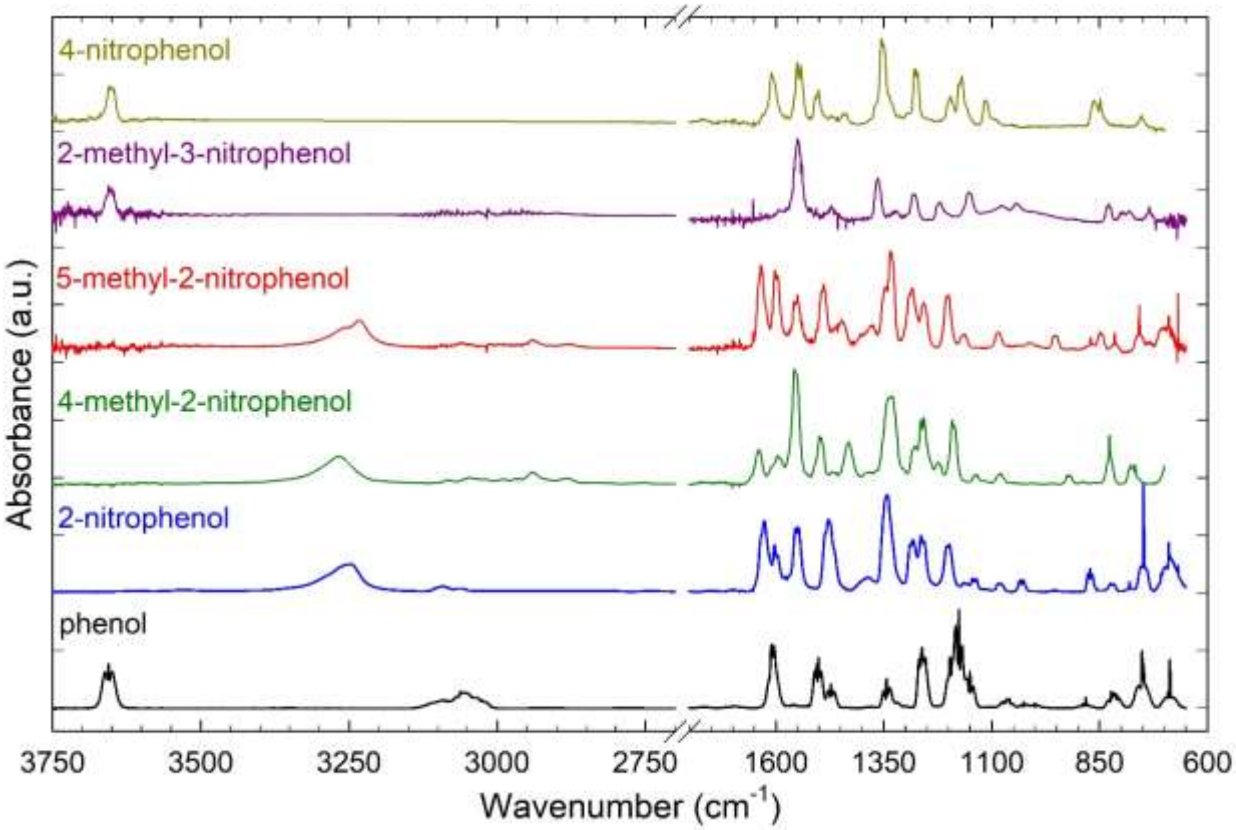

Figure S5: Gas-phase IR spectra of phenol, several 2-nitrophenols, 2-methyl-3-nitrophenol and 4-nitrophenol.

R1: It would be nice to add a table with the wavenumbers (and widths) of the bands assigned to OH and O…H bonds and to discuss these and their shifts, the removal of the doublet and shape in terms of bond strength and loss of symmetry. The position of the OH stretching vibration is also slightly shifted and may be taken as a measure of the bond energy and portion of the abstraction channel. This may add value to the mesomeric/electromeric effects discussed in figure 6. In fact, the description of the addition of OH to monosubstituted monocyclic aromatics by electrophilic addition in the gas phase became accessible in 1980 and 1981 by determining the rate constants for OH + biphenyl, chlorobenzene, benzonitrile and nitrobenzene by research students who enabled us to determine the reaction constant for gas-phase addition of OH. Together with the rate constants for aniline and phenol determined by Rinke and Wahner this led to the regression log (k/cm^3s^{-1}) = -11.7 – 1.41 $\Sigma\sigma^+$ for the available literature data (excluding benzaldehyde, where abstraction was known to predominate) (Zetzsch, 1982, see below). The extension to disubstituted and polysubstituted monocyclic aromatics then included our own data for *o*- and *m*-dichlorobenzene and 1,2,4-trichlorobenzene and various mono- and polysubstituted benzenes from literature and led to the regression log (k/cm^3s^{-1}) = -11.6 – 1.39 $\Sigma\sigma^+$. That regression, updated, adopted and properly cited by Kwok and Atkinson (1995), represented the available data within a factor of two and was enabled by the careful selection of the Hammett constants for electrophilic substitution by Brown and Okamoto (1958) from a large number of kinetic experiments in aqueous solution: Solvolysis of *t*-cumylchlorides, bromination, chlorination and nitration of aromatic derivatives, protonolysis of $ArylSiMe_3$, ionization of $Aryl_2CHOH$) and IR spectra of acetophenones and by the four "rules" in the conference abstract below. Brown and Okamoto pointed out that this database became extremely consistent if their σ^+ values were used rather than the "thermodynamic" σ values from equilibria. It would be most interesting to evaluate the impact of the H bonds on the sum of the Hammett constants for electrophilic addition according to Brown and Okamoto and to propose revised constants for such combinations of lone-pair substituents with the nitro substituent (if such a consideration is reasonable at all). The very impressive last column of Table 3 then deserves a better resolution than only one digit, and you might wish to extend the data in Table 3 and their discussion to polycyclic aromatics, such as nitronaphthalenes, attempting to estimate/predict the OH-reactivity of nitronaphthols.

