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Reaction Kinetics of Catechol (1,2-Benzenediol) and Guaiacol (2-Methoxyphenol) with Ozone

Atallah El Zein, Cécile Coeur,* Emil Obeid, Amélie Lauraguais, and Thomas Fagniez

Laboratoire de Physico-Chimie de l'Atmosphère (LPCA), EA 4493, Université du Littoral Côte d'Opale, Université Lille Nord de France, 32 Avenue Foch, 62930 Wimereux, France

Ⓢ Supporting Information

ABSTRACT: The kinetic reactions of 1,2-benzenediol (catechol) and 2-methoxyphenol (guaiacol) with ozone were studied in a simulation chamber (8 m³) under dark conditions. The rate coefficients were measured at 294 ± 2 K, atmospheric pressure and dry conditions (relative humidity, RH < 1%), except for 1,2-benzenediol where they were also measured as a function of relative humidity (RH = 1−80%). The concentrations of organic compounds were followed by a PTR-ToF-MS for a continuous monitoring of gas-phase species. The O_3 rate coefficients were obtained using both the pseudo-first-order and relative rate methods. The values (in cm^3 $molecule^{-1}$ s^{-1}) determined for catechol and guaiacol under dry conditions are $(13.5 \pm 1.1) \times 10^{-18}$ and $(0.40 \pm 0.31) \times 10^{-18}$, respectively. The rate coefficient of catechol was found to be independent of RH below 20% and above 60%, whereas for RH between 20% and 60% it decreases with increasing RH. The determined rate coefficients have been used to evaluate the atmospheric lifetime of each compound with respect to O_3. To our knowledge, this study represents the first determination of the ozone rate coefficient with guaiacol and is also the first kinetic investigation for the influence of the relative humidity on the oxygenated aromatic ozonolysis.
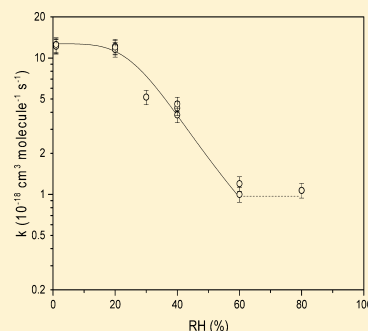
INTRODUCTION

It has become increasingly clear that our troposphere contains large quantities of volatile organic compounds (VOCs) emitted from anthropogenic and biogenic sources.[1] Aromatic hydrocarbons are an important class of VOCs emitted mainly from anthropogenic activities (from motor vehicles exhaust emissions and solvent use).[2]

In the atmosphere, aromatics react mainly with hydroxyl radicals, and the reaction of phenol and cresols with OH has been shown to produce catechols in yields of about 80%.[3,4] In addition, catechol can be directly emitted into the atmosphere from anthropogenic sources such as wood combustion.[5,6] Once released or formed in the atmosphere, the oxygenated aromatics can therefore be chemically transformed due to their reactivity toward the most important oxidants in air such as hydroxyl radicals,[1,7] nitrate radicals,[1,8] and/or chlorine atoms.[9,10] Ozonolysis of aromatic compounds is, however, known to be slow, excepted for catechols[11] and aromatics with alkene side chains.[12,13] The available information on the tropospheric reactivity of catechol and guaiacol is still scarce. In the literature, rate coefficients have been reported for the reaction of catechol with OH,[10,14] NO₃,[8] and O₃[11] and also for guaiacol with Cl[9] and OH.[15] Recent works have also shown their role in the formation of secondary organic aerosols through their reaction with ozone[15,16] or hydroxyl radicals.[17,18]

Natural wood consists of three basic polymers: cellulose (40−50%), lignin (18−35%), and hemicelluloses (25−35%).[19−21] Pyrolysis of lignin releases methoxyphenols,[22,23] mainly syringol (2,6-dimethoxyphenol), guaiacol, and their

derivatives. In this regard, guaiacol is emitted in the atmosphere from natural fires, human-initiated burning of vegetation, and residential wood combustion. Wood smoke particles are predominant in the inhalable size range and could be mutagenic and carcinogenic.[24] As a result, exposure to wood smoke can cause or exacerbate a wide range of adverse health effects related to respiratory problems.[25,26] Methoxyphenols were thought to be specific tracers for woodsmoke emissions.[5,27] The atmospheric lifetimes and hence the effectiveness of methoxyphenols as stable molecular tracers for wood combustion are governed by the rates of their atmospheric degradation.

