#### **RESEARCH PAPER**

## Kinetics and mechanisms of reactions of the nitrate radical $(NO_3)$ with substituted phenols in aqueous solution

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## Second order rate constants were obtained for the reactions of the nitrate radical (NO<sub>3</sub>) with substituted phenols in aqueous solutions at 298 K and pH = 0.5. The following compounds were investigated and the corresponding rate constants are reported: (1) 2-hydroxyphenol $[k_1 = (5.6 \pm 0.8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (2) 2-methylphenol $[k_2 = (8.5 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (3) 2-ethylphenol $[k_3 = (6.7 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (4) 2-methoxyphenol $[k_4 = (1.1 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (5) 2-nitrophenol $[k_5 = (2.3 \pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}]$ ; (6) 2-cyanophenol $[k_6 = (3.1 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (7) 2-fluorophenol $[k_7 = (5.5 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (8) 2-chlorophenol $[k_8 = (2.9 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (9) 2-bromophenol $[k_9 = (2.7 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (10) 2-phenylphenol $[k_{10} = (2.4 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (11) 4-hydroxyphenol $[k_{11} = (8.8 \pm 0.5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (12) 4-aminophenol $[k_{12} = (8.1 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ ; (13) 4-chlorophenol $[k_{13} = (1.7 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}]$ ; (14) 4-bromophenol $[k_{14} = (1.0 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}]$ ; (15) 4-hydroxybenzen ethyl ester $[k_{15} = (8.0 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}]$ . Moreover, the temperature dependence of the reaction of NO<sub>3</sub> with four *ortho*-substituted phenols, (a) 2-methylphenol, (b) 2-ethylphenol, (c) 2-hydroxyphenol and (d) 2-methoxyphenol were investigated in the temperature range of $278 \le T \le 318 \text{ K}$ and the corresponding activation parameters were obtained for the first time. A comparison of the reactivity of NO<sub>3</sub> towards other aromatics present in the tropospheric aqueous phase such as substituted benzenes and substituted benzoic acid was undertaken.

### 1. Introduction

Since the industrial revolution, a strong anthropogenic influence on the tropospheric composition has taken place. Many gases, originating entirely from anthropogenic sources, are at the parts per trillion levels but may still have significant effects on the environment. Some trace gases control or affect the Earth's climate and habitability.<sup>1,2</sup>

The gas phase oxidation of the aromatic hydrocarbons by light, OH,  $NO_x$  and  $O_3$  leads to products with increased polarity that might favour a phase transfer to the tropospheric liquid phase. Moreover, the low vapour pressure of many of these products initiates particle formation.<sup>3,4</sup> Most of the substituted benzenes have been identified as components of the atmospheric aerosol. These aromatic hydrocarbons are particularly interesting among the other volatile organic compounds (VOCs) due to their physical and chemical properties. Multiphase aromatic conversion mainly driven by radicals such as OH and NO3 could play an important role in multiphase tropospheric chemistry.5 Such chemistry might be involved in the multiphase formation of nitroaromatics following NO<sub>x</sub> emissions. Aromatic VOCs such as nitroaromatic compounds might have adverse effects on ecosystems and on human health.

In the present work, the rate coefficients for reactions of the nitrate radical  $(NO_3)$  with a number of *ortho-* and *para*-substituted phenols have been determined for the first time using the laser flash photolysis-long path laser absorbance (LFP-LPLA) technique. Rate constants for reactions of nitrate radical in aqueous solution have been studied mainly at 298 K and in some cases the temperature dependency of the rate constants have also been investigated.

### 2. Experimental

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A laser flash photolysis technique was used to produce  $NO_3$  in aqueous solution coupled with a long path laser absorption

setup to determine the initial concentration of the thus formed radicals and to observe their time dependent decay for kinetic studies.

The laser flash photolysis set-up consists of a multigas excimer laser (Mod. Compex 201, Lambda-Physik) operated at  $\lambda = 248$  nm (KrF gas fill, W = 700 mJ) with pulse durations of 10-40 ns. The optical detection system comprises a heliumneon laser (Mod. 35-2, Spindler and Hoyer) operated at 632 nm the light of which was passed into a combination of two dielectrically coated mirrors in White configuration<sup>6</sup> and folded 32 times through the reaction cell resulting in a total optical pathlength of d = 192 cm. The electrical output of the photodiode was amplified and fed to a digital storage oscilloscope (Mod. Delta Classic, Gould) connected to a computer. The timing of the experiment was controlled by a trigger generator. The thermostated reaction cell used in the present work consisted of a glass cylinder with an inner diameter of 50 mm and an inner length of 60 mm with a total volume of 118 ml. The front windows of the cell are plane plates made of fused silica. The experimental set-up is described in more detail elsewhere.

The formation of NO<sub>3</sub> following the flash photolysis of nitrate anions (0.01 M, pH = 0.5 with HClO<sub>4</sub>) at  $\lambda = 248$  nm occurs as follows:<sup>8</sup>

$$NO_{3}^{-} + h\nu (\lambda = 248 \text{ nm}) + H^{+} \rightarrow OH + NO_{2} \quad (R-a)$$
$$OH + HNO_{3} \rightarrow NO_{3} + H_{2}O \qquad (R-b)$$

The decays of NO<sub>3</sub> in the presence of variable amount of excess reagent were measured under pseudo-first order conditions, therefore the reactant concentrations were chosen to be at least ten times higher than the initial maximal radical concentrations, typically  $[NO_3]_0 = 1 \times 10^{-7}$  M. Normally, eight first order decay rate constants were determined and averaged for every reactant concentration. The errors stated throughout this work are statistical errors for a confidence interval of 95%.