Answer from authors: As already mentioned in the previous answers, the recently published article (Roman et al., 2022) from our group includes most of the information regarding the spectra characterization. Reviewer's suggestion about the spectral shift of the OH band from nitroaromatics with vicinal hydroxyl-nitro groups is presented there.

According to the reviewer's suggestions, **Table TS2** was additionally included in the SM. The k_{OH} estimated values for selected mononitro-aromatic compounds were taken into account considering the correction proposed in the manuscript at L326-328 (points 1 and 2) by using the SAR method of Kwok and Atkinson (1995). From the present data-base it is quite difficult to release new Hammett constants. However, we are in progress to synthesize additional nitroaromatics, which will be further investigated such as, to be possible to calculate new Hammett constants.

Reviewer's suggestion to improve Table 3 was taken into account and the manuscript was changed accordingly by addition of the last column. Table 3 was completed with information for nitronaphatalenes. For the estimation of the 2-nitro-1-naphthols rate constant, if we consider the average of the 2-nitrophenols $\mathbf{k_{NAHs}/k_{AHs}}$ ratio and the early recommendations for the k_{OH} for phenols and 1-naphthols (McGillen et al., 2020), the rate constant for 2-nitro-1-naphtol would be k(2-nitro-1-naphthol+OH)=3.74×10^{-11} cm^3×s^{-1}. On the other hand, using the updated SAR estimation method from Kwok and Atkinson (1995) with our experimental observations, by re-evaluating the equation for k_{add}, $\log(k_{add}$ / cm^3×s^{-1}) = -10.427 – 1.34 $\Sigma\sigma_i^+$, the k(2-nitro-1-naphthol+OH)=4.67×10^{-12} cm^3×s^{-1} would be obtained. The coefficient of -1.34 for $\Sigma\sigma_i^+$ remains unchanged while the new value for the intercept became -10.427 in steed of -11.71 considering the ratio of the naphthalene and benzene reactivities. These new estimated values are different by a factor of 8 and hence the attempt to correct the Hammett constants without new input data from further experimental support would not conclude to reliable information. Reviewer's suggestion to apply Jenkin et al. (2018) SAR approach is not applicable since the automated mechanism is created for monoaromatic compounds, although would be an interesting consideration for further investigations.

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(L609) Table 3: Rate coefficients at 298 K for aromatic hydrocarbons (AHs) and their correspondent nitroaromatic (NAHs) derivates for the gas-phase reaction with the OH radical.

Aromatic hydrocarbon (AHs)	**k_{OH} [10^{-12} cm^3× s^{-1}]**	**Nitroaromatic hydrocarbon (NAHs)**	**k_{OH} [10^{-12} cm^3× s^{-1}]**	**k_{NAHs}/k_{AHs} (%)**
benzene	1.22[a]	nitrobenzene	0.14[a,b]	11.48
toluene	5.63[a]	*m*-nitrotoluene	1.20[a]	21.31
phenol	26.3[a,d]	2-nitrophenol	0.90[c]	3.42
o-cresol	41[a,d]	6-methyl-2-nitrophenol	2.70[e]	6.59
m-cresol	68[a,d]	3-methyl-2-nitrophenol	3.69[e]	5.43
		5-methyl-2-nitrophenol	6.72[e]	9.88
p-cresol	50[a,c]	4-methyl-2-nitrophenol	3.59[e]	7.18
catechol	104[f]	3-nitrocatechol	3.41[g]	3.28
		4-nitrocatechol	1.27[g]	1.22
4-methylcatechol	156[f]	5-methyl-3-nitrocatechol	5.55[g]	3.56
		4-methyl-5-nitrocatechol	0.92[g]	0.59
naphthalene	23.00[a]	1-nitronaphthalene	5.40[h]	23.48
		2-nitronaphthalene	5.60[h]	24.35

[a]Calvert et al. (2002); [b]Witte et al., (1986), [c]Atkinson et al. (1992); [d]Atkinson (1989); [e]Bejan et al. (2007); [f]Olariu et al. (2000); [g]This work, [h](Atkinson et al., 1989).

