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

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Abstract. The Environmental Simulation Chamber made of Quartz from the University "Alexandru Ioan Cuza" from Iasi (ESC-Q-UAIC), Romania, was used to investigate for the first time the gas-phase reaction rate coefficients for four nitrocatechols towards OH radicals under simulated atmospheric conditions. Employing relative rate technique at a temperature of 298 ± 2 K and total air pressure of 1 atm, the obtained rate coefficients (in 10^{-12} $cm^3 \times s^{-1}$) were as followed: $k_{3NCAT} = (3.41 \pm 0.37)$ for 3-nitrocatechol, $k_{4NCAT} = (1.27 \pm 0.19)$ for 4-nitrocatechol, $k_{5M3NCAT} = (5.55 \pm 0.45)$ for 5-methyl-3-nitrocatechol and $k_{4M5NCAT} = (0.92 \pm 0.14)$ for 4-methyl-5-nitrocatechol. For the investigated compounds the photolysis rates in the actinic region, scaled to atmospheric relevant conditions, were evaluated as well. In this case the photolysis rate coefficient values were obtained only for 3-nitrocatechol and 5-methyl-3-nitrocatechol: $J_{3NCAT} = (3.06 \pm 0.16) \times 10^{-4}$ s^{-1} and $J_{5M3NCAT} = (2.14 \pm 0.18) \times 10^{-4}$ s^{-1}, respectively. 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. Results are discussed in terms of the reactivity of the investigated four nitrocatechols towards OH-radical initiated oxidation and their structural features. The rate coefficient values are also compared with those estimated from the structure-activity relationship for monocyclic aromatic hydrocarbons. Additional comparison with similar compounds is also presented underlining the implications towards possible degradation pathways and atmospheric behavior.

1. Introduction

Aromatic hydrocarbons (AHs) are a class of volatile organic compounds (VOCs) present as primary pollutants in the atmosphere mainly because of the anthropogenic activities. In urban areas, AHs are present due to the use of solvents, incomplete combustion of fossil fuels, car engines emissions and industrial processes (Piccot et al., 1992). Various monocyclic aromatics occur from biomass burning in rural and remote areas (Schauer et al., 2001). Atmospheric removal of these compounds occurs via reactions with different oxidants (Finlayson-Pitts and Pitts, 2000) and by wet and dry deposition (Calvert et al., 2002). The gas-phase oxidation initiated by the OH radicals is the main reaction responsible for the atmospheric sink of aromatic hydrocarbons. The chemical degradation of AHs forms oxidation products which further could be aromatic in nature or could lead to open ring compounds. AHs are known also as important contributors to the photo-oxidants and secondary organic aerosols (SOA) formation in the atmosphere (Calvert et al., 2002; Jenkin et al., 2017).

Hydroxylated aromatic compounds, such as phenols, cresols, dimethyl-phenols, trimethyl-phenols, methoxy-phenols and catechols are the most reactive species towards OH radicals (Atkinson et al., 1992; Bejan et al., 2012; Berndt and Böge, 2003; Coeur-Tourneur et al., 2006; Lauraguais et al., 2015; Olariu et al., 2000; Sørensen et al., 2002; Thüner et al., 2004). According to Master Chemical Mechanism (MCM), version 3.3.1, which describes the detailed gas-phase chemical processes involved in the tropospheric degradation of a series of primary emitted VOCs, the major oxidation pathway for monocyclic aromatic compounds is the addition of the OH radical to the aromatic ring that may lead to the ring retaining products. The distribution of the hydroxylated isomers varies for each monocyclic aromatic compound depending on the stability of its OH-adduct (Bloss et al., 2005). Thus, the OH-addition reactivity channel in the case of benzene and toluene will lead to the formation of phenol and cresols with a range of yields from 5 to 50%. These formation yields are very much affected by the levels of NO_x ($NO_x = NO + NO_2$) in the reaction mixture and the formation yields of the mono-hydroxylated aromatic compounds is decreasing in the presence of high NO_x concentration (Atkinson and Aschmann, 1994; Klotz et al., 1998, 2002; Volkamer et al., 2002). The hydroxylated products, when photo-oxidized by the OH radicals under atmospheric conditions, in turn form catechols with formation yields of about 65 to 90% (Olariu et al. 2002). Formation of nitrophenols and nitrocatechols from the oxidation of phenols and catechols initiated by the HO radicals is assigned to the H-atom abstraction pathway from the phenolic hydroxyl group, accounting for about 10% in the mono-hydroxylated aromatic compounds and for about 30% in the di-hydroxylated aromatic compounds (Atkinson et al., 1992; Finewax et al., 2018; Olariu et al., 2002). High formation yields of nitrophenols (more than 50%) and nitrocatechols (close to 100%) were reported from the gas-phase reactions of the NO_3 radical with the phenols and catechols, which may support the fact that the NO_3 chemistry may have an important role in the formation of such nitroaromatic compounds (Finewax et al., 2018; Olariu et al., 2004, 2013).

Nitroaromatic compounds (NAHs) have been found in rainwater, clouds, water, soil and fog (Belloli et al., 2006; Delhomme et al., 2010; Grosjean, 1991; Harrison et al., 2005; Herterich, 1991; Herterich and Herrmann, 1990; Leuenberger et al., 1988; Richartz et al., 1990; Rubio et al., 2012) and even in remote areas as in Terra Nova Bay, Antarctica (Vanni et al., 2001). More recently, nitroaromatics have been reported in aerosols composition from urban area (Ikemori et al., 2019; Lanzafame et al., 2021; Vidović et al., 2018; Wang et al., 2021). Nitrocatechols have been found as tracer compounds in particulate matter emitted during biomass burning, correlating well with the levoglucosan and NOx levels (Kitanovski et al., 2012b, 2012a; Salvador et al., 2021). In organic aerosols the 4-nitrocatechol concentration exceeds in some cases 150 ng × m^{-3} while for methylated nitrocatechols the overall concentration is as high as 821 ng × m^{-3} (Iinuma et al., 2010; Kitanovski et al., 2020). These high concentrations of nitrated monoaromatic hydrocarbons were determined in the winter season and have been correlated with household wood burning use. However, in these studies, all identified nitrocatechols seem to cover up to 96% of the nitrated monoaromatic hydrocarbons found in PM10 samples (Kitanovski et al., 2020). 4-nitrocatechol was

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found in the reaction of guaiacol initiated by the OH radicals in the presence of NO_x (Lauraguais et al., 2014). Besides 4-nitro-, 3-nitro- and 6-nitroguaiacol formed as oxidation products occurrence of 4-nitrocatechol was explained via the -*ipso* addition channel of OH radical to the methoxy group. Schwantes et al. (2017) report the formation of highly oxygenated low-volatile products from the chamber studies of *o*-cresol oxidation under high NO_x conditions. The signal with m/z = 169 detected by mass spectrometric techniques has been attributed to methyl-dihydroxy-nitrobenzene. Finewax et al. (2018) have reported 4-nitrocatechol in secondary organic aerosol (SOA) composition from the gas-phase oxidation of catechol initiated by both OH (30%) and NO_3 (91%) radicals, respectively. Atmospheric production of nitroaromatic compounds, including nitrophenols, dinitrophenols and nitrocatechols, is of great concern of interest as they play a significant role in the formation of brown carbon and aerosols (Lin et al., 2016). Their low atmospheric reactivity and high ability to absorb large amounts of near-UV, visible and infrared radiation could lead to positive radiative forcing (Bejan et al., 2007; Zhang et al., 2017).

The present study aims to determine and discuss, for the first time upon our knowledge, the OH kinetic rate coefficients for four nitrocatechols: 3-nitrocatechol (3NCAT), 4-nitrocatechol (4-NCAT), 5-methyl-3-nitrocatechol (5M3NCAT) and 4-methyl-5-nitrocatechol (4M5NCAT) by using the Environmental Simulation Chamber made by Quartz from University “Alexandru Ioan Cuza” from Iasi, Romania (ESC-Q-UAIC). Based on the ESC-Q-UAIC facilities, the photolysis frequencies of the investigated compounds were evaluated and scaled to the relevant atmospheric conditions. Detailed investigations with impact on the reactivity of highly substituted nitro-aromatic compounds are also depicted in this work.

