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Rate Coefficients for the Gas-Phase Reaction of NO₃ Radicals with Selected Dihydroxybenzenes

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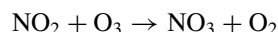
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ABSTRACT: Using a relative kinetic technique, rate coefficients have been determined at (298 ± 2) K and atmospheric pressure for the gas-phase reactions of the NO₃ radical with three vicinal dihydroxy aromatic compounds. The experiments were carried out in a 1080-l quartz glass reactor at the Bergische Universität Wuppertal and in the European Photoreactor (EUPHORE), Valencia, Spain. The rate coefficients obtained (in units of cm³ molecule⁻¹ s⁻¹) using 2,3-dimethyl-2-butene as the reference hydrocarbon were $k_{\text{NO}_3}(\text{1,2-dihydroxybenzene}) = (9.8 \pm 5.0) \times 10^{-11}$, $k_{\text{NO}_3}(\text{1,2-dihydroxy-3-methylbenzene}) = (17.2 \pm 5.6) \times 10^{-11}$, and $k_{\text{NO}_3}(\text{1,2-dihydroxy-4-methylbenzene}) = (14.7 \pm 6.5) \times 10^{-11}$. This study represents the first kinetic investigation of the reactions of the NO₃ radical with dihydroxybenzenes. © 2004 Wiley Periodicals, Inc. *Int J Chem Kinet* 36: 577–583, 2004

INTRODUCTION

The gas-phase chemistry of the nitrate radical and its important role in atmospheric chemistry have been extensively discussed in the literature [1–6]. The nitrate radical is in many situations an important nighttime ox-

idizing species, removing, for example, hydrocarbons, which would otherwise be available for daytime ozone formation. NO₃ is generated in the atmosphere by the reaction of NO₂ with O₃ and temporarily stored as N₂O₅ in an equilibrium rapidly established with NO₂:



Aromatic hydrocarbons such as benzene and alkyl-substituted benzenes are important constituents of gasoline, automobile exhaust, and urban air [4]. In the atmosphere, benzene and the alkyl-substituted benzenes react mainly with the OH radical and this

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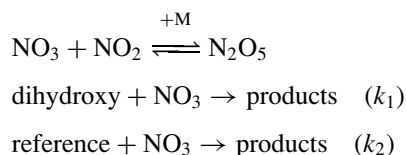
OH-radical-initiated photooxidation leads to hydroxylation of the ring. In the cases of benzene and toluene the addition of OH to the aromatic ring is known to produce phenol and the cresol isomers with yields of about 25 to 50% [8–11] and 20% [4,12–14], respectively. While phenol and the cresol isomers react only slowly with O₃ [4,15], their reaction with OH [4,16] and NO₃ [4,16] radicals is rapid. Recently it has been shown that the OH-radical-initiated photooxidation of phenol [17,18] and the cresol isomers [17] leads to the formation of (alkyl)-1,2-dihydroxybenzenes in high yields. The various vicinal dihydroxybenzenes have been shown to react rapidly with the OH radical [19] and moderately fast with ozone [20], with room temperature rate coefficients in the range $(1.04\text{--}2.05) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ for reactions with the OH radical and $(0.96\text{--}2.81) \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ for reactions with ozone. To date, no kinetic data are available on either gas or aqueous phase reactions of the NO₃ radical with (alkyl)-dihydroxybenzenes.

As part of systematic studies on the atmospheric chemistry of dihydroxybenzenes, we present here investigations on the kinetics of the reactions of the NO₃ radical with three dihydroxybenzenes, 1,2-dihydroxybenzene, 1,2-dihydroxy-3-methylbenzene, and 1,2-dihydroxy-4-methylbenzene, performed in two large-volume chamber facilities.

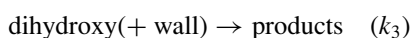
EXPERIMENTAL

Experiments were performed in the photoreactor systems at (i) the Bergische Universität Wuppertal [21] and (ii) the European Photoreactor (EUPHORE), Valencia, Spain [22]. Complete descriptions of these facilities can be found in the references given, and only details relevant to the present study will be given here.

In the kinetic method used in both chambers, the relative disappearance rates of a dihydroxybenzene (dihydroxy) and a reference compound were monitored in the presence of NO₃ radicals, which were generated by the thermal decomposition of N₂O₅.