In Fig. 1a a typical decay trace of nitrate radical in the presence of 2-bromophenol  $(2 \times 10^6 \text{ M})$  at 298 K and pH = 0.5 is shown.

As can be seen from the logarithmic decay reported in Fig. 1b, in the time range of the kinetic measurements a good linearity is obtained, and under pseudo-order conditions the first order rate constant could be obtained from the regression line.

All solutions were freshly prepared before every single experiment and the reagents used in this study were purchased from Sigma-Aldrich at the highest purity available (>99.9%).

The phenols are known to absorb strongly in the UV-region and they might have a relative absorption maximum also in the visible depending upon the ring substituent, therefore, before any kinetic measurements, the UV spectra of the compounds considered in this study were taken in order to avoid possible interference with both excimer ( $\lambda = 248$  nm) and analytical  $(\lambda = 632.8 \text{ nm})$  light. To better understand the effect of the substituent on the reactivity of the phenolic moiety, a larger number of compounds was considered in this study. Tentative determinations of the second order rate constant for the reactions of polysubstituted phenols such as 2,6-dimethylphenol, 2,6-dimethoxyphenol and 1,2,3-trihydroxybenzene were performed. An offset of about 10% was observed for all three compounds and this might lead to an underestimation of the observed rate constant. Hence, the presented experimental data all refer to phenols which do not absorb light significantly at  $\lambda = 248$  and  $\lambda = 632.8$  nm.

#### 3. Results and discussions

The rate coefficients for the reactions of NO<sub>3</sub> with a number of *ortho-* and *para*-substituted phenols have been determined using the LFP-LPLA technique.



**Fig. 1** (a) Intensity radical decay trace and (b) logarithm of absorbance decay of nitrate radical ( $\lambda = 632.8$  nm) from the flash photolysis of nitrate in the presence of 2-bromophenol (pH = 0.5, *T* = 298 K, 8 averages).



**Fig. 2** Measured  $k_{1st}$  vs. [reactant] for the reaction of NO<sub>3</sub> with: (a) 2-methylphenol; (b) 2-ethylphenol.

The reaction pathways, which are generally possible in reactions of NO<sub>3</sub> with aromatics in aqueous solution, involve four different competitive classes of reactions, *i.e.* (a) H-abstraction at the side-chains or phenolic H-atom, (b) H-abstraction at the aromatic ring, (c) addition–elimination and (d) direct single electron transfer (SET) from the aromatic ring.<sup>7,10</sup>

The electronic effect of the substituents could influence (a) reactions occurring according to an electron transfer mechanism by changing the electron density of the aromatic ring as well as (b) the OH bond strengths of the phenolic moiety in the case of the *ortho-* and *para*-substituted phenols.

#### 3.1. Reactions of NO<sub>3</sub> with ortho-substituted phenols at 298 K

First order rate constants were measured for 5 different reactant concentrations (generally in the range from  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$  M) to obtain second order rate constants from plots of  $k_{1st}$  against the reactant concentration as shown in Figs. 2 and 3. The investigations were performed at 298 K and pH = 0.5 (with HClO<sub>4</sub>).

In Fig. 3 the rate coefficients determined for the three *ortho*halogenated phenols show that the reaction proceeds faster for the phenol containing the most electronegative substituent and follows the series F > Cl > Br. However, the formation of a radical cation carrying a positive charge as reaction intermediate is expected in an electron transfer reaction. Therefore, electron withdrawing substituents might destabilise the positive charge carried by the aromatic ring resulting in a smaller rate constant for the 2-fluorophenol. Moreover, electron



**Fig. 3** Measured  $k_{1st}$  vs. [reactant] for the reaction of NO<sub>3</sub> with: (a) 2-fluorophenol; (b) 2-chlorophenol; (c) 2-bromophenol.

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withdrawing substituents, such as F, Cl and Br, are considered to withdraw electron density from the O–H bond and thereby increase its strength. Hence, a possible contribution from an Habstraction mechanism could not explain the order of reactivity observed in this work.

Thus, it can be concluded that for the case of *ortho*-halogenated phenols the steric effect prevails over the electronic effect in the reaction of  $NO_3$  (see also Section 3.5 and Table 3).

The phenol with the nitro group as a substituent shows the lowest rate constant for the reaction with NO<sub>3</sub>. The obtained rate coefficient is 100 times slower than for the reaction of NO<sub>3</sub> with the unsubstituted phenol and one order of magnitude slower than the other investigated phenols here. The two main reasons for this are: (a) a high bond dissociation energy (BDE) for the phenolic hydrogen (366 kJ mol<sup>-1 11</sup>) which leads to a very slow H-abstraction reaction and (b) the deactivating effect of the nitro goup on the aromating ring.

A  $\Delta G_R$  of -72.5 kJ mol<sup>-1</sup> was calculated (see Section 3.5.2 and eqn. (3)) for the electron transfer reaction of NO<sub>3</sub> with 2-nitrophenol which is the lowest among the phenols considered in the present work, as presented in Table 3.

In further experiments, the rate coefficient for the *ortho*substituted phenol with a cyano group as substituent was obtained (Fig. 3). In contrast to expectations, the 2-cyanophenol reacts as fast as the other slightly activated phenols. The high bond dissociation energy of the phenolic hydrogen  $(371.3 \text{ kJ mol}^{-1}$ , see Table 3), limits the contribution (<7%) of the H-abstraction channel to the observed rate constant.