Added in supplementary material:

The substituents interactions and their influence in the gas-phase OH-reactivity of nitrocatechols and nitrophenols were extensively discussed in the manuscript. Additionally, **Table TS2** presents the updated values of Kwok and

Atkinson (1995) SAR method with respect to the electrophilic substituents σ_i^+ contribution used in estimation of the kOH addition pathway and considerations given in other investigations (Brown and Okamoto, 1958; Rinke and Zetzsch, 1984; Zetzsch, 1982). In the case of 3-nitrocatechol and 5-methyl-3-nitrocatechol, the value with the most negative $\Sigma\sigma_i^+$ corresponds to *o*- and *p*- positions relative to the NO_2 substituent group. This is attributed to the fact that the OH placed next to the NO_2 could not influence the addition pathway since its shielding prevails. Very good estimated rate values are obtained in using this attempt for 3NCAT, 5M3NCAT and 4M5NCAT. However, for 4NCAT and nitrophenols this updated estimation tends to under evaluate the experimental data. Unfortunately, given the fact that in the catechol structure, the second OH group has no contribution to the addition pathway, the σ^+ for *meta* and/or *ipso* positions being neglected, no relevant new updated values could be now performed for σ^+ for the lone-pair NO_2 substituents.

Table TS2: Rate coefficients for the reaction of nitroaromatic compounds with OH radicals at room temperature calculated from Kwok and Atkinson (1995) SAR updated for the internal effects observed in nitrophenols and nitrocatechols, along with the electrophilic substituents constants proposed by Brown and Okamoto (1958) and Zetzsch (1982).

Compound	**σ_i^+**	**$\Sigma\sigma_i^+$**	**$k_{abs}\times10^{13}$**	**$k\times10^{12}$ ($cm^3 \times s^{-1}$)**
Nitrobenzene	0.674 [m-(NO_2)]	0.674	-	0.244
m-nitrotoluene	-0.311 [p-(CH_3)] 0.79 [p-(NO2)]	0.479	1.36 (CH_3)	0.581
2-nitrophenol	0.674 [m-(NO_2)]	0.674	-	0.244
3-methyl-2-nitrophenol	-0.311 [p-(CH_3)] 0.674 [m-(NO_2)]	0.363	1.36 (CH_3)	0.772
5-methyl-2-nitrophenol	-0.311 [p-(CH_3)] 0.674 [m-(NO_2)]	0.363	1.36 (CH_3)	0.772
4-methyl-2-nitrophenol	-0.311 [p-(CH_3)] 0.79 [p-(NO_2)]	0.479	1.36 (CH_3)	0.581
6-methyl-2-nitrophenol	-0.311 [p-(CH_3)] 0.79 [p-(NO_2)]	0.479	1.36 (CH_3)	0.581
3-nitrocatechol	-0.92 [o-(OH)] 0.79 [p-(NO_2)]	-0.130	1.4 (OH)	3.052
4-nitrocatechol	0.674 [m-(NO_2)]	0.674	1.4 (OH)	0.384
5-methyl-3-nitrocatechol	-0.92 [o-(OH)] -0.311 [p-(CH_3)] 0.79 [p-(NO2)]	-0.441	1.4 (OH) 1.36 (CH_3)	7.878
4-methyl-5-nitrocatechol	-0.311 [p-(CH_3)] 0.674 [m-(NO_2)]	0.363	1.4 (OH) 1.36 (CH_3)	0.912

R1: The SAR predictions of Table 4, adopting the procedures of Jenkin et al., adjusting the parameters to the experimental data, appear to underpredict the phenols and overpredict the catechols (4M5NCAT remains to be an unexplained extreme case). The different success of the SAR methods needs an additional figure to illustrate this limitation on the basis of the constants for electrophilic addition (and/or those of Jenkin et al.). Additional experimental and theoretical work on this topic is highly encouraged.

Answer from authors: In order to answer reviewer's request, an additional Figure was included for the correlations between SAR estimates values according to Jenkin et al. (2018) and Kwok and Atkinson (1995) with $\Sigma\sigma_i^+$ and $\Sigma\sigma_i^+$ calculated for the observed interactions. Also, correlation parameters were determined for the values estimated in the original form and for the re-evaluated form on the base of new experimental data. Additional fitting parameters were determined for the correlation between both SAR methods.

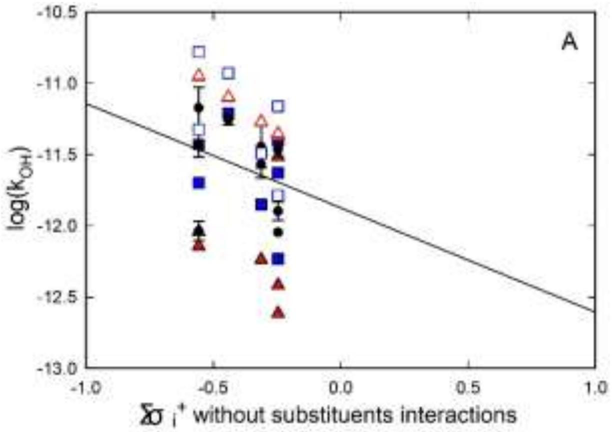
Changes in the manuscript/supplement text:

Changes in the manuscript:

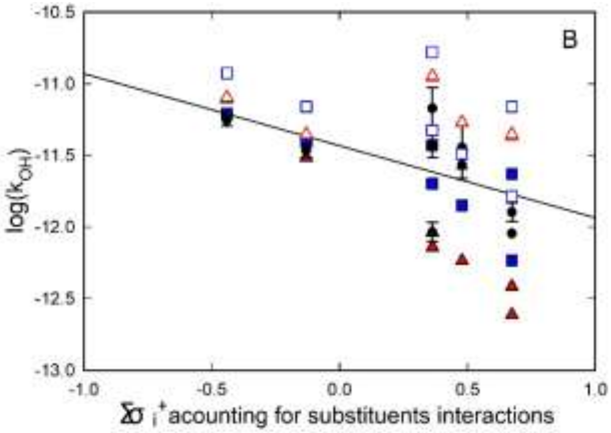
(L339) Table TS2 from the supplementary material presents the revised estimated k_{OH} values for several nitroaromatic compounds using Kwok and Atkinson (1995) SAR model updated with recent observations. Accounting for these experimental observations revisions for SAR model proposed by Jenkin et al. (2018b) were also performed. Figures 8 present the correlation analyses between the experimental, the original estimated and the revised estimated rate coefficients values. Thus, Figure 8A present such correlation *versus* the variation of the $\Sigma\sigma^+$ calculated without substituents interactions, while Figure 8B present this correlation *versus* the variation of the $\Sigma\sigma^+$ calculated when substituents interactions are taken into account. Data presented in both figures show that the main data cluster would be shifted to positive $\Sigma\sigma^+$ when substituent interactions are considered in compliance with experimental values.

Figure 8C reflect the correlations between the estimated and experimental determined rate coefficient values for the interest nitrophenols and nitrocatechols. From Figure 8C it is evident that the estimated revised values show reduce outspread throughout correlation lines. Moreover, the correlation between estimated k_{OH} values derived from using group factors (Jenkin et al. 2018) *versus* estimated k_{OH} values derived using electrophilic substituents (Kwok and Atkinson, 1995) is presented in Figure 8D. From the Figure 8D it is obvious that the original estimates values from both SAR methods present a poor correlation compare with the case when the same estimated k_{OH} values were generated after the revision based on the new obtained experimental data. The corrections introduced to account for the presence and influence of the H-bond to the rate coefficients values are reflected by the improvement in the Pearson coefficient value rising up from r = 0.463 for the original estimates to r = 0.888 for the revised estimates. However, the revised data seems to underestimate the experimental rate constant values for nitrophenols and overestimate those for nitrocatechols. Under these circumstances, it is strongly believed that new experimental values for the rate coefficients of nitroaromatics with OH radicals would further help to better estimate the rate coefficient values for nitroaromatic compounds.

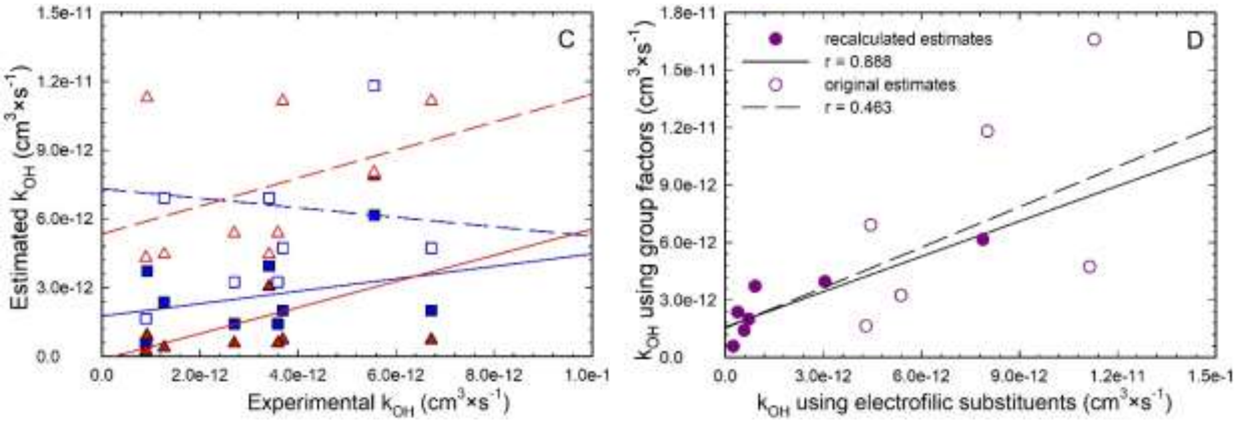
L(599)



Legend 8A: (●) k_{OH} experimental data of nitrophenols and nitrocatechols; (■) revised data of SAR estimates from Jenkin et al. (2018b) (see text); (▲) revised data of SAR estimates from Kwok and Atkinson (1995) (see text); (□) original SAR estimates data from Jenkin et al. (2018b); (△) original SAR estimates data from Kwok and Atkinson (1995);



Legend 8B: (●) k_{OH} experimental data of nitrophenols and nitrocatechols; (■) revised data of SAR estimates from Jenkin et al. (2018b) (see text); (▲) revised data of SAR estimates from Kwok and Atkinson (1995) (see text); (□) original SAR estimates data from Jenkin et al. (2018b); (△) original SAR estimates data from Kwok and Atkinson (1995);



Legend 8C: (■) revised data of SAR estimates from Jenkin et al. (2018b) (see text); (▲) revised data of SAR estimates from Kwok and Atkinson (1995) (see text); (□) original SAR estimates data from Jenkin et al. (2018b); (△) original SAR estimates data from Kwok and Atkinson (1995).

Legend 8D: (●) re-evaluated data; (○) original data.

Figure 8: Correlation analyses between the experimental, the original estimated and the revised estimated rate coefficients values.

Technical corrections, minor questions and suggestions:

R1: I feel that an alphabetical order of the references in the text is more justified than a chronological order. Wherever possible, avoid cumulated references in order to acknowledge the contribution of each reference individually.