Control experiments showed that the dihydroxybenzenes were also subject to losses in the absence of NO₃ radicals, mainly due to wall adsorption.



No wall-deposition losses were observed for the reference hydrocarbon. On the basis of the above reactions the following rate laws are valid for the compounds under investigation:

$$-\frac{d[\text{dihydroxy}]}{dt} = k_1[\text{NO}_3][\text{dihydroxy}] + k_3[\text{dihydroxy}] \quad (1)$$

$$-\frac{d[\text{reference}]}{dt} = k_2[\text{NO}_3][\text{reference}] \quad (2)$$

Integration and combination of Eqs. (1) and (2) leads to

$$\ln \frac{[\text{dihydroxy}]_{t_0}}{[\text{dihydroxy}]_t} - k_3(t - t_0) = \frac{k_1}{k_2} \ln \frac{[\text{reference}]_{t_0}}{[\text{reference}]_t} \quad (3)$$

where k_1 and k_2 are the rate coefficients for the reactions of the dihydroxybenzene and reference compound with NO₃ radicals, respectively. The terms $[\text{dihydroxy}]_{t_0}$, $[\text{dihydroxy}]_t$, $[\text{reference}]_{t_0}$, and $[\text{reference}]_t$ give the concentrations of the dihydroxybenzene and reference hydrocarbon at the times t_0 (initial concentration) and t (during the experiment). Plots of $\ln([\text{dihydroxy}]_{t_0}/[\text{dihydroxy}]_t) - k_3(t - t_0)$ as a function of $\ln([\text{reference}]_{t_0}/[\text{reference}]_t)$ for each individual dihydroxybenzene and reference hydrocarbon should yield a straight line with slope k_1/k_2 . The rate coefficient k_1 can be placed on an absolute basis using the known rate coefficient for the reference hydrocarbon, k_2 . 2,3-Dimethyl-2-butene with a rate coefficient of k (298 K) = $(5.72 \pm 0.21) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ [16] was employed as the reference hydrocarbon for the experiments in both chambers. This compound was chosen as the reference hydrocarbon because it is one of the few compounds that have a well-established rate coefficient of a magnitude similar to that expected for the reaction of NO₃ with the dihydroxybenzenes. In addition, 2,3-dimethyl-2-butene was chosen because it has interference-free adsorption in the infrared and its absorption bands do not overlap with those of the aromatic compounds under study.

Two different ways of adding the N₂O₅ were used in the experiments in both chambers. First, experiments were performed in which N₂O₅ was added as prepared, and second, experiments were performed in which extra NO₂ was added to N₂O₅ from the beginning of the experiments in an attempt to drive the equilibrium between N₂O₅, NO₂, and NO₃ radicals toward N₂O₅ and ensure that the reaction times were prolonged beyond the N₂O₅ mixing time. As can be seen from the NO₃ radical steady-state concentrations given

below, a considerable variation in the NO₃ concentration was obtained in the Wuppertal experiments, but only a marginal change was observed in the Euphore experiments.

Studies at the Bergische Universität Wuppertal

The experiments were performed in a darkened cylindrical quartz glass reactor with a volume of 1080 L. The reactor consists of two tubes connected by a central flange, has a length of 6.2 m and an inner diameter of 0.47 m, and is closed at both ends by aluminum flanges. The reactor can be evacuated to a pressure of $<10^{-3}$ mbar by a turbo molecular pump system. To ensure homogeneous mixing of the reactants, three fans with Teflon blades are mounted inside the reactor.