No direct comparison with literature data is possible since almost all of the reported rate constants here were determined for the first time. Very few literature data are available for the reaction of NO<sub>3</sub> with substituted phenols.<sup>8</sup> This may be due to the fact that former studies of nitrate radical kinetics in solution used strong oxidizing precursors which tend to oxidise phenol and its derivatives.<sup>12,13</sup>

However, *ortho*-substituted phenols were shown to react rapidly with NO<sub>3</sub> radicals. All the *ortho*-substituted phenols considered in the present work present smaller rate coefficients with respect to the reaction of NO<sub>3</sub> radicals with the unsubstituted parental compound. Umschlag *et al.*<sup>8</sup> have recently obtained a second order rate of  $(1.8 \pm 0.3) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for the reaction of NO<sub>3</sub> with phenol at 298 K and pH = 0.

Furthermore, the investigated compounds are shown to react more slowly than the corresponding *para*-substituted phenol, as shown in Table 1.

#### 3.2. Reactions of NO<sub>3</sub> with *para*-substituted phenols at 298 K

The second order rate constants for the reaction of  $NO_3$  with five different *para*-substituted phenols were obtained. All experiments were carried using the same experimental protocol as reported above. In Fig. 4 the corresponding plots are shown and the obtained coefficient rates are summarised in Table 1.

As already noted the *para*-nitrophenols react faster than the corresponding *ortho*-isomers. This observation is justified for different reasons. First, the steric hindrance is not influencing the mechanism of the reaction in the case of the para-substituted phenols and consequently the reaction might proceed faster than phenols, which present a bulky group close to the reaction centre. Secondly, the inductive effect of the group in *para* position exerts a lower effect on the aromatic ring. Finally, the effect of the resonance stabilisation (mesomeric effect) on the intermediate of the reaction plays an important role with para-substituted phenols. In phenols containing substituents which may conjugate with the aromatic system, electrondonating groups (alkyl chains, amino group, ...) induce weakening of the OH bond by a combination of effects, *i.e.*, the destabilisation of the phenol and stabilisation of the phenoxyl radical by delocalisation of the unpaired electron.<sup>1</sup>

Table 1 Second order rate constants for the reactions of NO<sub>3</sub> with *ortho-* and *para*-substituted phenol in aqueous solution at 298 K and pH = 0.5

Reaction no.	Compound	$k_{2nd.\ 298\ K}/M^{-1}\ s^{-1}$
R-1	2-Hydroxyphenol	$(5.6 \pm 0.8) \times 10^8$
R-2	2-Methylphenol	$(8.5 \pm 0.2) \times 10^8$
		$(1.1 \pm 0.3) \times 10^{9} a$
R-3	2-Ethylphenol	$(6.7 \pm 0.4) \times 10^8$
R-4	2-Methoxyphenol	$(1.1 \pm 0.1) \times 10^8$
R-5	2-Nitrophenol	$(2.3 \pm 0.4) \times 10^7$
R-6	2-Cyanophenol	$(3.1 \pm 0.3) \times 10^8$
<b>R-7</b>	2-Fluorophenol	$(5.5 \pm 0.4) \times 10^8$
R-8	2-Chlorophenol	$(2.9 \pm 0.3) \times 10^8$
R-9	2-Bromophenol	$(2.7 \pm 0.1) \times 10^8$
R-10	2-Phenylphenol	$(2.4 \pm 0.4) \times 10^8$
R-11	4-Hydroxyphenol	$(8.8 \pm 0.5) \times 10^8$
		$(1.6 \pm 0.6) \times 10^{9} a$
R-12	4-Aminophenol	$(8.1 \pm 0.3) \times 10^8$
R-13	4-Chlorophenol	$(1.7 \pm 0.2) \times 10^9$
R-14	4-Bromophenol	$(1.0 \pm 0.4) \times 10^9$
R-15	4-Hydroxybenzene ethyl ester	$(8.0 \pm 0.4) \times 10^8$
<sup>a</sup> Ref. 8.		

The rate constants for the reaction of NO<sub>3</sub> with 4-hydroxyphenol (R-11, Table 1) obtained here turn out to be two times slower than the value obtained by Umschlag *et al.*<sup>8</sup> This disagreement can be explained by the different experimental conditions applied in the two studies. In their study, Umschlag *et al.* determined the second order rate constants using the flash photolysis of nitrate at  $\lambda = 248$  as in the present work but at pH = 0 (with HClO<sub>4</sub>) instead of pH = 0.5 and a concentration



**Fig. 4** Measured  $k_{1st}$  vs. [reactant] for the reaction of NO<sub>3</sub> with: (a) 4-bromophenol; (b) 4-chlorophenol; (c) 4-hydroxyphenol; (d) 4-aminophenol; (e) 4-hydroxybenzene ethyl ester.

of nitrate ten times higher ( $[NO_3^-] = 0.1 \text{ M}$ ) than used here. Thus, the corresponding ionic strength differs by a factor three. It was observed that the ionic strength might influence the progress of the reaction exerting a positive or negative effect on the experimental second order rate constant.<sup>15,16</sup> In particular, the reaction of NO<sub>3</sub> with phenol is shown to proceed at a faster rate at higher ionic strengths. In an ionic strength range between I = 1.14 M and I = 2 M, the reaction rate increases linearly with increasing ionic strength reaching a plateau at I =2.2 M.<sup>8,16</sup> However, the small number of measurements to compare with does not allow further considerations. More experimental efforts are needed in order to better characterise the influence of the ionic strength on the reactions of NO<sub>3</sub> with phenols in the aqueous phase.