The present work concerns the experimental kinetic study for the reaction of catechol and guaiacol with ozone. For the former, the influence of the relative humidity (from 1 to 80%) has also been studied. To the best of our knowledge, this work represents the first determination of the ozone rate coefficient with guaiacol and is also the first kinetic investigation for the effect of the relative humidity on oxygenated aromatic ozonolysis.

EXPERIMENTAL SECTION

The kinetic experiments of guaiacol and catechol with O_3 were performed in a chamber consisting of a PMMA (poly(methyl methacrylate)) cube with an internal dimension of 2.0 m giving a total volume of 8 m³. The chamber is described in detail in

Lauraguais et al.;[28] briefly, it includes a fan with Teflon blades mounted inside the chamber and working sequentially to ensure an homogeneous mixing of the reactants. Multiple outlet ports for gas/particle sampling and in situ monitoring (by various analytical instruments) are located on the reactor walls. The chamber was operated using purified dry air and was flushed for at least 12 h before each experiment. VOCs were introduced into the chamber through a heated glass impinger system resulting in concentrations around 200 ppbv. The organic compounds were introduced in the reaction chamber using an inlet system in which measured amounts of the substances were gently heated in a small flow of purified air. Ozone was produced by passing pure oxygen (99.99%) through an electrical discharge generator (C-Lasky, C-L010-DTI).

The concentration of ozone into the chamber varied between 1 and 4 ppmv; they were measured by an UV photometric analyzer (Thermo Electron Corp. O_3 analyzer, Model 49C). Aromatics are known to interfere with ozone measurements as they also absorb in the UV. In order to test for such interferences, 200 ppbv of catechol or guaiacol were introduced separately into the chamber without ozone and were monitored with the ozone analyzer. The corresponding concentrations were about 2 and 34 ppbv, respectively, and were negligible compared to that of ozone used for our experiments (1−4 ppmv).

The loss rate of gas-phase organic species was monitored online throughout the experiments using a PTR−ToF−MS (proton transfer reaction−time of flight−mass spectrometry; Ionicon PTR-ToF 1000) allowing a continuous VOC quantification (one measurement every 3 s). The inlet line of the PTR-ToF-MS was heated at 60 °C to reduce the losses of oxygenated aromatics during their sampling.

The ozonolysis of alkene produces OH radicals,[1,12] so it is required to add hydroxyl radical scavenger into the chamber to suppress secondary reactions with OH.[11,29] In the present study, cyclohexane and 1,3,5-trimethylbenzene (TMB) were both used as OH scavengers. Their concentrations were determined to satisfy the relationship $v(OH + scavenger)_0/v(OH + VOC)_0 \geq 100$, where v refers to the rate of the corresponding reaction.

The rate coefficients have been determined at 294 ± 2 K, atmospheric pressure, and dry conditions using the pseudo-first-order (with an excess of ozone) and relative rate methods. The time scale of the experiments varied between 20 and 60 min. Tests were performed without ozone in the simulation chamber to verify that catechol, guaiacol, and the references were solely removed via the reaction with ozone (the wall losses of these organics were considered as negligible). For catechol, the rate coefficient has also been studied as a function of the relative humidity (from 1 to 80%). To vary the relative humidity within the chamber, deionized water was introduced using a heated line connected to the chamber. The relative humidity and temperature were measured with a digital sensor (605-H1, Testo). It is known that oxygenated aromatics (especially catechol) are sticky and the PTR-MS sensitivity influenced by the relative humidity.[30] Therefore, to assess the analytical artifacts which could occur during the measurement of catechol concentrations, preliminary experiments were performed to control the linearity of the PTR-MS by injecting measured amounts of catechol into the chamber. The calibrations were performed for different relative humidity (from 1 to 60%), and for each RH we observed a linear response of the PTR-MS. The sensitivity was, however, reduced

when the relative humidity increased, but this does not affect the ratio $\ln(C_0/C)$ used for the determination of the rate coefficient.