Answer from authors: Reviewer's suggestion included in the manuscript.

R1: L. 28: Are there appropriate original papers or reviews available for the topics of wet and dry deposition? The monograph by Peter Warneck: Chemistry of the natural atmosphere might be an additional source of detailed information

Answer from authors: Reviewer's suggestion included in the manuscript.

R1: L. 122: Question: Can the values, observed for k4 for the compounds of this study, be listed somewhere, say table 2? Are the wall-loss constants in the corresponding photolysis experiments similar?

Answer from authors: The wall loss constants are represented as an average value from data recorded prior to photolysis and kinetic experiments. They have been found quite similar and are presented in the text added in the manuscript. Errors represent 2σ from the linear regression analysis.

Changes in the manuscript/supplement text:

Changes in the manuscript:

(L172) ESC-Q-UAIC reactor ($J_{\text{NO2 - atmosphere}}$/ $J_{\text{NO2 – ESC-Q-UAIC chamber}}$ = 8.5×10^{-3} s^{-1} / 4.3×10^{-3} s^{-1} ≈ 2). The wall loss (k_4) measured for 3NCAT and 5M3NCAT was about $(3.2 \pm 0.4) \times 10^{-4}$ s^{-1}, while for 4NCAT and 4M5NCAT of about $(0.7 \pm 0.3) \times 10^{-4}$ s^{-1}. However, the wall loss was relatively constant over different experiments employed in this study. The wall loss rate constant values are consistent with our previous determinations (Roman et al., 2022).

R1: L. 144: Question: Have the retaining (or ring opening) products been identified and can you estimate their yields from IR spectra?

Answer from authors: Unfortunately, we could not identify relevant products formation from photolytic experiments and from OH radical initiated photodegradation of nitrocatechols. However, photolysis seems to rise up a band at 2130-2140 cm^{-1} in the IR spectra which could be assumed to correspond most probably to a ketene type compound. Further studies will be conducted to identify gas-phase products from the OH radical initiated oxidation of these compounds. Figure S4 from the supplementary material highlight these preliminary findings.

R1: Suggestion: The extremely valuable discussion on the potential impact of hydrogen bonds could be extended to other nitro-compounds observed as atmospheric reaction products in polluted and even more so remote regions and to pesticides and herbicides such as pendimethalin, DNOC and metabolites. L. 309: The authors should contact the US EPA or the authors of AOPWIN (Philip Howard, Syracuse, NY) about a possible serious error of the AOPWIN software package.

Answer from authors: In the supplementary material we briefly discuss some relevant examples of nitrophenols. We thank the reviewer for the suggestion and we shall proceed accordingly in the near future.

R1: L. 274-278: (suggestion) => …OH radicals, the Hammett constants for electrophilic addition, σ+, given by Brown and Okamoto (1958) have been proposed by Zetzsch (1982) and updated by Kwok and Atkinson (1995) to fit to the equation

log (kadd /cm3s-1) = -11.71 – 1.34 $\sum \sigma^+$,

where the most negative value of the sum $\sum \sigma^+$ has to be considered alone and any interaction among the substituents is neglected.

Answer from authors: Reviewer suggestion was assimilated in the manuscript. Similar approach has been discussed in a previous answer.

R1: L. 587: One might draw the attention to the weak, broadened band at 3100 wavenumbers (CAT and MCAT) from the H bond between the OH groups that increases with the influence of the nitro group and improve the figure by separating it into the two components for 4NCAT and 4M5CAT. This is required for precise determination of the band positions. It would be convenient to repeat the rate constants (or the ratios) of Table 3 in the spectra and beneath the structure in Figure 7 B.

Answer from authors: We thank both reviewers for this helpful suggestion. Figure 5 presenting IR spectra of the investigated compounds is now divided into distinct groups, in compliance with reviewers suggestion. Also, in the Figure 7B the OH-rate constants were placed inside the figure box.

Changes in the manuscript/supplement text:

Changes in the manuscript:

(L593)