The consumption of reactants and reference compound were monitored by long-path Fourier transform infrared (FT-IR) spectroscopy using an optical path length of 484.7 ± 0.8 m and a resolution of 1 cm^{-1} . The experiments were performed at 1000 mbar total pressure of synthetic air and at temperature 298 ± 2 K. The experimental procedure was as follows. The 1,2-dihydroxybenzene compound under investigation and the reference hydrocarbon, 2,3-dimethyl-2-butene, were injected into the chamber under reduced pressure. The chamber was then pressurized to 1000 mbar with synthetic air. For the first 5 min the concentration–time behaviors of the two compounds were monitored by FT-IR spectroscopy; i.e., 5 spectra derived from 64 interferograms co-added over a period of 1 min were recorded. N₂O₅ was then flushed into the chamber through a Teflon line at a flow rate of 50–100 mL/min for 15 min by evaporating solid N₂O₅. This procedure delivered N₂O₅ to the chamber at a rate of about 20–25 ppbV/min. N₂O₅ was prepared by the method of Schott and Davidson [23]. In total, the measurement time period for one experiment was about 30 min. On the basis of the decay of the reference compound 2,3-dimethyl-2-butene, a variation in the NO₃ radical steady-state concentrations of between 0.36×10^7 and 3.25×10^7 molecule cm⁻³ was obtained by variation in the concentration of NO₂ added to N₂O₅, i.e., a concentration change of approximately a factor of 8.

The initial reactant concentration range was $(1.2\text{--}4.8) \times 10^{13}$ molecule cm⁻³ for the 1,2-dihydroxybenzene compounds and reference hydrocarbon. As discussed above, in some experiments, up to 2.4×10^{13} molecule cm⁻³ of NO₂ was added. A minimum of five experiments was performed for each dihydroxybenzene compound.

Control experiments showed that wall loss of the 1,2-dihydroxybenzenes in 1 atm of air in the chamber

was typically between 35 and 40% h⁻¹. To obtain the wall loss typically, the compound (about 0.5 ppm) was introduced alone into the reaction chamber and synthetic air was added as diluent gas to a total pressure of around 1000 mbar. The gas mixture inside the chamber was then left for some minutes to ensure homogeneous mixing. The decay of the compound was monitored using its infrared absorption bands. Spectra were recorded by co-adding 128 scans per spectrum over a period of 2 min and collecting 15 such spectra during 30 min. The wall loss rate (k_3) for the compound was then derived from the slope of plots of $\ln([C_0]/[C_t])$ against time, where C_0 is the initial concentration of the compound at $t = 0$ and C_t its concentration at time t .

Between experiments the chamber was evacuated to approximately 10^{-3} mbar using the pumping system. Blank experiments after pumping showed that there was no off-gassing of the dihydroxybenzenes or reaction products from the chamber walls. No wall deposition loss was observed in the case of reference hydrocarbon.

Studies at the EUPHORE Chamber

The European Photoreactor (EUPHORE) is located on top of the building of the Centro de Estudios Ambientales del Mediterraneo (CEAM) near Valencia, Spain. EUPHORE consists of two reaction chambers of identical size. Chamber A, positioned at the northwest side of the building, was used for the experiments presented here. The chamber consists of a hemispherical FEP bag with a volume of about 200 m³ and a surface-to-volume ratio of about 0.96 m^{-1} . Purified air and chemical reactants are introduced through ports located on the floor, and gas mixtures are homogenized using mixing fans. A White mirror system, located inside the chamber and operated at an optical path of 326.8 m, was used for in situ monitoring of reactants and products by FT-IR spectroscopy. The FT-IR spectrometer (Nicolet Magna 550) equipped with a liquid nitrogen cooled MCT detector was operated at a spectral resolution of 1 cm^{-1} .

The experiments were performed at atmospheric pressure and at temperature 296 ± 2 K in purified air. Four kinetic experiments were performed on 1,2-dihydroxybenzene and three on the methyl isomers. The experimental procedure was as follows. The chamber was flushed with purified air overnight for approximately 10–12 h before the start of each experiment. The dihydroxybenzene compounds were added to the chamber using a spray inlet system. Prior to injection, a weighed amount of dihydroxybenzene was first dissolved in 5 mL of distilled water. 2,3-Dimethyl-2-butene and NO₂ were injected by means of a syringe

into a glass tube (impinger) connected to the chamber via a Teflon line. The initial reactant concentration range was $(5\text{--}7.2) \times 10^{12}$ molecule cm^{-3} for the reactant compounds and reference hydrocarbon. In some experiments, up to 7×10^{12} molecule cm^{-3} of NO_2 was added. N_2O_5 was produced by titration of a flow of NO_2 with O_3 prior to entry into the chamber and was added continuously to the chamber through a Teflon line. This procedure resulted in a delivery rate of about 1.2 ppbV/min for N_2O_5 to the chamber. On the basis of the decay of the reference compound 2,3-dimethyl-2-butene, a variation in the NO_3 radical steady-state concentrations of between 0.72×10^6 and 1.1×10^6 molecule cm^{-3} was obtained by variation in the concentration of NO_2 added to the chamber, i.e., less than a factor of 2.