The compounds used in this study, their manufacturer, and stated purity were as follows: catechol (Sigma-Aldrich, 99%), guaiacol (Alpha Aesar, 98%), isoprene (Fluka, 98%) and β-pinene (Fluka, 99%).

■ RESULTS AND DISCUSSION

Pseudo-First-Order Kinetics. In the present study, a series of experiments were performed with the pseudo-first-order method (with an excess of ozone, at least a factor of 10) to determine the rate coefficients for the reaction of catechol and guaiacol with ozone. As described below, the aromatic hydrocarbon decay is due to the reaction with O_3:

$$\frac{d[aromatic]}{dt} = -k[O_3][aromatic] \quad (I)$$

In this case, the equation can be simplified by replacing $k[O_3]$ by the pseudo-first-order rate coefficient, k'

$$\frac{d[aromatic]}{dt} = -k'[aromatic] \quad (II)$$

which on integration gives

$$\ln\frac{[aromatic]_0}{[aromatic]_t} = -k't \quad (III)$$

The rate coefficient k' is deduced from the straight line of the plots of $\ln([aromatic]_0/[aromatic]_t)$ as a function of time (t). The experiments were performed with different ozone concentrations, and k was then extracted from the slope of the regression line of k' versus $[O_3]$. Data generated from the reactions were plotted in the form of eq III in Figures 1 and 2 for catechol and guaiacol, respectively. The uncertainties on the measurements of k' have been determined from the linear regression analysis of the slope $\ln[aromatic]_0/[aromatic]_t$ versus the time; they are in the range 1−2% for catechol
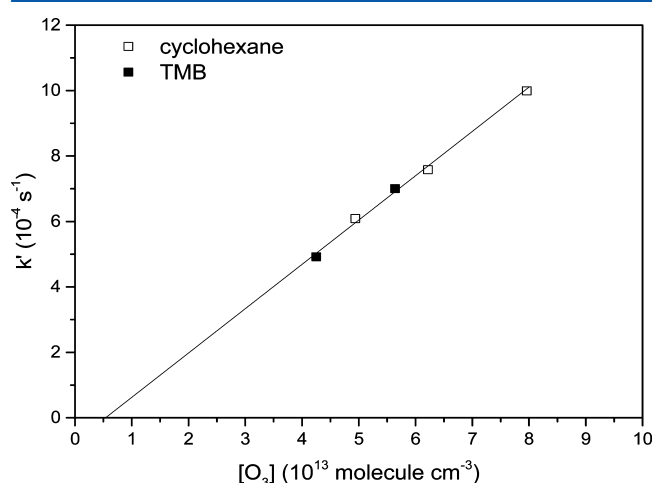
Figure 1. Plot of the pseudo-first-order rate coefficients (k') for the reaction of O_3 with catechol as a function of the initial ozone concentration: T = 294 ± 2 K, P = 1 atm, [catechol] $\cong$ 200 ppbv. Hydroxyl radical scavengers are cyclohexane (□) and 1,3,5-trimethylbenzene (TMB) (■). The uncertainties on the measurements of k' are in the range 1−2%, so the error bars are omitted in this figure.
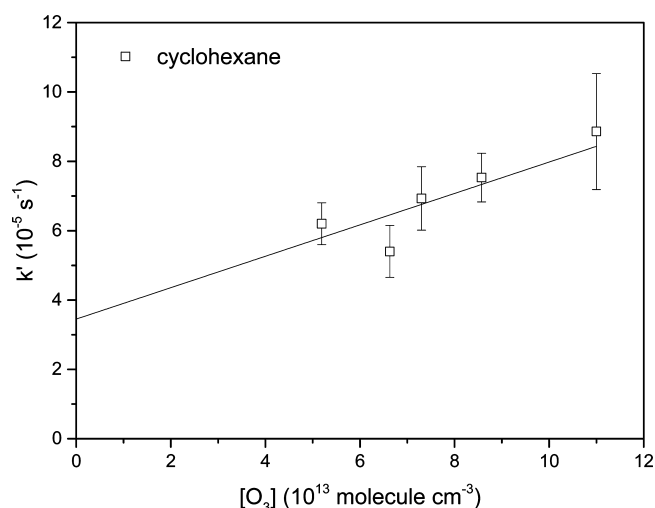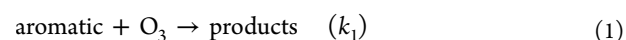
Figure 2. Plot of the pseudo-first-order rate coefficients (k') for the reaction of O_3 with guaiacol as a function of the initial ozone concentration: $T = 294 \pm 2$ K, $P = 1$ atm, [guaiacol] $\cong 200$ ppbv. Cyclohexane ($\square$) was used as OH scavenger. The error bars vary in the range 10−20% and reflect the uncertainties on the measurements of k'.