2. Experimental

Gas phase rate coefficients of the studied nitrocatechols towards OH radicals have been determined using the relative kinetic method. For this purpose, the ESC-Q-UAIC reactor, a 760 L and 4.2 m long cylindrical photoreactor consisting of three quartz tubes surrounded by 32 Philips TL-DK 36W (with λ_{max}= 365 nm) and 32 UV-C TUV 30W/G30 T8 (with λ_{max}= 254 nm), has been employed. Experiments were performed at 1 atm of air and temperature of 298 ± 2 K. Decay of the nitrocatechols and reference compounds in the reactor vessel was monitored by IR spectroscopy using a Bruker Vertex 80 FTIR coupled to a White type mirrors system mounted inside the chamber, providing a total optical path of 492±1 m. Solid nitrocatechols were transferred into the reactor at low pressure, via a preheated glassware port. A steam of nitrogen flowing over the heated nitroaromatic compound was used to carry the reactants and reference compounds inside the reaction chamber. Two Teflon blade fans were used to ensure homogeneous mixture. Dimethyl ether (C_2H_6O), cyclohexane (C_6H_{12}) and methanol (CH_3OH) were chosen as reference compounds in the relative kinetic study due to theirs IR spectral features and rate coefficients values towards OH radicals close to those of the investigated compounds: $k_{C2H6O} = (2.80 \pm 0.56) \times 10^{-12}$ $cm^3 \times s^{-1}$ (Atkinson et al., 2004), $k_{C6H12} = (6.38 \pm 0.56) \times 10^{-12}$ $cm^3 \times s^{-1}$ (Wilson et al., 2006) and $k_{CH3OH} = (0.90 \pm 0.18) \times 10^{-12}$ $cm^3 \times s^{-1}$ (Atkinson et al., 2004). Dimethyl ether (DME) was used as reference hydrocarbon for all the investigated nitrocatechols while cyclohexane was used for the kinetic studies involving 3-nitrocatechol and 5-methyl-3-nitrocatechol. Methanol was employed for the kinetic experiments of 4-nitrocatechol and 4-methyl-5-nitrocatechol. The OH radicals were

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generated *in situ*: (1) via photolysis of a mixture of CH_3ONO/NO at 365 nm as showed in R1.1 to R1.4 reactions, when NO has been added in excess to suppress ozone formation and potential interference processes in the reaction kinetics:

$CH_3ONO + h\nu\,(365nm) \rightarrow CH_3O\cdot + NO$ (R1.1)

$CH_3O\cdot + O_2 \rightarrow HCOH + HO_2$ (R1.2)

$HO_2\cdot + NO \rightarrow HO\cdot + NO_2$ (R1.3)

$O_3 + NO \rightarrow NO_2 + O_2$ (R.1.4)

and (2) via photolysis of H_2O_2 at 254 nm for 4-nitrocatechol and 4-methyl-5-nitrocatechol as presented in R2.1 reaction

$H_2O_2 + h\nu\,(254\ nm) \rightarrow 2\ HO$ (R2.1)

Preliminary tests showed that nitrocatechols photo-dissociate under experimental conditions. Corrections to reactants' concentration are needed to be made due to the photolysis and wall deposition, as presented in the following reactions sequence:

reactant + OH → products (k_1)

referent + OH → products (k_2)

reactant + $h\nu$ (365/254 nm) → products (k_3) (J)

reactant → wall (k_4)

By representing the total decay of both reference and reactant in time, with respect to the correction mentioned above, the following kinetic expression shown in Eq. 1 could be used to determine the nitroaromatic rate coefficients:

$$\ln\frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t} - (k_3 + k_4)(t - t_0) = \frac{k_1}{k_2}\ln\frac{[\text{referent}]_{t_0}}{[\text{referent}]_t} \qquad (\text{Eq. 1})$$

where $[\text{reactant}]_{t_0}$ and $[\text{referent}]_{t_0}$ are the initial concentrations of nitrocatechols and the reference compound at t_o, and $[\text{reactant}]_t$ and $[\text{referent}]_t$ are the concentrations of nitrocatechols and the reference compounds during the reaction time "t", k_1, k_2 are the gas phase rate coefficients for the OH radical reactions with the reactants and reference compounds respectively, k_3 is the photolysis frequency (J) of the reactants at 365/254 nm and k_4 is the wall loss rate coefficient. The ratio of k_1/k_2 determined from the slope of the linear regression is used further to obtain the rate coefficient k_1 by using well determined k_2 rate coefficients of the reference compounds. No wall loss or photolysis was observed for the reference hydrocarbons used in this study.

However, the photolysis of nitrocatechols at 254 and 365 nm have been measured using CO as OH radical scavenger. Photolysis rate coefficients are corrected for wall loss and used to correct further rate coefficients from the reactions of nitrocatechols with OH radicals.

Initial concentrations of reactants in the reactor were: 6.5×10^{13} cm^{-3} for DME, 4.8×10^{13} cm^{-3} for cyclohexane, 12.5×10^{13} cm^{-3} for methanol, 12.9×10^{13} cm^{-3} for NO, 16.2×10^{13} cm^{-3} for CH_3ONO, a maximum of 25.2×10^{13} cm^{-3} for H_2O_2. For the investigated nitrocatechols their initial concentration varied between $(2.5 \div 7.7) \times 10^{13}$ cm^{-3}.

3. Chemicals

Chemical compounds used in the present study were: DME >99.9% (suitable for GC analysis, Sigma-Aldrich), cyclohexane >99.5% (anhydrous, Sigma-Aldrich), methanol (anhydrous, >99.9% suitable for HPLC analysis, Sigma-Aldrich), NO (2.5 purity, Linde), H_2O_2 (40% solution in water, Sigma-Aldrich), CO (4.7 purity, Linde). CH_3ONO was prepared in our laboratory using an adapted method from Taylor et al. (1980). All nitrocatechols have been synthesized using two methods of nitration according to available literature information (Iinuma et al., 2010; Palumbo et al., 2002; Rosenblatt et al., 1953). Thus, both 3-nitrocatechols have been obtained by treating an anhydrous diethyl ether solution of the corresponding catechols with freshly prepared fuming nitric acid. 4-nitrocatechol and 4-methyl-5-nitrocatechols were prepared by treating a cooled aqueous solution of catechol and sodium nitrite with sulfuric acid. Extractions and purifications of the synthesized compounds were conducted by means of sublimation and recrystallization. The purity of the synthesized compounds from H-NMR analysis was found to be about 98%.

4. Results

Kinetic results for the reaction of nitrocatechols with OH radicals are presented in Figures 1 to 4. For each compound, a minimum of four experiments have been performed. Despite difficulties in handling these low volatile compounds, their slow reactivity towards OH radicals, and the difficulties encountered in the IR spectra evaluation, the plots depicted in Figures 1 to 4 show good linearity. Total conversion of nitrocatechols during the irradiation period was evaluated to be of about 25% to 55 %. Up to 30% of the nitrocatechols and reference compounds decay have been attributed to the reaction with OH radicals during the kinetic experiments.

In Table 1 are presented the kinetic data results from the present study. Relative ratios of k1/k2 determined from the kinetic plots (see Figures 1 to 4), gas-phase rate coefficient (k1) calculated for the OH reactions with the investigated nitrocatechols, and the average kinetic coefficients (k1average) are also indicated in Table 1. Uncertainties for the k1/k2 represent 2σ from the linear regression analysis. The k1 rate coefficient errors are given from a combination of 2σ values from the linear regression and an additional error from the reference compound uncertainty. As for the k1 (average) and its uncertainty, the weighted average was used to estimate the best interval that accommodates the highest confidence of the obtained data. Based on the daytime average concentration of the OH radicals in the atmosphere (Prinn et al., 1995), of 1.6×10^{6} cm^{-3}, Table 1 lists also the atmospheric residence time of the studied nitrocatechols. No significant differences were observed for 4-nitrocatechol and 4-methyl-5-nitrocatechol rate coefficient values when NO_x or NO_x-free conditions have been employed.