Each experiment on the dihydroxybenzene/reference/ N_2O_5 reaction system was performed over a period of approximately 2 h in darkness using in situ FT-IR spectroscopy to monitor the compounds. Infrared spectra were derived from 130 co-added scans, which yielded a time resolution of 2.5 min. The experiment was usually terminated when ca 70–80% of the reactant had been consumed. The reaction chamber was pressurized continuously during the experiments to compensate for losses due to leaks and air drawn by external analytical instrumentation. This dilution was monitored by FT-IR using SF_6 as an inert tracer gas. The dilution loss was typically $3\% \text{ h}^{-1}$. The sum of the surface deposition and dilution rates for the dihydroxybenzenes was determined by observing the decay of their IR absorption feature prior to addition of N_2O_5 and NO_2 . Loss rates of about $20\% \text{ h}^{-1}$ were measured. In the case of the reference hydrocarbon, no wall deposition loss was observed.

All the hydrocarbons studied (1,2-dihydroxybenzene, 1,2-dihydroxy-3-methylbenzene, and 1,2-dihydroxy-4-methylbenzene) as well as the reference hydrocarbon (2,3-dimethyl-2-butene) were used as supplied by Aldrich Chemical Company and had stated purities of >98%.

RESULTS AND DISCUSSION

Plots of the kinetic data according to Eq. (3) for the experiments performed in Wuppertal and the EUPHORE chambers are shown in Figs. 1–6. Reasonably linear plots were obtained in both chambers. As seen in all the figures, there is no discernable difference in the results between the experiments performed at low or high NO_2 for both chambers; i.e., the kinetic behavior was independent of the $[\text{N}_2\text{O}_5]/[\text{NO}_2]$ ratio supporting the

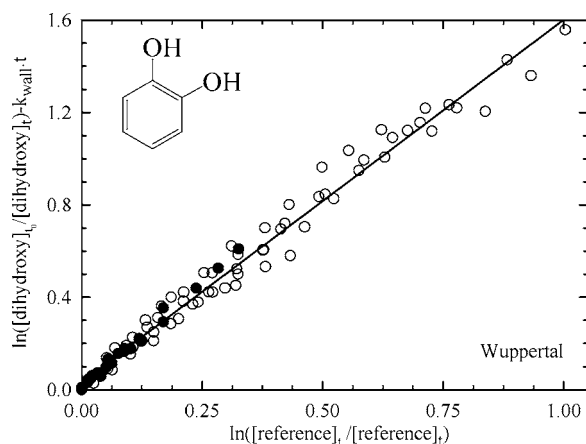


Figure 1 Plot of the kinetic data according to Eq. (3) for the reaction of 1,2-dihydroxybenzene with NO_3 radicals in the 1080 l quartz glass reaction chamber. The reference hydrocarbon is 2,3-dimethyl-2-butene: (○) low NO_2 ; (●) high NO_2 .

conclusion that the reaction of 1,2-dihydroxybenzenes takes place with NO_3 radicals and not with N_2O_5 or with NO_2 .

The k_1/k_2 ratios determined from the slopes of the straight-line plots in the figures are listed in Table I. The values of the rate coefficients k_1 for the reaction of NO_3 with the various dihydroxybenzenes have been put on an absolute basis using k_2 (298 K) $= (5.72 \pm 0.21) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [16]. The errors quoted in Table I are a combination of the 2σ statistical errors from the linear regression analysis, the error given for the recommended value of the reference compound in the literature, and the errors arising from the subtraction procedure and from the