(Figure S.1, Supporting Information) and 10−20% for guaiacol (Figure S.2). Plots in Figures 1 and 2 display good linearity; for catechol (Figure 1), it shows near-zero intercept, whereas for guaiacol there is a y-axis intercept. This y-axis intercept is probably linked to the uncertainties on the rate coefficients k' due to the slowness of the reaction (the guaiacol wall losses were verified and were considered as negligible). The ozone reaction with guaiacol is slow and the rate coefficient difficult to

measure accurately, so the y-axis intercept could be attributed. The derived rate coefficients are listed in Table 1, and the determined rate coefficients are $k_{catechol} = (13.4 \pm 1.0) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} and $k_{guaiacol} = (0.54 \pm 0.31) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}. The indicated errors are twice the standard deviation arising from the least-squares fit of the data.

Relative Rate Plot. The rate coefficients for the ozonolysis of catechol and guaiacol were also determined with the relative rate method; these experiments were performed with cyclohexane and TMB as OH scavengers. The reference compounds used were as follows: for catechol, isoprene ($k_{isoprene} = 12.7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}),[1] and β-pinene ($k_{\beta\text{-pinene}} = 15 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1})[1] and for guaiacol, p-cresol ($k_{p\text{-cresol}} = 5 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}),[12] and o-cresol ($k_{o\text{-cresol}} = 3 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}).[12] A minimum of three experiments were performed for each reference.

Addition of ozone into the chamber initiates the following reactions:

$$\text{aromatic} + O_3 \rightarrow \text{products} \quad (k_1) \tag{1}$$

$$\text{reference} + O_3 \rightarrow \text{products} \quad (k_2) \tag{2}$$
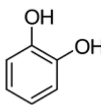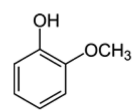
Kinetic treatment of these reactions yields to the following relationship

$$\ln \frac{[\text{aromatic}]_0}{[\text{aromatic}]_t} = \frac{k_1}{k_2} \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \tag{IV}$$

where k_1 and k_2 are the rate coefficients for reactions 1 and 2, and the subscripts 0 and t indicate the concentrations at time $t = 0$ and t, respectively. Plots in the form of eq IV should yield a straight line with zero intercept and slope k_1/k_2. Data generated from the reactions were plotted in the form of eq IV and show

Table 1. Rate Coefficients for the Reaction of O_3 with Catechol and Guaiacol at 294 $\pm$ 2 K, Dry Conditions, and Associated Atmospheric Lifetimes)*