Direct photolysis of the hydroxylated nitroaromatics under similar conditions as those used in this study have been shown to produce HONO (Bejan et al., 2006). Photolysis of HONO is a well-known source of OH radicals. To properly evaluate the photolysis rate coefficients at 365 nm and 254 nm for the investigated nitrocatechols, by accounting for possible interference of the secondary chemistry due to the OH radicals' reactions, a series of individual experiments were performed using carbon monoxide (CO) as OH scavenger. To cut off the low reactivity of the scavenger ($k_{CO+OH} = 2.41 \times 10^{-13}$ $cm^3 \times s^{-1}$)

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(DeMore et al., 1994), a high amount of CO was introduced into the reactor vessel (of about 1.17×10^{17} cm^{-3}) to ensure a scavenging efficiency of more than 98%. Photolysis rates for all four nitrocatechols at 365 nm (J365) were evaluated. At this wavelength, no significant photolysis for 4-nitrocatechol and 4-methyl-5-nitrocatechol were observed while for 3-nitrocatechol and 5-methyl-3-nitrocatechol photolysis frequency of $(1.53 \pm 0.08) \times 10^{-4}$ s^{-1} and $(1.07 \pm 0.09) \times 10^{-4}$ s^{-1}, respectively, has been measured. Additionally, since for 4-nitrocatechol and 4-methyl-5-nitrocatechol the reaction rate coefficients were measured under NO_x free condition by using H_2O_2 photolysis as OH radical precursor, photolysis rate coefficients at 254 nm of these two compounds were evaluated. For 4-nitrocatechol the photolysis rate (J_{254}) was $(6.71 \pm 0.99) \times 10^{-5}$ s^{-1} and that for 4-methyl-5-nitrocatechol was $(3.18 \pm 0.32) \times 10^{-5}$ s^{-1}. However, for 3-nitrocatechol and 5-methyl-3-nitrocatechol corrections have been also performed because of their high wall loss and their photolysis at 365 nm. Photolysis rate coefficients are presented in Table 2, beside the average lifetime with respect to photolysis under atmospheric conditions. Photolysis rate coefficients at 365 nm for 3-nitrophenols has been scaled to the atmospheric conditions, as Klotz et al. (1997) has described for 40° N latitude noontime and clear sky conditions, with a factor of 2 obtained from the NO_2 photolysis frequency measured in atmospheric conditions versus the ESC-Q-UAIC reactor ($J_{\text{NO2 - atmosphere}} / J_{\text{NO2 – ESC-Q-UAIC chamber}} = 8.5 \times 10^{-3}\ s^{-1} / 4.3 \times 10^{-3}\ s^{-1} \approx 2$).

5. Discussion

The rate coefficients obtained from the kinetic investigations of a series of nitrocatechols with OH radicals are reported for the first time in this study. No significant differences have been observed between the two reference compounds that have been employed to achieve the quality of the rate coefficient values. Based on collision theory and the standard gas kinetic theory, Sørensen et al. (2002) showed that the presence of inorganic aerosols does not influence the OH radicals concentration, with less than 0.1% of the total OH being deactivated by the aerosol surface. Possible SOA formation from the irradiation of nitrocatechols is expected following a similar process as the one reported by Bejan et al. (2020) for nitrophenols. However, these would not influence the kinetic data even if expected effects on the gas phase nitrocatechols concentration due to the gas-particle equilibrium are not excluded. Taken into account estimations for Henry`s law constant of $(2 \div 8) \times 10^{-13}$ atm × m^3 × $mole^{-1}$ at 25°C this effect is unlikely to make significant differences over the nitrocatechols concentrations used in the present study (Hine and Mookerjee, 1975; Meylan and Howard, 1991).

A comparison with literature data is not possible. However, there are reported rate coefficients values for nitrophenol and methylated nitrophenols reaction with OH radicals (Atkinson et al., 1992; Bejan et al., 2007). Additionally, kinetic rate coefficients of the OH radical initiated oxidation of nitronaphtalene have been studied by Atkinson et al. (1989). For the OH radical reactions with the nitroaromatics compounds, however, all the reported values of the rate coefficients in the literature have the same order of magnitude as those presented in this work.

5.1. Electromeric effect of aromatic ring substituents

Prior to initiate the discussions on the kinetic results we should emphasize the influence of the substituent position on the aromatic ring for all the nitrocatechols and their effect on the reactivity. The electromeric effects influencing reactivity could be easily noticed on the structure of infrared spectra. Figure 5 presents the gas-phase infrared spectra of catechol (CAT), 4-methylcatechol (4MCAT) and all four nitrocatechols investigated in the present study. Infrared spectra clearly show the presence of the H-bonds between OH and NO_2 groups substituents attached to the aromatic ring in the nitrocatechols as follows: the compounds 3NCAT and 5M3NCAT exhibit a H-bond between the OH and one of the O atom from the NO_2 vicinal group; 4NCAT presents a H-bond between the H from the C1-linked OH and O atom from the C2-linked OH; and 4M5NCAT reveal a H-bond bond between the H from the C2-linked OH and O atom from the C1-linked OH in 4M5NCAT similar to 4NCAT. One could notice the existence of similar structure of vicinal OH groups in catechol and 4-methylcatechol. However, these H-bonds are not present in CAT and 4MCAT, as both OH groups are highlighted in the gas phase IR spectra. H- bond occurring in the nitrocatechols should be evaluated in the light of the existent nitro group that acts with its deactivating electromeric E- effect on the ring, withdrawing the electrons from its *-ortho* and *-para* positions. For the 3-nitrocatechols, the chemical structures reveal the presence of one OH group placed between the OH and NO_2 groups. This hydroxyl group will be affected by the NO_2 electron withdrawing effect and in consequence the O-H bond weakens results in an H-atom that is more susceptible to form a H-bond with O from the NO_2 group. This bond can be observed also in the structure of 2-nitrophenols (Bejan et al., 2007, 2020; Bejan, 2006; Olariu et al., 2002, 2013). As shown in the spectra from Figure 5 the structure of CAT and 4MCAT exhibit the presence of OH groups one next to the other and no visible H-bond between these substituents. These suggest that for 1,2-dihydroxybenzenes the E+ effect is less diminished through the presence of the vicinal OH in *-ortho* to the first one.

In Figure 6, 3NCAT has been chosen as a master example to emphasize the electromeric effects manifested by NO_2 and OH groups on the aromatic ring, in order to identify also their possible implications on the molecule stability. For 3NCAT structure one could observe that the OH substituent next to NO_2 group would produce an H bond which is shielded to manifest its E+ effect on the ring. As reported by Bejan et al. (2006, 2020) photolysis of methylated 2-nitrophenols leads to HONO formation via H-transfer from the hydroxyl group its vicinal nitro group. For 4NCAT and 4M5NCAT, where both OH are linked in the H-bonds, no significant photolysis at 365 nm and no E+ effect to enhance electron density on the aromatic ring occur.

5.2. Reactivity trends

It is well known that the presence of a nitro group has a high deactivating effect on the aromatic ring as the reactivity of nitroaromatic compounds are approximatively 5-20 time lower than theirs parent compounds. Some OH rate coefficients at 298 K for AHs and theirs corresponding NAHs are presented in Table 3 (Atkinson, 1989; Atkinson et al., 1992; Bejan et al., 2007; Calvert et al., 2002; Witte et al., 1986). The reactivity of catechols against OH radicals drops even more than two order of magnitude when a nitro group is attached to the ring (Olariu et al., 2000). Such a sudden loss in reactivity is due to the inhibition of the addition channel in aromatic hydrocarbons as discussed in the present study. Ring retaining product studies from the gas phase OH-radical initiated oxidation of phenol and cresols show that the addition pathway is the dominant oxidation mechanism, occurring between 65% up to 90% of the overall reactions, nitrophenols being formed via phenolic H-atom abstraction channel accounting for 5% to 10 % (Olariu et al., 2002). Gas phase reactions with NO_3 radicals leads to a yield of ~50% of nitrocatechols and almost 100% of nitric acid suggesting that the H-atom abstraction channel represents at least half of the overall reactions (Olariu et al., 2013). In the gas phase oxidation of catechol with OH radical at high NO_x conditions, Finewax et al. (2018) found 4NCAT in the SOA composition with a molar yield of 30%. At least 90% molar yield has been obtained in their study in the oxidation initiated by NO_3 radicals. These results suggest that H-atom abstraction channel has a greater contribution in catechols reactivity rather than abstraction channel from phenol or cresols oxidation.