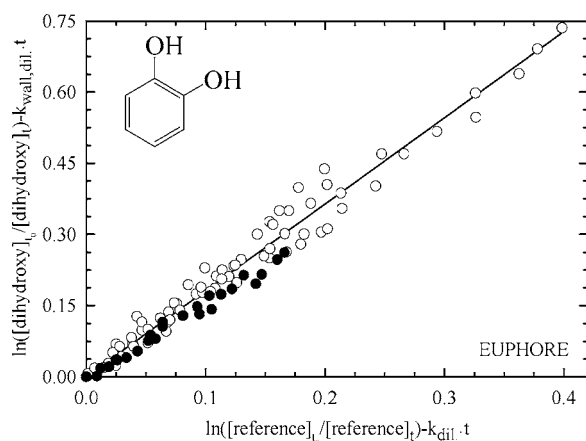


Figure 2 Plot of the kinetic data according to Eq. (3) for the reaction of 1,2-dihydroxybenzene with NO_3 radicals in the EUPHORE chamber. The reference hydrocarbon is 2,3-dimethyl-2-butene: (○) low NO_2 ; (●) high NO_2 .

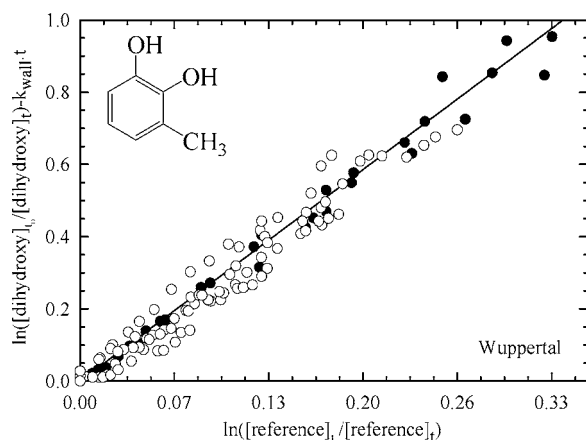


Figure 3 Plot of the kinetic data according to Eq. (3) for the reaction of 1,2-dihydroxy-3-methylbenzene with NO₃ radicals in the 1080 l quartz glass reactor chamber. The reference hydrocarbon is 2,3-dimethyl-2-butene: (○) low NO₂; (●) high NO₂.

wall-deposition correction of the reactant. The corrections for wall deposition in the Wuppertal chamber experiments were approximately 40% compared to NO₃ reaction; in the Euphore chamber the correction for wall and dilution loss was also typically 40% compared to NO₃ reaction.

Since the values of the rate coefficients determined in the two chambers are indistinguishable within the experimental uncertainties, we choose to quote final values ($k_{1(\text{average})}$) in Table I, which are the average of the individual measurements, together with error lim-

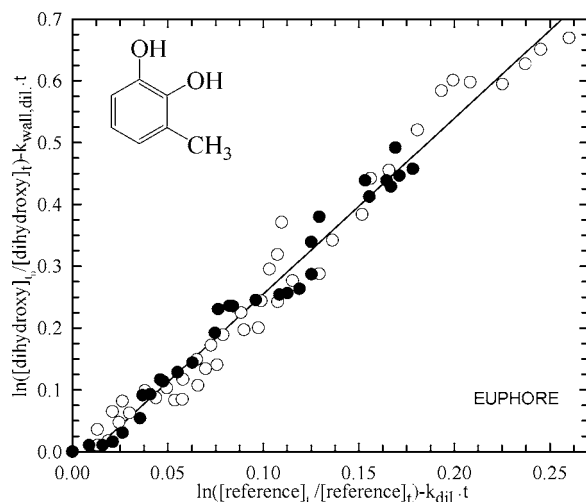


Figure 4 Plot of the kinetic data according to Eq. (3) for the reaction of 1,2-dihydroxy-3-methylbenzene with NO₃ radicals in the EUPHORE chamber. The reference hydrocarbon is 2,3-dimethyl-2-butene: (○) low NO₂; (●) high NO₂.