Compound	Method	Reference	k_1/k_2	k_1[e] ($\times 10^{-18}$)	k_1[e, f] ($\times 10^{-18}$)	$k_{1(average)}$[e, g] ($\times 10^{-18}$)	τ_{O_3}[h]
Catechol （OH, OH)	Pseudo first order	–	–	13.4 ± 1.0	–	13.5 ± 1.1	8.4 h
	Relative rate	β-pinene[a]	0.86 ± 0.03	12.9 ± 0.5	13.6 ± 0.6		
		Isoprene[b]	1.12 ± 0.02	14.2 ± 0.3			
Guaiacol （OH, OCH3)	Pseudo first order	–	–	0.54 ± 0.31	–	0.40 ± 0.31	11.8 d
	Relative rate	p-cresol[c]	0.54 ± 0.04	0.27 ± 0.02	0.25 ± 0.02		
		o-cresol[d]	0.75 ± 0.03	0.22 ± 0.01			

*Notes: The indicated errors are twice the standard deviation arising from the least-squares fit of the data displayed in Figures 1−4 and do not include the uncertainty in the reference rate coefficients (estimated at 20% for β-pinene and isoprene and 100% for p-cresol[12]). [a]$k_{\beta\text{-pinene}} = 15 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.[1] [b]$k_{isoprene} = 12.7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.[1] [c]$k_{p\text{-cresol}} = 5 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}.[12] [d]$k_{o\text{-cresol}} = 3 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}.[12] [e]k is expressed in the unit cm^3 molecule^{-1} s^{-1}. [f]Average rate coefficient for both references. [g]Average rate coefficient for both methods. [h]Lifetime: $\tau_{O_3} = 1/k_{O_3}[O_3]$, where $[O_3] = 2.46 \times 10^{12}$ molecules cm^{-3} (100 ppbv; polluted atmosphere).[31]

good linearity with near zero intercepts (Figures 3 and 4). As already observed for guaiacol with the pseudo-first-order
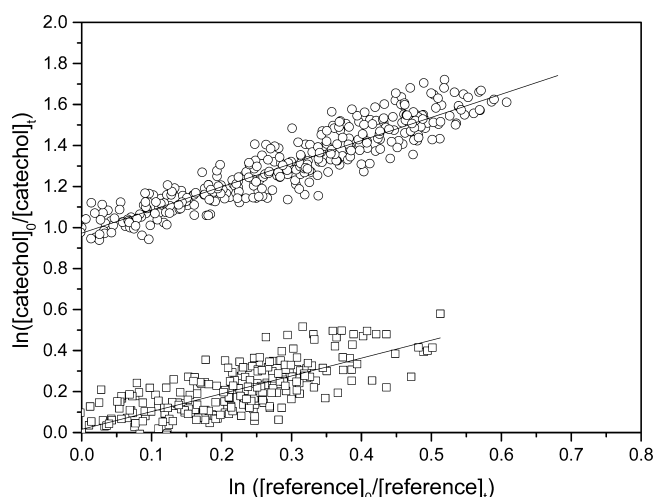
Figure 3. Relative rate plots for the reaction of O_3 with catechol at 294 $\pm$ 2 K, 1 atm and dry conditions. Reference compounds are β-pinene ($\square$) and isoprene ($\bigcirc$). Isoprene data have been vertically shifted by 1 unit for clarity. TMB was used as OH scavenger.
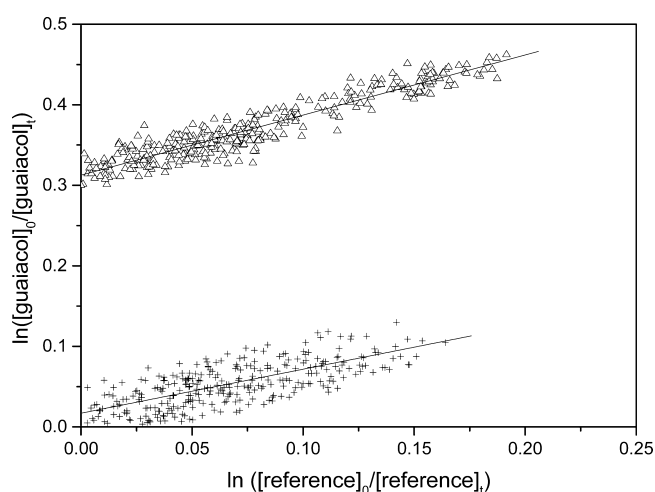
Figure 4. Relative rate plots for the reaction of O_3 with guaiacol at 294 $\pm$ 2 K, 1 atm and dry conditions. Reference compounds are o-cresol ($\triangle$) and p-cresol ($+$). O-cresol data have been vertically shifted by 0.3 unit for clarity. Cyclohexane was used as OH scavenger.

method, Figure 4 shows an y-axis intercept which can also be attributed to uncertainties on the rate coefficients due to the slowness of the reaction.