The gas phase rate coefficients in the investigated series of nitrocatechols vary as follow: $k_{5M3NCAT} > k_{3NCAT} > k_{4NCAT} \sim k_{4M5NCAT}$. 4NCAT and 4M5NCAT could assume a little effect from the methyl group but little distinguished from experimental determined rate coefficients values from this study. A distribution of possible free attack sites by OH radicals on the aromatic ring, accounted also by the substituent's effects, is represented in Figure 7 A. The NO_2 group deactivates the aromatic ring towards OH attack by the E- effect. By it's I+ effect, the $-CH_3$ substituent will probably influence the electrophilic addition, although its effect is diminished by the E- from $-NO_2$ substituent. According to Figure 7 A the most stable adduct is the 4M5NCAT-OH, and one could propose an OH radical addition to the 3rd position of the ring. However, this is not the case since the experimental data shows that 4M5NCAT is the least reactive compound in this series. Differences between the reactivity of 3NCAT and 5M3NCAT in reaction with an electrophile suggest two determining pathways to occur: addition to the ring in the NO_2-deactivated 4th or 6th position oriented by the E+ electromeric effect of OH (C1) and I+ effect from CH_3, and H-atom abstraction from the C1 linked OH group. While the difference between 3NCAT and 5M3NCAT is comparable with the difference between 2-nitrophenol (2NPh) and 4-methyl-2-nitrophenol (4M2NPh), we may consider that the E+ effect of OH (C1) is less present due to the same orientation of the E- effect of NO_2. Comparing the reactivity of 2NPh with those of methyl-2-nitrophenols, an increase in the reactivity of 2 up to 7 times is observed which is attributed to CH_3 group presence and orientation. The most reactive compound is 5-methyl-2-nitrophenol (5M2NPh) with a $k_{5M2NPh} = 6.72 \times 10^{-12}$ cm^3 × s^{-1}, where the methyl I+ effect is manifested on both *-ortho* positions relative to itself and is not affected by the NO_2 E- deactivating effect. In comparison, 4M2NPh, $k_{4M2NPh} = 3.59 \times 10^{-12}$ cm^3 × s^{-1}, both *-ortho* positions to methyl are likely deactivated by the NO_2. In the methylated nitrophenol series, Bejan et al. (2007) found that the least reactive is 6-methyl-2-nitrophenol (6M2NPh) compound, $k_{6M2NPh} = 2.70 \times 10^{-12}$ cm^3 × s^{-1}, with just one *-ortho* and one *-para* position that are both deactivated by NO_2. Following the trend for 3-nitrocatechols with respect to the internal electromeric effects of the OH and NO_2 groups, considering the reactivity trend in methyl-2-nitrophenols and the implication of the methyl group on the addition of OH radical to the (hydroxylated) aromatic hydrocarbons, rate coefficient for 6M3NCAT (not

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measured in this study) was estimated to fall between (5.0 ÷ 6.5) × 10^{-12} cm^3× s^{-1}, similar to 5M3NCAT (Aschmann et al., 2013; Bejan et al., 2007, 2012; Klotz et al., 1998; Olariu et al., 2000).

For 4NCAT and 4M5NCAT the difference in the reactivity is not obvious since both OH groups involved in H-bond have their E+ effect shielded by the H-bond. If OH group could manifest its electromeric effect, the most reactive compound should be 4M5NCAT. However, the supplementary I+ effect of methyl group, *-para* orientated from the C1-linked OH in 4M5NCAT, seems to strengthen the C1 O-H bond making harder the H abstraction. Even if H-abstraction from CH_3 could be an option for 4M5NCAT, the overall reactivity of this compound is smaller or at least the same as 4NCAT, H-abstraction from the OH group C1-linked being the main degradation path. Seeking the trend in 4-nitrocatechols and 5-nitrocatechols based on these experimental observations we could estimate that for 3M4NCAT the OH rate coefficient falls in between (0.5 ÷ 0.9) × 10^{-12} cm^3× s^{-1} and for 3M5NCAT in between (1.0÷1.4) × 10^{-12} cm^3× s^{-1}. However for all 4-nitrocatechols and 5-nitrocatechols the rate coefficients could be considered around 1×10^{-12} cm^3× s^{-1}. These estimations should be treated carefully, since few experimental data are available at this time.

5.3. Comparison with SAR estimated values

There are two Structure-Activity-Relationship (SAR) models for estimating kinetic rate coefficients of aromatic hydrocarbons, both based on substituent factor analysis that influence the reactivity at atmospheric relevant conditions. The general model proposed by Kwok and Atkinson (1995) (used mainly for aliphatic hydrocarbons) considers four cumulative reactions pathways for the OH-initiated oxidations: H-atom abstraction from ring substituents, OH radical addition to the unsaturated aliphatic (double or triple) bond of the substituents, OH radical addition to the aromatic ring and OH radical interactions with ring heteroatoms. The rate coefficient for the total reaction is assumed as a sum of rate coefficients from these four pathways. As for aromatics, this model proposes standard values for H-atom abstraction for the group rate coefficients and substituents factors. For addition to the aromatic ring of the OH radicals the electrophilic substituent scale factors are proposed assuming a fit to the following equation: $\log k_{add} = -11.71 - 1.34 \times \Sigma\sigma^+$. Factors needed in the evaluation of the OH addition pathway (σ^+) represents the electrophilic substituent constants given by Brown and Okamoto (1958). The SAR estimation model from Jenkin et al. (2018a, 2018b) updates the factors used in the calculation of rate coefficients and branching ratios for the gas-phase reactions of the OH radicals with monocyclic aromatic compounds. A scaling parameter for the OH radical addition to each carbon atom in the aromatic cycle relative to positions of the ring substituents was introduced. Additionally, for the addition pathway, 17 possible ring substituents adjustment factors were introduced, including nitro and hydroxyl groups. In the H-atom abstraction pathway from aliphatic substituents another scaling factor for group rate coefficients of exp(140/T) is recommended to be used when alkyl substituents are present in *-ortho* or *-para* position relative to the attack site. Based on previous studies (Bejan et al., 2007, 2012; Lauraguais et al., 2015; Olariu et al., 2000, 2002) on hydroxylated aromatic compounds, an abstraction rate coefficient from the phenolic OH of k_{abs} (Ph-OH) = 2.6 × 10^{-12} cm^3× s^{-1} is being proposed by Jenkin et al. (2018b), rate coefficient that is 20 times larger than those observed in aliphatic alcohols (Jenkin et al., 2018a). This has a great impact on the overall reactivity and the branching ratios of aromatic hydroxylated monocyclic compounds. Observations from the kinetic data of nitro containing aromatic hydrocarbons result in re-evaluation of the H-atom abstraction channel from the OH substituent, and a more suitable value for the reactions occurring at 298K is k_{abs} (Ph-OH) = 1.4×10^{-13} $cm^3 \times s^{-1}$. EPI Suite – AOPEWIN software 4.11 was developed based on Kwok and Atkinson (1995) observations by United States Environmental Protection Agency (US-EPA). Data in Table 4 shows that each SAR tends to overestimate the OH gas phase reactivity of hydroxylated nitro-benzenes. Along with nitrocatechols rate coefficient values obtained in the present study, Table 4 lists also the experimental kinetic rate coefficients for 2-nitrophenols determined by Bejan et al. (2007) and the estimated SAR values. The 2-nitrophenols estimated rate coefficient values of Jenkin et al. (2018b) fits better with the experimental data compared with other SARs, due to the use of substituent adjustment factors R(Φ) for the substituent factors F(Φ) updated to the available literature and the rescaled of abstraction rate coefficient previously assigned to -OH groups in aliphatic compounds of k_{abs} (Ph-OH) = $1.28 \times 10^{-12} \times \exp(-660/T)$ $cm^3 \times s^{-1}$ (1.4×10^{-13} $cm^3 \times s^{-1}$ at 298 K). In the case of nitrocatechols, Jenkin et al. (2018b) SAR values are a factor of 1.5 higher compared with the values of Kwok and Atkinson (1995). The difference between the estimated values is consider to appear due to the k_{add} estimation in Kwok and Atkinson (1995) SAR, where the electrophilic substituent coefficient τ^+ for the OH orientated in *-meta* position has no attributed contribution. For 1,2-dihydroxybenzenes molecules the addition pathway might count only for one phenolic hydroxyl. This is in agreement with the experimental explanation given for 3-nitrocatechols reactivity, where the E+ effect of the OH group from C2 has no electromeric effect on the aromatic ring as visible in infrared spectra. Consistency between the rate coefficient values is given as both SARs assume that the addition pathway is at least 94% of the overall reactivity. Based on the observations of Bejan et al. (2007) on methylated 2-nitrophenols this assumption is reasonable.