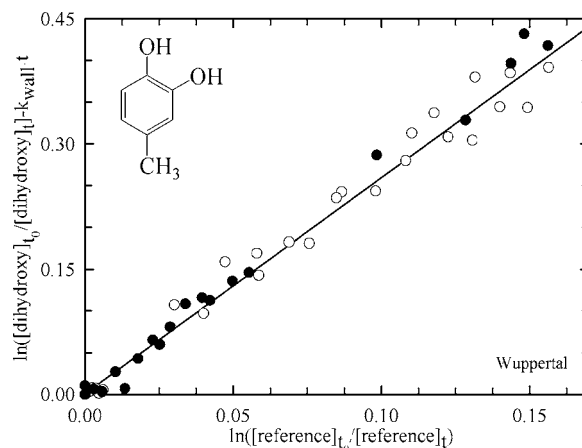


Figure 5 Plot of the kinetic data according to Eq. (3) for the reaction of 1,2-dihydroxy-4-methylbenzene with NO₃ radicals in the 1080 l quartz glass reactor chamber. The reference hydrocarbon is 2,3-dimethyl-2-butene: (○) low NO₂; (●) high NO₂.

its, which encompass the extremes of the individual measurements.

This study represents the first determination of the rate coefficients for the reaction of NO₃ radicals with 1,2-dihydroxybenzene, 1,2-dihydroxy-4-methylbenzene, and 1,2-dihydroxy-3-methylbenzene, and therefore a comparison with literature values is not possible.

As seen from Table I, the reactivity of the 1,2-dihydroxybenzenes takes the following order: k_{NO_3} (1,2-dihydroxybenzene) < k_{NO_3} (1,2-dihydroxy-4-methylbenzene) < k_{NO_3} (1,2-dihydroxy-3-methylbenzene). Since the reaction of NO₃ with phenolic compounds is believed to proceed via an overall H-atom

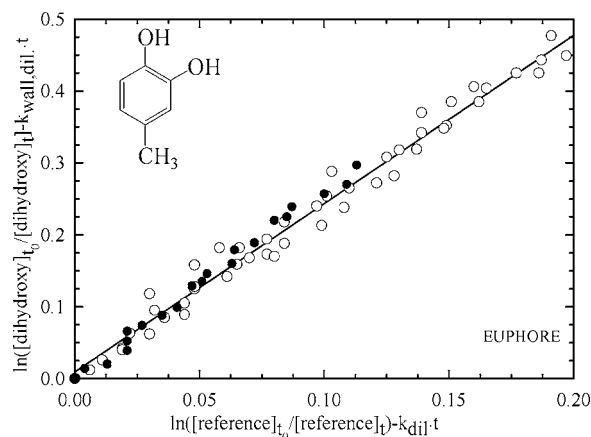
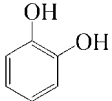
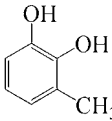
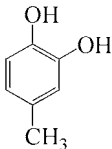


Figure 6 Plot of the kinetic data according to Eq. (3) for the reaction of 1,2-dihydroxy-4-methylbenzene with NO₃ radicals in the EUPHORE chamber. The reference hydrocarbon is 2,3-dimethyl-2-butene: (○) low NO₂; (●) high NO₂.

Table I Rate Coefficients for the Reaction of NO₃ radicals with 1,2-Dihydroxybenzene, 1,2-Dihydroxy-3-methylbenzene, and 1,2-Dihydroxy-4-methylbenzene

Compound	10801 Reactor		EUPHORE Chamber		$k_1(\text{average})$ (10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹)	$\tau_i = 1/k_i$ [NO ₃]
	k_1/k_2	k_1 (10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹)	k_1/k_2	k_1 (10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹)		
 1,2-Dihydroxybenzene	1.58 ± 0.07	9.03 ± 3.7	1.88 ± 0.11	10.6 ± 4.3	9.8 ± 5.0	42 s
 1,2-Dihydroxy-3-methylbenzene	3.01 ± 0.10	17.3 ± 5.6	2.93 ± 0.06	17.1 ± 4.8	17.2 ± 5.6	24 s
 1,2-Dihydroxy-4-methylbenzene	2.80 ± 0.10	16.0 ± 5.2	2.36 ± 0.06	13.4 ± 5.0	14.7 ± 6.5	28 s

abstraction mechanism, which is preceded by an electrophilic addition of NO₃ to the aromatic ring [4], this order is what would be expected from a consideration of the structures of the compounds. The faster rate coefficients for the reactions of the methylated 1,2-dihydroxybenzenes compared to 1,2-dihydroxybenzene can be attributed to the positive inductive effect of the methyl group.