A summary of the slopes derived from the plots and the calculated O_3 rate coefficients is provided in Table 1. For catechol and guaiacol there is a good agreement between the values of the rate coefficients obtained using both reference compounds, so we calculate the average value of these two determinations. The indicated errors on $k_{catechol}$ and $k_{guaiacol}$ are twice the standard deviation arising from the least-squares fit of the data and do not include the uncertainty in the reference rate coefficients (estimated at 20% for β-pinene and isoprene and 100% for p-cresol and o-cresol[12]).

The rate coefficient for the reaction of catechol with ozone obtained with both references are in very good agreement, and they are also in accordance with that obtained using the

pseudo-first-order method which validates the determined value. Moreover, the experimental catechol rate coefficients can also be compared with literature data. As far as we know, the only previous work investigating the kinetic reaction of O_3 with catechol has been published by Tomas et al.[11] Using an FT-IR analytical method for monitoring the reactants, the authors employed the relative rate and pseudo-first-order methods to determine the rate coefficient for the reaction of O_3 with selected benzenediols. The value determined by Tomas et al. is $k_{catechol} = (9.60 \pm 1.12) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, where the quoted error represents only the statistical error (2σ) from the average of the rate coefficients of all individual experiments. The uncertainties in the FT-IR subtraction procedure and those attributed to the reference rate coefficients were not taken into account. Thus, they estimate a global uncertainty for each O_3 reaction rate coefficient determined in their work around 30–40%. Based on these considerations, we can infer that the rate coefficient for the catechol reaction with ozone determined in our work ($k_{catechol} = (13.5 \pm 1.1) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}) is in good agreement with the literature data.

For guaiacol, the rate coefficients determined with the pseudo-first-order method ($k_{guaiacol} = (0.54 \pm 0.31) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}) are twice the value measured with the relative method ($k_{guaiacol} = (0.25 \pm 0.02) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}). However, if we take into account the uncertainties (the given uncertainties for the relative method do not take into account those on the reference compounds, p-cresol and o-cresol, which are estimated at 100%), we can consider that the rate coefficient obtained with both methods are in agreement.

The comparison of $k_{catechol}$ and $k_{guaiacol}$ shows that the reactivity of catechol toward ozone is more than 1 order of magnitude higher than that for guaiacol. Broadly speaking, the ozonolysis of aromatic compounds is typically slow,[12,32] and the rate coefficients are generally lower than 10^{-19} cm^3 molecule^{-1} s^{-1}.[11] To our knowledge, the only exceptions to this general rule are catechol, methylcatechols, and styrenes.[11] In their article, Tomas et al.[11] attribute the high reactivity of catechol with O_3 to the presence of the two neighboring OH groups that raise the electron density at these sites and facilitate the electrophilic addition of O_3 to the ring across the carbons bearing the OH groups. They also propose that if such assumptions are correct, then enhanced gas-phase reactivity toward O_3 would be expected for other 1,2 disubstituted aromatics containing electron-donating groups such as OCH_3. Based on these speculations, we would have expected a higher value for the rate coefficient of guaiacol with ozone. Thus, our results suggest that the hydroxyl group activates the electrophilic addition of O_3 on the aromatic ring much more strongly than the methoxy group. However, if we consider the rate coefficients for the OH reaction with catechol ((10.4 ± 2.1) $\times 10^{-11}$)[29] and guaiacol ((7.53 ± 0.41) $\times 10^{-11}$),[15] which proceed mainly by addition of OH on the aromatic ring,[4,12] we can note that they are in the same range, suggesting that the activating effects of $-OCH_3$ and $-OH$ substituents are comparable; the hydroxyl group is, however, slightly more activating than the methoxy.[15] These two different behaviors suggest that the reaction of catechol and guaiacol with ozone and OH proceeds via different mechanisms. With the hydroxyl radical, the first step is known to be the OH addition on the aromatic ring, which is activated by electron donor groups in the ortho and para positions. With ozone, the reaction starts with the ozone addition on the C=C double bond and the formation of a Criegee intermediate (CI). The highest reactivity of catechol