As data in Table 4 show no differences were observed between the rate coefficient values estimated by the EPI Suite – AOPWIN and Kwok and Atkinson (1995) approach since the programme is based on the model calculation proposed study. However, for nitrocatechols there is a difference between the rate coefficients values. This difference is observed since the programme could not choose the correct parameters of the nitro group to proper calculate $T\sigma^+$. Instead of choosing the lowest value for NO_2 substituent *-meta* orientated, it chooses the electrophilic substituent group constant from *-ortho* and *-para*, that gives the highest $T\sigma^+$, not the lowest as it is recommended. However, in further discussions we will no longer consider EPI Suite – AOPWIN software data.

In SAR approaches, the estimated rate coefficients values do not consider the interactions between the nitro and its vicinal OH group or between OH groups, thus all having a tendency to overestimate the gas phase OH rate coefficients for hydroxylated nitro monocyclic automatics. However, Jenkin et al. (2018b) propose a substituent adjustment factor for NO_2 group of 0.024 for the *-ortho* and *-para* relative to each of the addition sites on the ring and of 0.07 for the *-ipso* and *–meta* positions. In Kwok and Atkinson (1995) SAR estimations assign a NO_2 group substituent factor of + 0.790 in *-ortho* or *-para* and of +0.674 for *-meta* or *-ipso*. All of these factors are calculated based on previous experimental data to fit alkyl substituted or low substituted aromatic compounds. Although the updated SAR of Jenkin et al. (2018b) is more complex, interactions between the substituents are not taken into consideration. These limitations lead in the case of 4NCAT or

4M5NCAT to differences of 5 and 18 times higher. For the 3NCAT and 5M3NCAT the estimated rate coefficient values are more consisted with the present experimental data, values being only ~2 times larger. Differences between experimental values of 4NCAT and 4M5NCAT in comparison with those estimated by SAR model suggest that the addition pathway is of lower importance compared with the H-atom abstraction from hydroxyl groups due to the inhibition of the E+ effect of phenolic hydroxyls, and limited contribution from the presence of the CH_3 group.

If substituents interactions are taken into account by: (1) excluding the OH substituent effect on the addition channel (one substituent effect in 3NCAT, 5M3NCAT and both substituents in 4NCAT and 4M5NCAT); (2) removing one H-atom abstraction channel in all the nitrocatechols; (3) considering the methyl group inhibiting the H-atom abstraction channel in 4M5NCAT; and (4) using a new neighbouring group factor for α-H-atom abstraction from the deactivated phenolic group F(-Ph deactivated) = 0.5, then the automated mechanism construction propose by Jenkin et al. (2018b) would emphasize new estimated rate coefficient values approaching the experimental data obtained in this study as follows: for 3NCAT a rate of 3.95×10^{-12} $cm^3 \times s^{-1}$ with a $k_{add}/k_{tot} = 0.67$, for 5M3NCAT a rate of 6.15×10^{-12} $cm^3 s^{-1}$ with a $k_{add}/k_{tot} = 0.73$, for 4NCAT a rate of 2.36×10^{-12} $cm^3 \times s^{-1}$ with a $k_{add}/k_{tot} = 0.45$ and for 4M5NCAT a rate of 3.71×10^{-12} $cm^3 \times s^{-1}$ with a $k_{add}/k_{tot} = 0.69$. However, based on Jenkin et al. (2018b) study and the behaviour of the investigated nitrocatechols it is probably better to use 0.5 value of the new parameter for the H-atom abstraction for deactivated phenyl group F (-Ph deactivated) when k_{abs}(Ph-OH) = 2.6×10^{-12} $cm^3 \times s^{-1}$ is considered. In this case the H-atom abstraction from phenolic hydroxyl will gain significant importance, and will be in agreement with previous kinetic studies of hydroxylated aromatic compounds. The new estimated values obtained within the present work are listed in Table 4 besides those of methylated nitrophenols, for which systematic lower values are reported. However, more kinetic studies are necessary to be performed on nitro-aromatic compounds in order proper to evaluate all needed parameters in the development of a unified OH-SAR for aromatic hydrocarbons.

5.4. Atmospheric implications

The estimated photolysis frequencies for the 3NCAT and 5M3NCAT extrapolated to atmospheric conditions (see Table 2) are comparable with those proposed by Bejan et al. (2007) for 2-nitrophenols. Photolysis of nitrocatechols with NO_2 and OH groups in vicinal position would be the dominant atmospheric sink being almost 10 times faster than reaction with OH radicals. Similar values of photolysis frequencies have been also reported for nitro-naphthalenes and methyl-nitro-naphthalenes (Phousongphouang and Arey, 2003). Based on the obtained data, it may be suggested that all the nitroaromatic compounds that have the NO_2 group in vicinal position with a large electron density area, might easily undertake photolysis which maybe is the main sink pathway in the atmosphere. Similar to 4-nitro and 5-nitrocatechols, dry or wet deposition seems to be the most probable atmospheric removal process, with little or no photolysis in the boundary layer and with high chemical residence time regarding atmospheric oxidative degradation initiated by the OH radicals.

6. Conclusions

Gas-phase reaction rate coefficients of OH radicals with four nitrocatechols have been investigated for the first time by using the ESC-Q-UAIC chamber facilities. The reactivity of all investigated nitrocatechols is strongly influenced by the formation of the intramolecular H-bonds that are directly influenced by the deactivating electromeric effect of the NO_2 group. For the 3-nitrocatechols compounds, the electromeric effect of the "free" OH group is diminished by the deactivating E- effect of NO_2 group. Thus, the rate coefficients of 3-nitrocatechols compounds are higher than the rate coefficients values of 4-nitrocatechol or 4-methy-5-nitrocatechol where no electromeric effect of the OH group seems to be active. In consequence, in 4-nitro or 5-nitrocatechols the H-abstraction pathway seems to play an important role for the entire OH radical reaction while in 3-nitrocatechols case the OH-addition path remains dominant.

For 3-nitrocatechols the atmospheric average lifetime seems o be controlled by the photolysis processes, similar to 2-nitrophenols, with an average day-time lifetime of about one hour. Reaction with OH radicals is the main atmospheric process for 4-nitrocatechols. Atmospheric day lifetimes of 4-nitro and 5-nitrocatechols are higher than 48 hours because of the OH radical initiated oxidation, being susceptible to long-range transport at atmospheric conditions.

As presented in the current study, the automated mechanism construction for OH rate coefficients SAR estimations is further recommended to consider the internal interactions between vicinal substituents. Moreover, all approaches tend to overestimate the gas phase reactivity of highly substituted nitro containing aromatic compounds. Use of an average rate coefficient for the H-atom abstraction from the O-H group $k_{abs(Ph\text{-}OH)} = 2.6\times10^{-12}$ $cm^3 \times s^{-1}$ is encouraged, along with a scaling parameter for deactivated aromatic phenyl group, estimated to be 0.5 at 298 K. Also, the substituent adjustment factors R(Φ), relative to the F(Φ) values for nitro group should be re-evaluated, R(Φ) average for all possible addition sites being ~ 0.009. However, more studies are required to support the proposed reactivity for nitrocatechols and to move further the knowledge of the gas-phase aromatic chemistry.