#### 3.3. Reactivity comparison with OH radical

Since OH is considered the most important radical for its high reactivity towards organic compounds in the tropospheric aqueous phase a comparison between the reactivity of OH and  $NO_3$  towards aromatic compounds in aqueous solution is presented in Table 2.

As can be seen, OH radical reacts one order of magnitude faster than NO<sub>3</sub> with aromatic compounds in most cases. Exceptions are the rate constants derived for 4-chlorophenol and 4-bromophenol, which are comparable with the ones obtained for OH radicals. This is a further confirmation of the role played by the substituent. In fact the availability of unshared  $\pi$  orbitals belonging to the halogen-substituent in *para*-position allows a stabilization of the reaction intermediate for resonance effects.

# 3.4. T-dependent studies of reactions of $NO_3$ with 2-methylphenol, 2-ethylphenol, 2-hydroxyphenol and 2-methoxyphenol

Rate constants for reactions of the NO<sub>3</sub> radical in aqueous solution have been studied mainly at room temperature.<sup>7,8,16</sup> Since temperature might influence strongly the rate coefficients for a given reaction and no literature data are available concerning the temperature dependences of the rate constant for the reaction of nitrate radicals with *ortho*-substituted phenols, in the present work the rate constants of the reaction of NO<sub>3</sub> with (a) 2-methylphenol, (b) 2-ethylphenol, (c) 2-hydroxyphenol and (d) 2-methoxyphenol were studied in the range of temperatures from 278 K to 328 K.



**Fig. 5** Arrhenius plot for the reaction between NO<sub>3</sub> radicals and: (a) 2-ethylphenol; (b) 2-methylphenol; (c) 2-hydroxyphenol; (d) 2-methoxyphenol.

The reaction rate constant investigated as a function of the temperature delivers kinetic data which can be described by the Arrhenius equation.<sup>15</sup> The equation is commonly applied in the linearised form and an Arrhenius plot of log k against 1/T yields a line with y = mx + b, where  $y = \ln k$ , x = 1/T, m (slope) =  $-E_A/R$  and b (intercept) =  $\ln A$ .

Fig. 5 reports the Arrhenius plots observed for the investigated reactions and Table 3 shows the corresponding activation parameters.

Just a few data are available from the literature for a comparison to the kinetic data obtained here. However, the activation energies ( $E_A$ ) are in good agreement with the ones measured for reactions of NO<sub>3</sub> with aromatic compounds and they are very close to the values determined for phenol and 4-methylcresol by Umschlag *et al.*<sup>8</sup> (see Table 3).

The Gibbs free energies of activation are all in the range of  $22-27 \text{ kJ mol}^{-1}$  for the *ortho*-substituted phenols and in the range of  $18-38 \text{ kJ mol}^{-1}$  for the phenols studied so far. These values are quite similar to the values present in literature.<sup>6</sup>

The entropies of activation ( $\Delta S^{\ddagger}$ ), where  $\Delta S^{\ddagger} = R \times (\ln A - \ln (k_{\rm B}T/h) - 1)$ , show negative values that indicate that for most of the systems studied the reaction might proceed through the formation of an activated complex which is more highly ordered than the initial reactants. However, the obtained values are three times more positive than the activation entropies obtained for the H-abstraction reactions of NO<sub>3</sub> with

Table 2	Comparison	of the reactivity	between	OH and NO	3 for the	reactions	with are	omatic comp	ounds in	solution
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	$k_{\rm 2nd,\ 298\ K}/{ m M}^{-1}\ { m s}^{-1}$		$k_{2nd, 298 \text{ K}}/\text{M}^{-1} \text{ s}^{-1}$		
Compound	ОН	Ref.	NO <sub>3</sub>	Ref.	
Benzene	$7.8 \times 10^{9}$	15	$(4.0 \pm 0.6) \times 10^8$	7	
Toluene	$5.1 \times 10^{9}$	18	$(1.2 \pm 0.3) \times 10^9$	7	
Phenol	$1.4 \times 10^{10}$	19	$(1.9 \pm 0.3) \times 10^9$	8	
2-Chlorophenol	$1.2 \times 10^{10} a$	20	$(2.9 \pm 0.3) \times 10^8$	This work	
4-Chlorophenol	$7.6 \times 10^{9} a$	21	$(1.7 \pm 0.2) \times 10^9$	This work	
4-Bromophenol	$5.7 \times 10^{9} a$	22	$(1.0 \pm 0.4) \times 10^9$	This work	
2-Methylphenol	$1.1 \times 10^{10} a$	23	$(8.5 \pm 0.2) \times 10^8$	This work	
4-Methylphenol	$1.2 \times 10^{10}$	24	$(8.2 \pm 0.3) \times 10^8$	8	
2-Methoxyphenol	$2.0 \times 10^{10}$	25	$(1.1 \pm 0.1) \times 10^8$	This work	
4-Methoxyphenol	$2.6 \times 10^{10}$	25	$(6.6 \pm 1.8) \times 10^8$	This work	
2-Nitrophenol	$9.2 \times 10^{9} a$	23	$(2.3 \pm 0.4) \times 10^7$	This work	
4-Nitrophenol	$3.8 \times 10^{9}$	26	$(7.1 \pm 0.4) \times 10^7$	8	
2-Hydroxyphenol	$1.1 \times 10^{10} a$	23	$(5.6 \pm 0.8) \times 10^8$	This work	
4-Hydroxyphenol	$2.1 \times 10^{10}$	27	$(8.8 \pm 0.5) \times 10^8$	This work	
4-Hydroxybenzoic acid	$9.0 \times 10^{9 \ b}$	28	$(5.0 \pm 1.3) \times 10^8$	8	
<sup>a</sup> Measurement performed at pH	I > 9. <sup>b</sup> Measurement performe	ed at $pH = 7$ .			