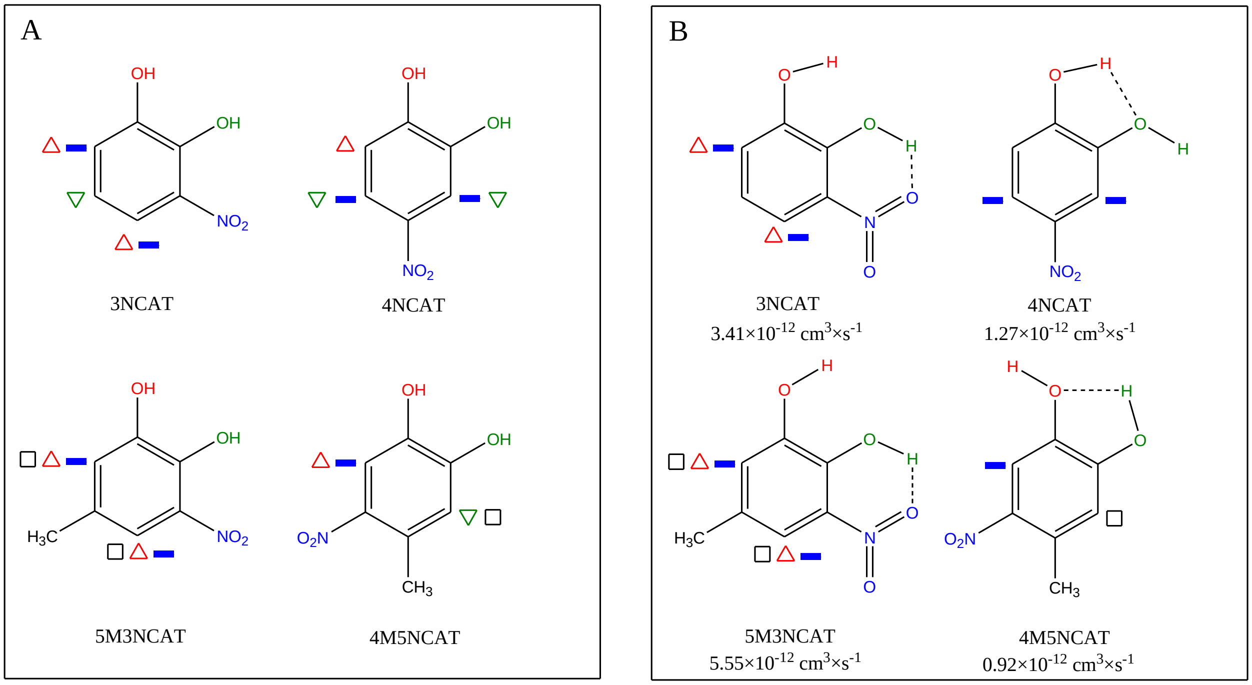


Figure 7: Electromeric effect distribution on the aromatic ring for the all investigating nitrocatechols in the present study: (A) active sites toward electrophilic attack by hydroxyl (1st OH△ / 2nd OH ▽), nitro (▬) and methyl (□)

groups; (B) internal interactions of the substituents and consequences on the reactivity based on the gas phase FT-IR spectra.

R1: L. 12: …technique => techniques

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 13: …followed => follows

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 14: results the => results, the

Answer from authors: Reviewer suggestion was assimilated in the manuscript to line 17.

R1: L. 15-16: => …scaled to atmospheric relevant conditions by NO2 photolysis, were evaluated for 3-nitrocatechol and 5-methyl-3-nitrocatechol:

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 17: results our => results, our

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 21: aromatic hydrocarbons. Additional… => aromatic hydrocarbons and discussed with gas-phase IR spectra of the nitrocatechols. Additional…

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 26: car engines emissions => car-engine emissions

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 34: => methoxy-phenols, and

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 34-35, 54-55, 56-57, 132, 205, 219-220, 254-255, 283-284: I feel that an alphabetical order of the references in the text is more justified than a chronological order. Wherever possible, avoid cumulated references in order to acknowledge the contribution of each reference individually.

Answer from authors: For L34-35, 54-55, 56-57, 132, 205, 254-255, 283-284 authors managed to comply to the reference suggestions, by splitting, where possible, the references, in order to acknowledge the contribution individually. In L 219-220 we eliminate references and let them only on the footnote of table 3. References have been arranged in alphabetical order, as ACP Journal recommendations.

R1: L. 36 (instead of L. 40): 3.3.1 (Bloss et al., 2005)

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 40, 41: move “in the case of benzene and toluene” to the end of the sentence

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 43: => mixture, and

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 55: => aerosol

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 60: => concentration can be as high as 820…

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 64: => by OH radicals..

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 65: => products, occurrence

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 76: => made of Quartz…at the

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 90: => their

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 91: => and well-known rate coefficients for the reaction with OH radicals…

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 96: => nm, as shown in….., where..

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 99: Question: => H2C=O (formaldehyde), or do you want to indicate the isomerization of CH3O to CH2OH as an intermediate?

Answer from authors: It is a simple mechanism to suggest formation, and presence in the reactor vessel, of formaldehyde from R1.2 reaction.

R1: L. 115: => *t,*

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 121: => …has been…..OH-radical scavenger …(a series of three nouns with hyphen)

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 129-130: => NO: > 99.5%....CO (99.997%

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 142: => was evaluated to range from about..

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 143: => Up to 30% of the decays of the….and the…

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 145: => Table 1 presents the…

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 156: => nitrocatechols by

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 158: cut off => override

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 161-163: => was observed, while…….frequencies…, have been measured.

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 170: has => have

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 178: The number of 0.1 requires information about the aerosol density obtained in your experiments?

Answer from authors: The reviewer is right and we updated the discussions in the manuscript considering these suggestion. Therefore, using the following equations derived from the standard gas kinetic theory, knowing (i) the total surface and volume of aerosols as presented in an earlier study (Roman et al., 2022) referring to similar experimental conditions as those employed in the present manuscript, (ii) the gas-phase OH-rate constants and (iii) the concentrations of nitrocatechols in the reactor, an upper limit for the OH radicals deactivation rate for each investigated nitrocatechols was calculated.