could be attributed to the CI, which would be much more stabilized by −OH than by −OCH$_3$ groups. Another explanation could be the steric hindrance of the −OCH$_3$ substituent compared to that of the −OH, which induces a slower reactivity for guaiacol than for catechol. The characterization of oxidation products formed during these reactions would be very helpful to bring information about the chemical mechanisms involved in the reaction of catechols with ozone; these aromatics are the only ones known to react with ozone with such high rate coefficients.

RH Dependence. In this series of experiments, the rate coefficient of catechol toward O$_3$ was measured as a function of the relative humidity (1−80%) in order to test the influence of such a parameter on the catechol reactivity. This study was performed using the pseudo-first-order method; water was added into the chamber before the introduction of catechol and OH scavenger (cyclohexane). The ozone rate coefficients of catechol determined versus de relative humidity are displayed in Figure 5. As can be seen from Figure 5, the values of k
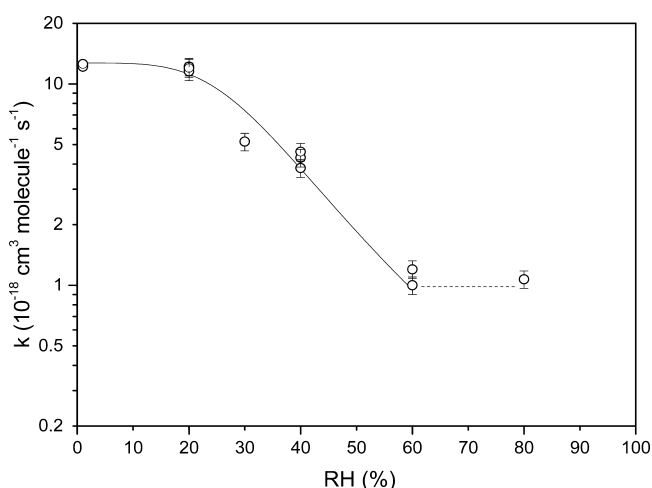
Figure 5. Rate coefficient for the reaction of O$_3$ with catechol as a function of relative humidity: $T = 294 \pm 2$ K, $P = 1$ atm. The error bars for RH in the range 20−80% represent an average uncertainty of 10% on the measurements of k.

remain independent of the relative humidity for RH ≤ 20%. Then, when RH exceeds 20%, the O$_3$ rate coefficient shows a negative dependence and reaches a value which is approximately 1 order of magnitude lower at 60% ($k \cong 1.0 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}) than at 20% ($k \cong 11.8 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}). Then, for RH between 60% and 80%, the rate coefficient does not vary significantly with RH.

The solid line in Figure 5 represents the fit to the experimental data according to the following empirical equation that describes the catechol rate coefficient with ozone for RH between 1 and 60%:

$$k = \frac{1.96 \times 10^{-11}}{1.54 \times 10^6 + RH^{4.1}}$$

We suggest that this effect of RH on the ozone rate coefficient of catechol could be attributed to intermolecular hydrogen bonds between the two hydroxyl (OH) groups of catechol and water molecules.[33,34] Indeed, it has been shown through theoretical calculations that the hydroxyl groups in catechol can interact with water molecules via intermolecular hydrogen bonds forming cyclic catechol−H$_2$O complexes.[34] Several