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Table 3 Summarising table of thermodynamic and kinetic data for the reactions of NO<sub>3</sub> with phenolic compounds in aqueous solution

Compound	$E_{ m A}/ m kJ$ $ m mol^{-1}$	$\Delta G^{\ddagger}/\mathrm{kJ}$ mol $^{-1}$	$\Delta H^{\ddagger}/\mathrm{kJ}$ mol $^{-1}$	$\frac{\Delta S^{\ddagger}_{}/J}{mol^{-1}K^{-1}}$	$k_{ m 2nd. 298/} M^{-1} { m s}^{-1}$	Ref.	BDE [O–H] <sup>a</sup> /kJ mol <sup>-1</sup>	$k_{\mathrm{H-abs. calc},b}/\mathrm{M}^{-1}$	$rac{k_{ m H}/k_{ m obs}}{(\%)}$	$E^\circ_{ m red}  {}^c/{ m V}$	$\Delta G_{ m R} {}^{d}/{ m kJ}$ mol $^{-1}$
Phenol	$17 \pm 4$	$21 \pm 8$	$15 \pm 3$	$-(21 \pm 3)$	$(1.8 \pm 0.3) \times 10^9$	8	371.3	$2.1 imes 10^7$	1.1	1.46	-94.2
2-Hydroxyphenol	$39 \pm 9$	$23 \pm 11$	$36 \pm 7$	$(45 \pm 15)$	$(5.6\pm 0.8) imes 10^8$	This work	341.3	$6.8 imes10^9$	> 100	1.20	-119.5
2-Methylphenol	$22 \pm 7$	$22 \pm 8$	$19 \pm 7$	$-(11 \pm 3)$	$(8.5\pm 0.2)  imes 10^8$	This work	362.3	$1.2 imes 10^8$	14.1	1.38	-102.7
1							357 [CH <sub>2</sub> -H] <sup>e</sup>	$3.2 imes10^8$	37.6		
					$(1.1 \pm 0.3) \times 10^9$	8	362.3	$1.2 imes10^8$	10.6		
							357 [CH <sub>2</sub> -H] <sup>e</sup>	$3.2 imes 10^8$	29.1		
2-Methoxyphenol	$25 \pm 4$	$27 \pm 8$	$22 \pm 3$	$-(11 \pm 2)$	$(1.1 \pm 0.1)  imes 10^8$	This work	354.3	$5.5 imes 10^8$	>100	1.24	-115.6
2-Nitrophenol					$(2.3 \pm 0.4)  imes 10^7$	This work	366.3	$5.4 imes10^7$	> 100	1.69	-72.5
2-Phenylphenol					$(2.4 \pm 0.4)  imes 10^8$	This work				1.41	-99.1
2-Fluorophenol					$(5.5\pm 0.4) imes 10^{8}$	This work	363.3	$9.6 imes10^7$	17.5	1.44	-96.1
2-Bromophenol					$(2.7 \pm 0.1) \times 10^8$	This work	364.3	$7.9 imes10^7$	29.3	1.51	-90.1
2-Chlorophenol					$(2.9\pm 0.3) imes 10^{8}$	This work	368.3	$3.7 imes 10^7$	12.6	1.50	-91.1
2-Cyanophenol					$(3.1 \pm 0.3)  imes 10^8$	This work	371.3	$2.1 imes 10^7$	6.6	1.65	-76.
2-Ethylphenol	$18 \pm 2$	$23 \pm 4$	$16 \pm 3$	$-(24 \pm 6)$	$(6.7 \pm 0.4) \times 10^8$	This work				1.38	-102.3
4-Methylphenol	$38 \pm 4$	$22 \pm 8$	$35 \pm 5$	$-(45 \pm 21)$	$(8.2\pm 0.3) imes 10^{8}$	8	363.3	$9.6 imes10^7$	11.7	1.33	-107.1
							357 [CH <sub>2</sub> -H] <sup>e</sup>	$3.2  imes 10^8$	39		
4-Nitrophenol					$(7.1\pm0.4) imes10^7$	8	396.3	$1.6  imes 10^5$	0.2	1.80	-62
4-Methoxyphenol					$(6.6\pm1.8) imes 10^{8}$	8	349.3	$1.4  imes 10^9$	> 100	1.13	-126.7
4-Hydroxyphenol					$(1.6 \pm 0.6)  imes 10^9$	8	344.3	$3.8 imes10^9$	> 100	1.07	-132.5
					$(8.8\pm 0.5)  imes 10^{8}$	This work			> 100		
4-Aminophenol					$(8.1 \pm 0.3) \times 10^8$	This work	331.3	$4.7 imes10^{10}$	> 100		
4-Bromophenol					$(1.7 \pm 0.2)  imes 10^9$	This work	373.3	$1.4 imes10^7$	0.8	1.53	-87.9
4-Chlorophenol					$(1.0\pm 0.4) imes 10^9$	This work	370.3	$2.5  imes 10^7$	2.5	1.51	-89.6
4-Hydroxybenzoic Acid					$(5.0\pm 1.3) imes 10^{8}$	8	$360^{f}$	$1.8 imes10^8$	36	1.64	-80.0
4-Hydroxybenzene ethyl ester					$(8.0\pm 0.4)  imes 10^8$	This work	378.3 <sup>g</sup>	$6.9  imes 10^{6}$	0.9		
<sup><i>a</i></sup> The bond dissociation energy ( potentials were obtained using t <sup><i>e</i></sup> Ref. 10. <sup><i>f</i></sup> Ref. 8. <sup><i>s</i></sup> Estimated	BDE) for the he correlatio equal to the	phenolic hydı n of Jonsson value reporte	ogen are taker <i>et al.</i> , <sup>40</sup> where d for the <i>meta</i>	I from ref. 39 if n $\sigma^+$ for the <i>orth</i> -substituted form	ot otherwise indicated. <sup>1</sup> -substituted phenols w 1. <sup>39</sup>	<sup>b</sup> The rate consta as estimated on	unts for abstractable h the basis of eqn. (4)	ydrogen were calculated (see text). <sup>d</sup> Calculated	l using eqn. (1) using eqn. (3)	$r^{7 c}$ The standa with $E^{0}$ (NO <sub>3</sub> )	rd reduction $= 2.44 \text{ V.}^{41}$