$$\frac{R_{coll}}{(R_{coll} + R_{reactant})} = \frac{\bar{v} \times A}{(\bar{v} \times A + 16k_1 \times [reactant])}$$

where, R_{coll} (in cm^{-3}×s^{-1}) is the gas kinetic rate at which OH radicals collide within the cross section of a spherical particle, $R_{reactant}$ (in cm^{-3}×s^{-1}) represents the gas kinetic rate at which OH radicals react with the investigated reactant in concentration $[reactant]$ (in cm^{-3}) at a rate coefficient k_1, $\bar{v}$ is the average velocity (in cm×s^{-1}) of the OH radicals colliding an surface at a given temperature calculated from the standard gas kinetic theory, $\bar{v} = \left(^{8RT}/_{\pi M}\right)^{1/2}$ and A is the aerosol surface area per unit air volume (in cm^{-1}). At 298 K the average velocity of OH radicals is 6.09×10^4 cm×s^{-1} (Sørensen et al, 2002). The table bellow presents the experimental conditions for the kinetic rate coefficient determinations. Assuming 100% efficiency for collision of the OH radical with particles followed by deactivating the OH, the ratios of collisions would vary between 0.04% and 0.22%, for 5-methyl-3-nitrocatechol and 3-nitrocatechol gas-phase systems. For the systems involving 4-nitrocatechol and 4-methyl-5-nitrocatechols, the aerosols being much more abundant as presented in Roman et al., (2022), the OH-deactivation by aerosol collisions could contribute up to 21% from the overall OH production rate. However, the radical concentration would be high enough to ensure reaction over the time-period of the kinetic experiments. Additionally, the radical concentration would not affect the relative kinetic technique used for the investigations of the gas-phase reaction rate coefficients of nitrocatechols with OH radicals, since the ratio of k_1/k_2 is equally influenced by experimental conditions.

Compound	**A** **(10^{-5} cm^{-1})**	$[reactant]$ **(10^{12} cm^{-3})**	k_1 **(10^{-12} cm^3×s^{-1})**	$\frac{R_{coll}}{(R_{coll}+R_{reactant})}$ **(%)**
3NCAT	7.60	38.00	3.41	0.22
4NCAT	55.60	23.20	1.27	6.70
5M3NCAT	2.15	37.80	5.55	0.04
4M5NCAT	47.50	7.69	0.92	20.35

Changes in the manuscript/supplement text:

Changes in the manuscript:

(L 176) Based on collision theory …… does not influence the value of the OH radicals rate coefficients when relative kinetic technique is used. Deactivation rate of the OH radicals due to the presence of aerosols in the reaction chamber was estimated by considering an OH radicals average velocity of about 6.09 × 10^4 cm × s^{-1} at 298 K (Atkins and de Paula, 2006) and the experimental conditions employed in this study, relative to the particles area per air unit volume initially formed into the system (Roman et al., 2022). Under these conditions, the contribution of the deactivation process is less than 1% for 3-nitrocatechol and 5-methyl-3-nitrocatechols and between 7-21% for 4-nitrocatechol and 4-methyl-5-nitrocatechol. However, even if such process occurs at higher rate, using of the relative kinetic technique, where the k_1/k_2 ratio is experimentally determined independent of the OH radical concentration of, no systematic errors rising up from the OH radical concentration would influence the kinetic data. On the other hand, possible……

R1: L. 182: => ,this

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 184: => coefficient

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 186: You mention nitronaphthalene, so naphthalene and nitronaphthalene might be added to table 3

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 187: => nitroaromatic

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 188: Please specify. What do you mean with “same order of magnitude”, a similar deactivating effect of the nitro group?

Answer from authors: The same order of magnitude refers to the comparison of rate coefficient values. In the text we try to explain that the rate coefficient values for the reaction of nitrocatechols with OH radicals obtained in this work are in the same order of magnitude of 10^{-12} $cm^3 \times s^{-1}$, as most of the nitroaromatic compounds, since the NO_2 E+ effect is decreasing the reactivity.

R1: L. 190: => results, we

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 196 => and the O atom

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 203: => …by the electron withdrawing effect of NO2, and in consequence, the weakened O-H bond results in an H atom that is more…

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 206: => Figure 5, the structures of CAT and 4MCAT..

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 210: => For the 3NCAT structure, one…

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 212: => , photolysis..

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L 217-218: => ring, as the reactivity…is approximately 5-20 times lower than that of their parent compounds.

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 219 => their

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 225-227: => Gas-phase reactions….lead to…. In the gas-phase oxidation of..

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 234: => its

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 237: => from the.. According to Figure A, the …

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 250: cancel "compound"

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 252-253: groups and considering….., the rate coefficient

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 256: => , the difference

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 262: => , we

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L 264: => nitrocatechols, the

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 281: …substituents, another..

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 285: => , a rate coefficient that is..

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 289: AOPEWIN => AOPWIN

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 291: => nitrobenzenes

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 294: fits => fit

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 299: = considered

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 300: => ·+ for the OH oriented in…..molecules,

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 305: => , this

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 306: => , no

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 309, 311: => · ·+

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 316: => groups

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 317: => , the SAR estimations assign the NO2 group substituent factors of Brown and Okamoto (1958) of ….

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 321: differences => different ratios of ….. 5M3NCAT, the

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 322: => consistent

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 323: => SAR models

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 326: => substituent

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 330: => proposed

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 334: => based on the study by Jenkin et al. …..to use a value of 0.5 as new parameter…for the deactivated

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 336: => In this case, the

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 337: => ..importance and will

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 339=> ..nitroaromatic……in order to evaluate all…

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 344: => sink, being

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 347: undertake => undergo

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 350: initiated by OH radicals.

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 354: of intramolecular

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 355: E-effect of the NO2 group.