isomers may account for the configuration of these catechol−H$_2$O clusters both in aqueous solution and in the gas phase.[34] Thus, in the present study, the inverse dependence of the rate coefficient on RH could be attributed to the formation of these catechol−H$_2$O intermediates in which the accessibility of the C=C double bond located between the two OH groups on the aromatic ring would be probably reduced and the O$_3$ addition disfavored. The increase in the relative humidity enhanced the steric hindrance of the C=C double bond and thus reduces the catechol ozone rate coefficient. Below 20% of RH, this effect does not seem to have any influence on the catechol reactivity as it is indicated by the stability of the ozone rate coefficient. Similarly, as above 60% of RH the k value does not decrease anymore, this would suggest that this steric hindrance has reached an upper limit. The interpretation of the role of water on the catechol rate coefficient with ozone is tricky and it would be very useful to investigate such an effect on other unsaturated 1,2-diols in order to clarify this issue.

■ ATMOSPHERIC IMPLICATIONS AND CONCLUSIONS

The rate coefficients determined in this work can be used to calculate the atmospheric lifetimes of catechol and guaiacol with respect to their reaction with ozone (Table 1). The atmospheric lifetimes (τ_{O3}, in s) can be calculated from eq V

$$\tau_{O_3} = \frac{1}{k_{O_3}[O_3]} \qquad (V)$$

where k_{O3} is the second order rate coefficient for the homogeneous gas-phase ozonolysis of the compound studied (in cm^3 molecule^{-1} s^{-1}) and [O$_3$] the ozone concentration (in molecules cm^{-3}). Thus, assuming an average O$_3$ concentration of 100 ppbv (2.46×10^{12} molecules cm^{-3}; polluted atmosphere),[31] the calculated atmospheric lifetime of guaiacol is 11.8 days (see Table 1) which is significantly longer than that with OH radicals (2.3 h[15]) or Cl atoms (18.7 h[9]). Thus, the OH oxidation is the dominant chemical removal pathway of guaiacol in the troposphere during daytime and the ozonolysis is a minor tropospheric sink. In order to complete our knowledge on the various competing atmospheric degradation pathways of this organic compound, kinetic data for its reaction with NO$_3$ radicals are still required.

For catechol, kinetic data were found to be inversely dependent on RH, with a slower O$_3$ reactivity observed above 20%. The formation of catechol−H$_2$O intermediates via intermolecular hydrogen bonds that induce steric hindrance has been proposed to explain such a reduction in the ozone reactivity. To our knowledge, this work represents the first study on the dependence of the ozone rate coefficients of VOCs with the relative humidity and precisely for an oxygenated aromatic (catechol). The atmospheric lifetime of catechol with respect to its reaction with ozone for RH ≤ 20% (τ = 8.4 h) can be compared to that of OH radicals (τ = 1.7 h),[14] Cl atoms (14.6 h),[10] and NO$_3$ radicals (τ = 20 s).[8] On the basis of these values, one can infer that the ozonolysis can be considered as a negligible removal pathway for catechol during the night. However, during daytime, this reaction has to be considered, especially in polluted environment (where high ozone levels can be encountered) under low RH level (<20%). Moreover, as for high RH level (≥60%), the O$_3$ rate coefficient of catechol is 1 order of magnitude lower than for RH below 20%, the corresponding lifetime is thus about 10 times longer

(τ = 102.6 h). Thus, this indicates that in many environments the ozonolysis is a minor sink for catechol also during the day, as its main sink is its reaction with OH.

Previous studies[11,35] have shown muconic acid as a gas-phase oxidation product for the catechol reaction with ozone, and a formation of secondary organic aerosols (with yields between 17% and 86%) was also observed.[16] Therefore, future works on the reactivity of catechol with ozone should be extended to include the identification and quantification of degradation products formed both in gas- and particle- phases. This will be helpful for a better understanding of the chemical mechanisms involved in the catechol ozonolysis.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Plots in the form of eq III for the reaction of O_3 with catechol (Figure S.1) and guaiacol (Figure S.2) at 294 ± 2 K, 1 atm, and dry conditions. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b00174.

AUTHOR INFORMATION

Corresponding Author

* Phone: +33 321996405. Fax: +33 321996401. E-mail: coeur@univ-littoral.fr.

Notes

The authors declare no competing financial interest.

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