aliphatic compounds which are in the range  $\Delta S^{\ddagger} = -40$  to -60 J mol<sup>-1</sup> K<sup>-1,7</sup> Furthermore, the values reported in Table 3 present less negative entropies of activation than the other aromatics.<sup>7</sup>

An interesting result is obtained for the reaction of NO<sub>3</sub> with 2-hydroxyphenol where a very positive value of entropy of activation was obtained, which is not common for the reactions of NO3 with organics in the aqueous phase.<sup>7</sup> The presence of two hydroxyl groups in ortho position might greatly influence the reactivity of this compound through the formation of a net of hydrogen bonds with a polar solvent such as water. Hence, the reactant might be in a very high ordered state before undergoing reaction with NO<sub>3</sub>. In the literature there are several studies concerning the determination of the absolute rate constants for hydrogen atom abstraction from phenols by peroxyl radicals<sup>29-34</sup> and by other oxygen- or nitrogen-centered radicals.35 Many of those rate constants have been measured in different solvents and found to show strong solvent effects in hydrogen bond accepting solvents (HBA), such as water. Furthermore, they do not depend on the nature of the attacking radical. These solvent effects have been attributed to hydrogen bond formation between hydroxylic hydrogen atom of the phenolic moiety and the HBA solvent<sup>36,37</sup> and it might play an important role with compounds such as 2-hydroxyphenol.

Finally, it was confirmed with the present study that steric crowding around the hydroxyl group is important in decreasing the reactivity of phenol and this influence might be more effective than the electronic effect due to the substituent as already observed in a study of the reactivity of substituted phenols towards alkyl radicals by Franchi *et al.*<sup>38</sup>

#### 3.5. Reactivity correlations

Chemical kinetics provide insights into the mechanism underlying a certain process because kinetics is concerned with changes in properties between an initial state and the transition state as shown for the temperature dependency studies reported in the previous section. Just a few kinetic data were available<sup>7,8,16</sup> for the reactions of NO<sub>3</sub> with phenols in the aqueous phase and no correlations are actually published in the literature.

3.5.1. Reaction mechanisms for the reaction of  $NO_3$  with substituted phenols: H-abstraction. The kinetic data obtained in the present work and the data collected from the literature were used to seek common reaction patterns and possibly distinguish between the different mechanisms involved in the oxidation process. In view of this, the available data were summarised in Table 3 and with the help of kinetic, thermodynamic data and extrathermodynamic relationship mechanistic considerations are undertaken.

As mentioned earlier,  $NO_3$  might react with a phenolic compound *via* different pathways, *i.e.* addition–elimination, electron-transfer or H-atom abstraction reactions. The rate coefficient of the latter reaction type is determined by the bond strength of the weakest X–H bond.

The analysis of all the available data led Santos and Simoes<sup>39</sup> to propose a set of recommended values for the O–H bond dissociation energies in phenols, which was used in the present study to derive the expected rate constant for an H-abstraction mechanism with the help of a correlation described in the literature<sup>7</sup> for the reactions of NO<sub>3</sub> with organics in aqueous solution (eqn. (1)), as reported in Table 3.

lg 
$$k_{\text{H-abs}}/\text{M}^{-1} \text{ s}^{-1} = (38.5 \pm 5.6) - (0.084 \pm 0.014)$$
  
× BDE/kJ mol<sup>-1</sup> (1)

with a database of 37 reactions considered and a correlation coefficient of R = 0.89.

However, Santos and Simoes recognise that their proposal may be controversial, particularly when large discrepancies exist between data for the same compound obtained from different experimental and theoretical methods. Furthermore, Santos and Simoes pointed out that the present knowledge on the energetics of the phenolic bond is still unsatisfactory. Even for the phenol itself and some of the compounds considered here the published values for the O–H bond dissociation energy vary over a wide range.