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 559, 568, 573, 589: => reference (figs. 1 -4)

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 563: => radical

Answer from authors: Reviewer suggestion was assimilated in the manuscript. Changed for all figures (1-4) radicals source => radical source.

R1: L. 607: hour => h

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: L. 614: => and SAR-estimated cate coefficients….with OH radicals.

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R1: References:

Add subscripts where required (L. 397, 404, 405, 475, 516, 538), add missing DOIs

Complete the references Bejan, I.G. (2006/7) (PhD thesis?) and Prinn et al.

Remove capitals in the title of Finewax et al. (journal name ?), same in L. 487, 488, 493, 494,

Finlayson-Pitts and Pitts: remove abbreviated title of monograph

Harrison et al.: correct initials of Olariu

Typos in names: Henry's, Simoneit, Dibb

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

B. Comments by Referee #2

R2: Which OH concentrations are typically reached in the chamber?

Answer from authors: The OH radical concentration used in the kinetic investigations is dependent to the OH radical precursor concentration. For the photolysis of CH_3ONO/NO mixture with lamps emitting light at 365 nm, the OH radical concentration reached in the ESC-Q-UAIC reactor is around (7 - 8) × 10^7 cm^{-3}. For the photolysis of H_2O_2 with lamps emitting light at 254 a higher OH concentration of (1 – 2) × 10^8 cm^{-3} is achieved.

R2: L122: How large are wall losses compared to photolysis?

Answer from authors: For 4NCAT the wall loss and photolysis contribute approximately equal to the total loss into the chamber, while for all others nitro compounds the wall loss dominates over the photolysis. The wall loss (k_4) has been measured for 3NCAT and 5M3NCAT in the range of (3.2 ± 0.4) × 10^{-4} s^{-1} and for 4NCAT and 4M5NCAT in the range of (0.7 ± 0.3) × 10^{-4} s^{-1} and has been found relatively constant over different experiments employed in this study. The text has been amended with the wall loss values as mentioned in a previous answer.

R2: L143: Can you be more specific? How large is the fraction which reacts with OH and how large are the contributions of dilution and wall loss compared to that? Could you add figures for the photolysis experiments? Did you perform any additional product measurements?

Answer from authors: There is no dilution associated with our experiments. In the following table are the wall deposition, photolysis and OH radical kinetic percentage for kinetic experiments of nitrocatechols occurring in the reactor. Values were averaged from individual kinetic and photolysis experiments.

Compound	WL (%)	Photo (%)	OH Kinetics (%)
3NCAT	45.74 ± 1.02	20.77 ± 2.17 (365 nm)	33.50 ± 3.63

4NCAT	21.28 ± 0.73	19.01 ± 3.35 (254 nm)	59.72 ± 8.93
5M3NCAT	38.39 ± 1.48	12.96 ± 2.18 (365 nm)	48.65 ± 4.21
4M5NCAT	27.22 ± 0.86	12.62 ± 2.52 (254 nm)	60.16 ± 9.15

Photolysis plots were included in the supplementary material. Moreover, the authors amended the text such as to include the reviewer's suggestion. In an attempt to preliminary evaluate the gas-phase products formed from the photolysis and from the OH radical initiated gas-phase reaction of nitrocatechols, the infrared residual spectra for these reactions were investigated. No ring-retaining or ring-opening products were identified from the photolysis or photooxidation of the investigated nitrocatechols. However, the residual photolysis product spectra illustrated in **Figure S4** show clear absorption features at 2139 cm^{-1} for 3NCAT and 2135 cm^{-1} for 5M3NCAT.

Minor and technical comments:

R2: Sometimes you write HO instead of OH (e.g., L.46., L100). Please check throughout the manuscript for consistency.

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R2: L53: Nitroaromatic compounds (NAHs) -> I would call it ''Nitroaromatic hydrocarbon (NAH) compounds''

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

L71: is of great concern of interest -> is of great interest

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R2: L116: Please give a reference for the k2 values that you used for the three reference compounds.

Answer from authors: The k2 values for the reference used in the kinetic investigations were given in L91-93 along with explicit literature citations.

R2: L126, L182, L254, L263: Why is the division sign used here? It is not common everywhere to use it to give a range of value. Maybe you can use an alternative.

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

L184: coefficient

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

R2: Fig. 7, panel A: please specify in the description, why you use the two different symbols for the OH attack sites

Answer from authors: We used two different symbols for the OH substituents in order to show clearly the orientation towards possible electrophilic substitutions due to the positive electromeric effects of the hydroxyl groups. Both, different colors and symbols, respectively, (for material printed in black and white) are used to distinguish the active sites.

Changes in the manuscript/supplement text:

Changes in the manuscript:

Figure 7: Electromeric effect distribution on the aromatic ring for the all investigated nitrocatechols in the present study:(A) active sites toward electrophilic attack by hydroxyl (1st OH△ / 2nd OH ▽), nitro (▬) and methyl (☐) groups; (B) internal interactions of the substituents and consequences on the reactivity based on the gas phase FT-IR spectra.

R2: Fig. 7, panel B is not referenced in the text. Where exactly do you want to use it?

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

Changes in the manuscript/supplement text:

Changes in the manuscript:

(L239-240) …..compound in this series, because of the substituent's interactions (see Figure 7 B).

R2: Check references for the use of subscript (e.g., NO_2, NO_3)

Answer from authors: Reviewer suggestion was assimilated in the manuscript.

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