Competing interests

The authors declare no conflict of interest. The founders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Author contribution

Claudiu ROMAN (Investigation, Formal analysis, Data curation, Writing – original draft, Writing – review& editing); Cecilia ARSENE (Data curation, Formal analysis, Funding acquisition, Writing – review & editing); Iustinian Gabriel BEJAN (Formal analysis, Funding acquisition, Writing – review & editing); Romeo-Iulian OLARIU (Conceptualization, Formal analysis, Data curation, Funding acquisition, Supervision, Writing – review & editing).

Code availability

Not applicable

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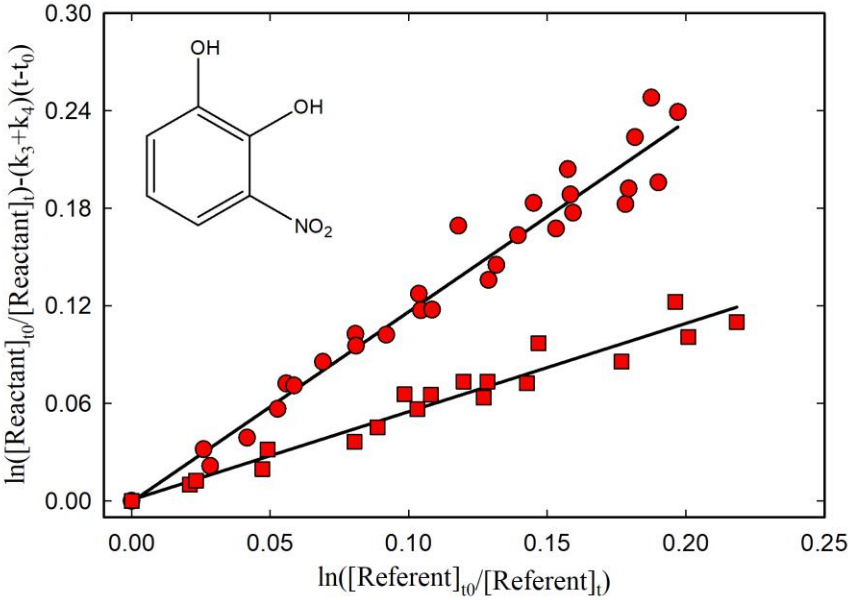

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Figure 1: Kinetic plot according to Eq. 1 for the reaction of 3-nitrocatechol with OH radicals relative to (●) dimethyl ether and (■) cyclohexane, using photolysis of CH_3ONO/NO mixture at 365 nm as OH radicals source.

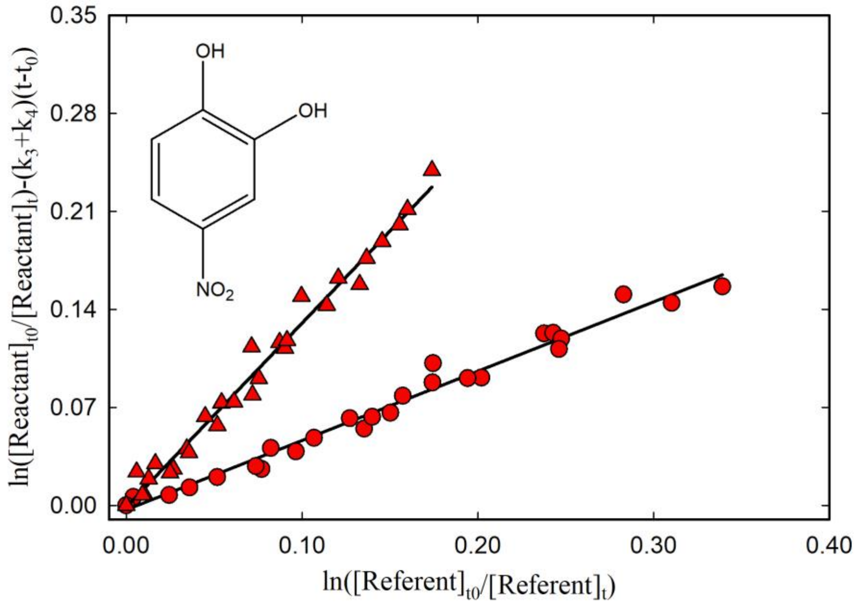

Figure 2: Kinetic plot according to Eq. 1 for the reaction of 4-nitrocatechol with OH radicals relative to (●) dimethyl ether, using photolysis of CH_3ONO/NO mixture at 365 nm as OH radicals source, and relative to (▲) methanol, using photolysis of H_2O_2 at 254 nm as OH radicals source.

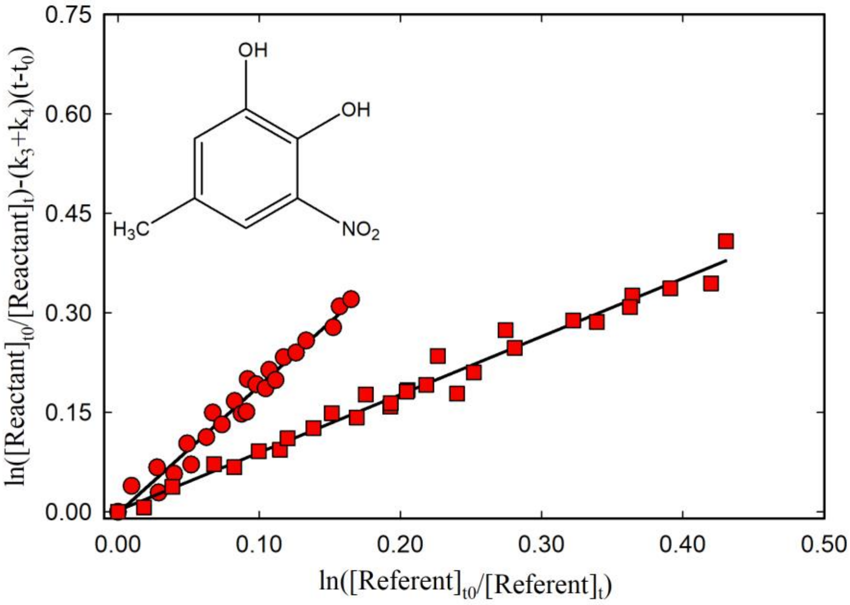

Figure 3: Kinetic plot according to Eq. 1 for the reaction of 3-nitro-5-methylcatechol with OH radicals
575 relative to (●) dimethyl ether and (■) cyclohexane using photolysis of CH_3ONO/NO mixture at 365 nm as OH radicals source.

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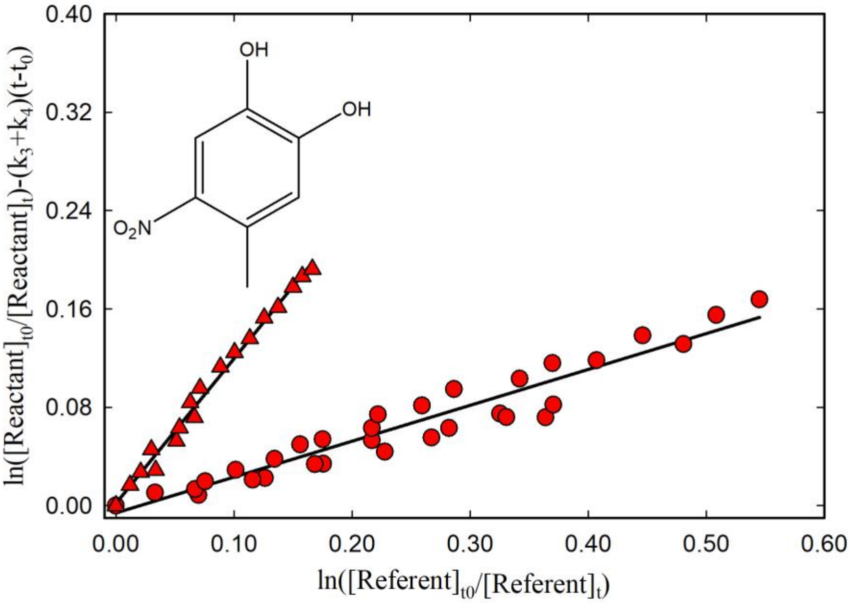


580 **Figure 4:** Kinetic plot according to Eq. 1 for the reaction of 4-nitro-5-methylcatechol with OH radicals relative to (●) dimethyl ether, using photolysis of CH_3ONO/NO mixture at 365 nm as OH radicals source, and relative to (▲) methanol, using photolysis of H_2O_2 at 254 nm as OH radicals source.