Evans and Polanyi found that the activation energy of an exothermic H-abstraction reaction changes linearly with the C–H bond energy.<sup>42</sup> According to the Arrhenius equation the logarithm of the rate constant depends linearly on the activation energy for a series of reactions which do follow the same reaction mechanism, such as the H-abstraction reactions of  $NO_3$  with aliphatic organic compounds. Therefore, the logarithm of the rate constants and the X–H bond energy should depend on each other linearly.

The correlation between the logarithm of the rate constant per equivalent abstractable H atom ( $k_{\rm H}$ ) and the bond dissociation energy BDE (Table 3) is shown in Fig. 6 for the compounds where the observed rate constant is fully explained by an H-abstraction mechanism according to the more recent thermochemical data mentioned before.

A correlation between the logarithm of the observed rate constant for the abstraction of the phenolic hydrogen and the corresponding bond dissociation energy (BDE) is provided (Fig. 6 and eqn. (2)) which might be used for the prediction of rate coefficients for H-abstraction reactions of substituted phenols with  $NO_3$  in aqueous solution:

log 
$$k_{\rm H}/{\rm M}^{-1}$$
 s<sup>-1</sup> = (23.7 ± 2) - (0.044 ± 0.01)  
× BDE/kJ mol<sup>-1</sup> n = 6 r = 0.88 (2)

where n is the number of compounds considered in the regression line and r is the corresponding correlation coefficient.

3.5.2. Reaction mechanisms for the reaction of NO<sub>3</sub> with substituted phenols: Electron transfer. Furthermore, in order to do a comparison between the possible reaction mechanisms involved and to explore the contribution of a single electron transfer (SET) on the observed rate constants, the standard free energy of the reaction  $\Delta G_R$  has been calculated for the reactions investigated in this study according to:

$$\Delta G_{\rm R} = -z \times F \times \Delta E^0 = -z \times F \times [E^0(\mathbf{X}^{\bullet}) - E^0(\text{reactant})] \quad (3)$$

Where z is the number of exchanged electrons, F is the Faraday constant and  $\Delta E^0$  is the standard electromotive force.  $\Delta E^0$  is



**Fig. 6** Plot of the logarithm of the  $k_{\text{H-abs}}$  versus the bond dissociation energy for the reaction of NO<sub>3</sub> with: (a) 4-aminophenol; (b) 4-hydroxyphenol; (c) 4-methoxyphenol; (d) 2-hydroxyphenol; (e) 2-methoxyphenol; (f) 2-nitrophenol.

the difference between the standard potentials of the redox couple where the reduction potential for  $(NO_3/NO_3^-)$  is 2.44 V.<sup>41</sup> The obtained Gibbs free energies are reported in Table 3.

The reduction potentials listed in Table 3 were calculated with the correlation proposed by Jonsson *et al.*<sup>40</sup> Experimentally determined one-electron reduction potentials and estimated values for mono-substituted benzene radical cations are available from literature as functions of the substituent Brown parameter  $\sigma_p^{+}$ .<sup>43</sup>

Jonsson *et al.*<sup>40</sup> derived a conditional  $\sigma_o^+$  scale for *ortho*-substituted phenols which is described by eqn. (4).

$$\sigma_o^{+} = 0.66 \times \sigma_p^{+} \tag{4}$$

The factor of 0.66 by which  $\sigma_p^+$  must be multiplied is a result of a comparison of *ortho* and *para* effects on O–H bond strengths.<sup>44,45</sup> Linear correlations between *ortho* and *para* substituent on phenols have been reported in the literature.<sup>45,46</sup>

More recently, the Jonsson *et al.* exercise was repeated by Santos and Simoes<sup>39</sup> using their recommended selected data for the monosubstituted *ortho* phenols and  $\sigma_p^+$  leading to eqn. (5):

$$\sigma_o^{+} = 0.62 \times \sigma_p^{+} \tag{5}$$

in good agreement with the first one determined by Jonsson *et al.*<sup>40</sup> Moreover, Santos and Simoes compared the two equations (eqns. (4) and (5)) with the full data set of monosubstituted phenols recognizing that the factor 0.66 proposed by Jonsson *et al.* better describes the available data, hence the factor of 0.66 was used throughout this work.

However, it should be underlined that due to irregular interactions between *ortho* substituents and the OH group, it is somewhat controversial to assign a  $\sigma_p^+$  value to them.

The logarithms of the observed rate constant were plotted against the obtained  $\Delta G_{\rm R}$ . According to the reaction scheme of an irreversible electron transfer:

$$\mathbf{A} + \mathbf{B} \xrightarrow[k_{-d}]{k_{0}} [\mathbf{A} \cdots \mathbf{B}] \xrightarrow{k_{p}} \mathbf{A}^{-} + \mathbf{B}^{+}$$

which may be applied for  $NO_3$  single electron transfer reactions studied in the present work, the following relation applies for the observed rate constant:

$$k_{\rm obs}/1 \,\,{\rm mol}^{-1} \,\,{\rm s}^{-1} = k_{\rm d}/\left(1 + \frac{k_{\rm -d}}{k_{\rm etr}}\right)$$
 (6)

The experimental data were modelled using eqn. (7), obtained as described in Herrmann and Zellner,<sup>7</sup> in order to obtain the expected electron transfer rate for a given Gibbs free energy of reaction.