At present there is no reliable method to quantitatively estimate rate coefficients for the reactions of the NO₃ radical with aromatic hydrocarbons. However, it is interesting to make a comparison with the recommended rate coefficients for the reaction of NO₃ radicals with mono-hydroxylated analogues at 298 K [4]. The rate coefficient for the reaction of NO₃ with 1,2-dihydroxybenzene at 298 K is about a factor of 24 higher than that for phenol [$k_{\text{NO}_3} = (3.8 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$]. For 1,2-dihydroxy-3-methylbenzene, the measured NO₃ rate constant is factors of 12.3 and 15.6 higher than those for the corresponding reactions of *o*-cresol [$k_{\text{NO}_3} = (1.43 \pm 0.16) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$] and *m*-cresol [$k_{\text{NO}_3} = (1.1 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$], respectively. For 1,2-dihydroxy-4-methylbenzene, the rate coefficient is a factor of 14.5 higher than that for *m*-cresol and *p*-cresol [$k_{\text{NO}_3} = (1.1 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$], respectively.

On average, the addition of the second hydroxyl group to phenol and the cresols to form 1,2-

dihydroxybenzenes increases the reactivity of the compounds toward the NO₃ radical by a factor of about 16. The observed differences in reactivity can be ascribed to the activating effect of the hydroxyl groups toward electrophilic reactions and the magnitude of the *o*- and *p*-site directing strength of the substituents.

CONCLUSIONS

1,2-Dihydroxybenzene and its methylated derivatives react rapidly with NO₃ radicals, and this almost certainly constitutes the major nighttime atmospheric sink for these compounds. Using the kinetic data obtained in the present study, in combination with a nighttime tropospheric nitrate radical concentration of [NO₃] = $2.4 \times 10^8 \text{ molecule cm}^{-3}$ [24], an estimated atmospheric residence time τ_i of a compound *i* due to reaction with NO₃ radicals can be calculated according to the relationship $\tau_i = (k_i[\text{NO}_3])^{-1}$. We consider that the NO₃ radical concentration chosen is that which is most likely to prevail in the polluted urban areas, where formation of 1,2-dihydroxybenzenes will predominate. The residence times thus obtained are presented in Table I. The 1,2-dihydroxybenzenes will have very short atmospheric lifetimes during nighttime and therefore can influence the chemical oxidant formation on a local scale.

The rate coefficients for the reaction of 1,2-dihydroxybenzene, 1,2-dihydroxy-4-methylbenzene, and 1,2-dihydroxy-3-methylbenzene with OH radicals are 1.04×10^{-10} , 2.05×10^{-10} , and $1.56 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, respectively [19]. Using this kinetic data for OH and the NO₃ kinetic data from the present study, the relative contribution of each species to the degradation of the dihydroxybenzenes during the daytime can be estimated. On the basis of a daytime average tropospheric OH radical concentration of $1.6 \times 10^6 \text{ molecule cm}^{-3}$ [25–27] and NO₃ radical concentration of $3.1 \times 10^6 \text{ molecule cm}^{-3}$ [24], it can be shown that 1,2-dihydroxybenzene will react during the daytime about 60% with OH and about 40% with NO₃ radicals. Therefore, reaction of 1,2-dihydroxybenzenes with NO₃ is also a potentially important daytime oxidation process for these compounds nearly on par with the OH-radical-initiated photooxidation. Finally an additional important sink for dihydroxybenzene compounds in the atmosphere will be removal by wet and dry deposition. Dihydroxybenzenes are polar molecules with very high Henry's law constants at 25°C [28] and can also be efficiently scavenged from the gas phase by rain and fog droplets.

As mentioned in the Results section, the mechanism of the reaction of NO₃ with 1,2-dihydroxybenzene and its methylated derivatives is probably initial addition of NO₃ to the ring followed by H-atom abstraction from an OH group. In any event the formation of products with low vapor pressures such as nitrodihydroxybenzene is highly probable. Therefore, the products from the NO₃-initiated oxidation of 1,2-dihydroxybenzenes (or their further oxidation products) are potentially important contenders as precursors for the formation of secondary organic aerosol (SOA). Detailed studies of the oxidation products from the NO₃-initiated oxidation of 1,2-dihydroxybenzenes, particularly with respect to quantification of their SOA formation potential, seem warranted.

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