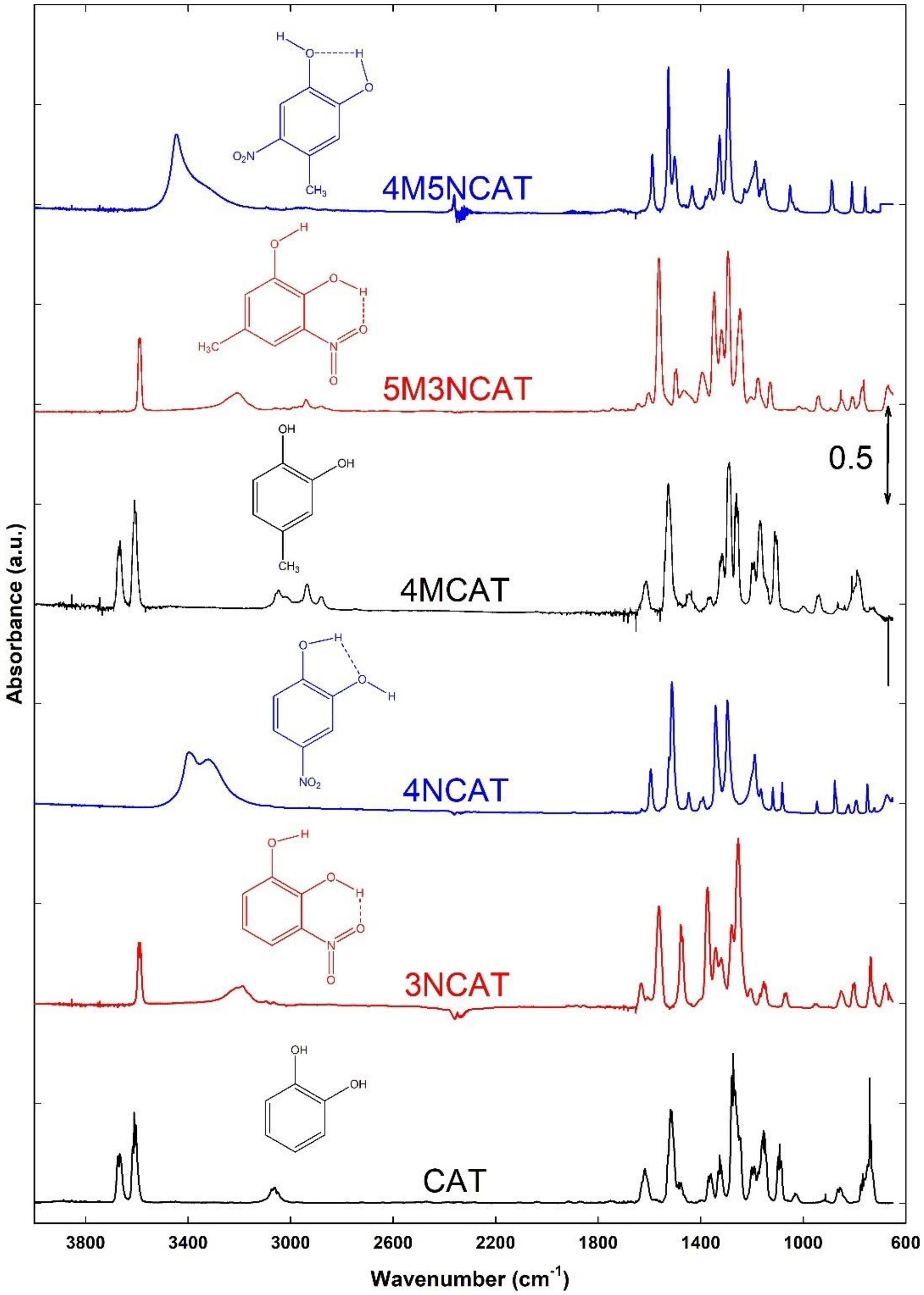
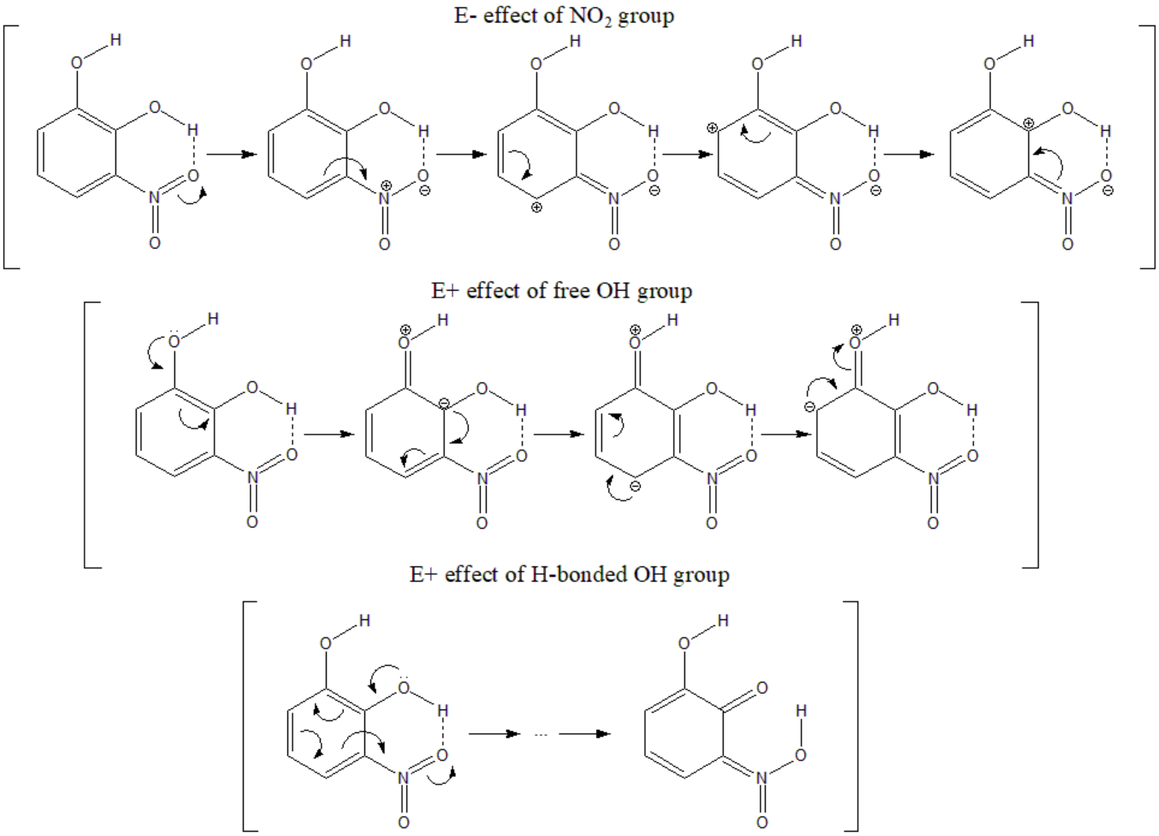


Figure 5: Gas-phase IR spectra of catechol, 4-methylcatechol, and all four investigated nitrocatechols. 585 Evidence for the intramolecular H-bond occurrence between the substituents: catechol and 4MCAT– both free OH present in the spectra; 3NCAT and 5M3NCAT – only one free OH; 4NCAT and 4M5NCAT – both OH involved in H-bond.


E- effect of NO_2 group

E+ effect of free OH group

E+ effect of H-bonded OH group

Figure 6: Electromeric effects of NO_2 and OH substituents from 3NCAT molecule.

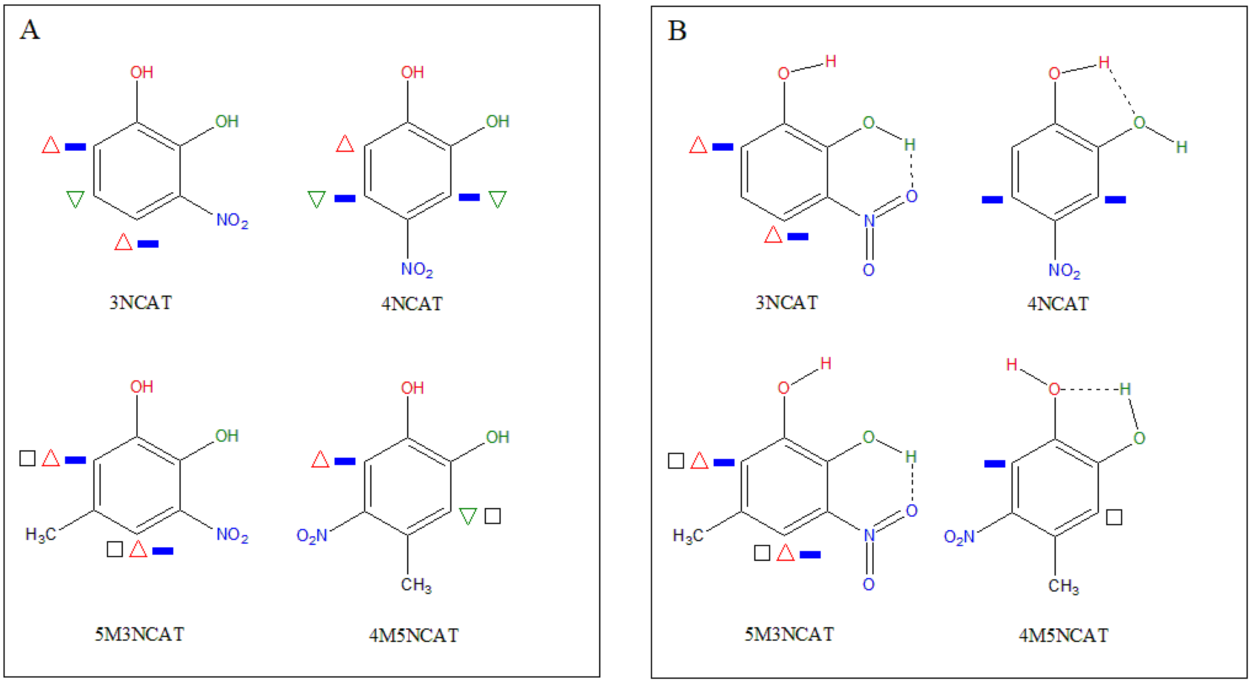


Figure 7: Electromeric effect distribution on the aromatic ring for the all investigating nitrocatechols in the present study:
(A) active sites toward electrophilic attack by hydroxyl (△/▽), nitro (▬) and methyl (□) groups;
(B) internal interactions of the substituents and consequences on the reactivity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

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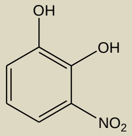
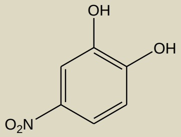
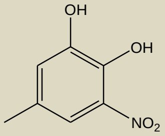
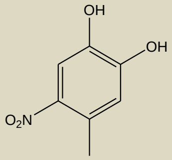
Table 1: Rate coefficient values of OH radical reactions with all investigated nitrocatechols in the present study.

Compound	Referent	k_1/k_2	k_1 [10^{-12} cm3×s^{-1}]	k_1 (average) [10^{-12} cm3×s^{-1}]	τ^a [h]
 **3-nitrocatechol**	DME	1.17±0.09	3.27±0.69	**3.41±0.37**	51.6
	Cyclohexane	0.54±0.06	3.46±0.44		
 **4-nitrocatechol**	DME	0.49±0.03	1.39±0.29	**1.27±0.19**	137.0
	Methanol	1.31±0.06	1.18±0.24		
 **5-methyl-3-nitrocatechol**	DME	1.92±0.13	5.37±1.14	**5.55±0.48**	31.3
	Cyclohexane	0.88±0.05	5.58±0.49		
 **4-methyl-5-nitrocatechol**	DME	0.29±0.03	0.82±0.18	**0.92±0.14**	189.6
	Methanol	1.18±0.06	1.06±0.22		

[a] calculated considering the average daytime OH radical concentration of 1.6 ×10^6 cm^{-3} (Prinn et al., 1995).

Table 2: Rate coefficients values for the photolysis of all nitrocatechols investigated in this study scaled to atmospheric conditions and their average atmospheric lifetimes due to the photolysis (at 365 nm).

Compound	**$J_{(NCAT)}$ – 254 nm [10^{-4} s^{-1}]**	**$J_{(NCAT)}$ – 365 nm [10^{-4} s^{-1}]**	**$\tau_{h\nu}$ (at 365 nm) [hour]**
3NCAT	not measured	3.06 ± 0.16	~0.91
4NCAT	0.67 ± 0.01	< 0.1	> 27.78
5M3NCAT	not measured	2.14 ± 0.18	~1.30
4M5NCAT	0.32± 0.03	< 0.1	> 27.78

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} $cm^3 \times s^{-1}$]**	**Nitroaromatic hydrocarbon (NAHs)**	**k_{OH} [10^{-12} $cm^3 \times s^{-1}$]**	**k_{NAHs}/k_{AHs}**
benzene	1.22[a]	nitrobenzene	0.14[a]	0.11
toluene	5.63[a]	*m*-nitrotoluene	1.2[a]	0.21
phenol	26.3[a,c]	2-nitrophenol	0.9[b]	0.04
o-cresol	41[a,c]	6-methyl-2-nitrophenol	2.7[d]	0.07
m-cresol	68[a,c]	3-methyl-2-nitrophenol	3.7[d]	0.05
		5-methyl-2-nitrophenol	6.7[d]	0.1
p-cresol	50[a,c]	4-methyl-2-nitrophenol	3.6[d]	0.07
catechol	104[e]	3-nitrocatechol	3.41[f]	0.03
		4-nitrocatechol	1.27[f]	0.01
4-methylcatechol	156[e]	5-methyl-3-nitrocatechol	5.55[f]	0.04
		4-methyl-5-nitrocatechol	0.92[f]	0.01

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

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Table 4: Experimental and estimated by SAR method rate coefficients of monoaromatic hydroxylated nitro compounds with the OH radical. In brackets are the ratios of the experimental data versus the estimated values (kcalc/kexp).

Compound	**Experimental data**	**SAR**				
		EPI Suite - AOPWIN	*Kwok and Atkinson 1995*	*Jenkin et al., 2018b* k_{abs}(Ph-OH)		**this work**
				2.6×10^{-12}	0.14×10^{-12}	
		$k_{(OH)}\times10^{12}$ [$cm^3\times s^{-1}$]				
3NCAT	3.41 ± 0.37	3.15 (0.92)	4.45 (1.30)	11.83 (3.47)	6.91 (2.03)	3.95 (1.16)
4NCAT	1.27 ± 0.19	3.15 (2.48)	4.45 (3.50)	11.83 (9.31)	6.91 (5.44)	2.36 (1.86)
5M3NCAT	5.55 ± 0.48	5.65 (1.02)	8.02 (1.45)	18.21 (3.28)	11.81 (2.13)	6.15 (1.11)
4M5NCAT	0.92 ± 0.14	7.90 (8.59)	11.29 (12.27)	22.99 (25.00)	16.60 (18.04)	3.71 (4.03)
3M2NPh	3.69 ± 0.70[a]	11.15 (3.02)	11.15 (3.02)	7.19 (1.95)	4.73 (1.28)	2.00 (0.54)
4M2NPh	3.59 ± 1.17[a]	5.38 (1.50)	5.38 (1.50)	7.17 (2.00)	3.24 (0.90)	1.41 (0.39)
5M2NPh	6.72 ± 2.14[a]	11.15 (1.66)	11.15 (1.66)	7.19 (1.07)	4.73 (0.70)	2.00 (0.30)
6M2NPh	2.70 ± 0.57[a]	5.38 (1.99)	5.38 (1.99)	7.17 (2.66)	3.24 (1.20)	1.41 (0.52)

[a] Values from Bejan et al. (2007): 3M2NPh- 3-methyl-2-nitrophenol; 4M2NPh- 4-methyl-2-nitrophenol; 5M2NPh- 5-methyl-2-nitrophenol; 6M2NPh- 6-methyl-2-nitrophenol.