$$k_{\rm obs} = \frac{k_{\rm d}}{1 + \frac{k_{-\rm d}}{A_0} \exp\left[\frac{Z_{\rm X} Z_{\rm R} e^2}{\varepsilon r_{12}} \frac{N_{\rm A}}{10^7} + \Delta G_0^{\frac{1}{4}} \left(1 + \frac{\Delta G_{\rm R}^0}{4\Delta G_0^{\frac{1}{4}}}\right)^2 / RT\right]}$$
(7)

where  $A_0$  is the preexponential factor.  $Z_X$  and  $Z_R$  are the formal charge of the radical (X<sup>•</sup>) and the reactant (R), respectively. *e* is the elementary charge in electrostatic units. *e* is the dielectric constant of the solvent,  $r_{12}$  is the sum of the reactant radii in the activated complex considering a spherical shape for both radical and reactant.  $N_A$  is Avogadro's number.  $\Delta G_R^0$  is the free enthalpy in the prevailing medium,  $\Delta G_0^{\dagger}$  is the component related to the reorganization of the solvent molecules surrounding the reactants during the proceeding of the reaction. *R* is the gas constant and *T* the absolute temperature.

In Fig. 7A and 7B, the comparison between the experimental data (symbols) and the calculated curve (line) is shown. Fig. 7A represents the outcome of a former study of Herrmann<sup>47</sup> where



**Fig. 7** Rate constants for the single-electron transfer of NO<sub>3</sub> reaction in aqueous phase with anions and aromatic compounds. (A)  $\bigcirc$  anions;  $\Delta$ : aromatics from refs. 47 and 7. (B)  $\bigcirc$ : anions;  $\Delta$ : aromatics same as plot A;  $\blacksquare$ : substituted phenols studied in the present work.

in the model calculations only the reactions of  $NO_3$  with anions in aqueous solution have been considered. In Fig. 7B the database of the model was extended also to aromatic compound and the substituted phenols considered in this work.

The kinetic data for the reactions of  $NO_3$  with anions and the aromatic compounds represented in Fig. 7 and used for the modelling calculation are taken from Herrmann<sup>47</sup> and Table 3 (this work).

A comparison between the two correlations shows substantial agreement. As can be seen from the experimental data, for  $\Delta G_{\rm R} < -50$  kJ mol<sup>-1</sup> the rate constants for both reaction with anions and aromatic compounds including the substituted phenols become essentially independent of the Gibbs free energy of reaction and are best described by an observed second-order rate constant in the range of 2 × 10<sup>9</sup> l mol<sup>-1</sup> s<sup>-1</sup> in both cases.

Towards the exergonic part of the axis the rate constants measured for the reaction aromatic compounds do not differ substantially from the ones obtained for the anions. Quite differently, the aromatic compounds show a different behaviour in the more endoergonic region of the plot. Hence, it is concluded that in the case of aromatic compounds the rate constants observed in the regime of  $\Delta G_{\rm R} > -50$  kJ mol<sup>-1</sup> do not reflect an electron transfer from the aromatic ring.

A zoom of the plot presented in Fig. 7B is shown in Fig. 8. Generally, the substituted phenols ( $\blacksquare$ ) considered in this work are in agreement with the calculated curve and the obtained second order rate constants are somewhat slower with respect to the predicted value provided from the fit. Moreover, the compounds ( $\blacksquare$ ) that show a large difference between the observed and the expected second order rate constant are suggested to react *via* the H-abstraction mechanism with NO<sub>3</sub> (see also Fig. 6).



Fig. 8 Zoom of the plot in Fig. 7B for single electron transfer reactions of  $NO_3$  radicals in the aqueous phase. Data and symbols as in Fig. 7A and 7B. See text for explanation of symbols.

**3.5.3.** Reaction mechanisms for the reaction of NO<sub>3</sub> with substituted phenols: Hammett-type plot. In the literature the Hammett treatment includes so far only substituents that are *meta* or *para* to the reaction site. When Hammett-plots are made with data for *ortho*-substituted reactants, scatter diagrams usually result. This failure is usually attributed to steric effects.<sup>48</sup> Taft first proposed the use of a correlation<sup>49</sup> similar to the Hammett correlation trying to separate the electronic effect from the steric effect introducing a series of substituent constants ( $E_s^0$ ) for a small number of substituents.<sup>15</sup> In this work, a tentative Taft-plot for the reactions of NO<sub>3</sub> with *ortho*-substituted phenols resulted in a very poor correlation (r = 0.59, n = 5) between the observed rate constants and the steric constants. This result is explained mainly because steric effects can be particularly difficult to define.

Whereas the contribution of steric effects is often unpredictable and results in a scatter plot, the *para*-substituted phenols allowed a better interpretation of the obtained data and better correlations are generally obtained. In Fig. 9, a Hammett plot for the reaction of NO<sub>3</sub> radical with *para*-substituted phenols and benzoic acids is shown.

A saturation behaviour is observed, even if the diffusion limit for the reaction of NO<sub>3</sub> with the hydroxyphenol is calculated to be  $k_{\text{diff}} = 7.5 \times 10^9 \text{ 1 mol}^{-1} \text{ s}^{-1}$  applying the Smoluchowski equation.<sup>50,51</sup> This trend is actually difficult to explain. A possible suggestion might be provided in Fig. 10



Fig. 9 Hammett-plot for the reaction of NO<sub>3</sub> with: ( $\Delta$ ) *para*-substituted benzoic acids and ( $\odot$ ) *para*-substituted phenols. See text for details, H-abstraction contributions are given in percent.



Fig. 10 Hammett-type plot for the reaction of OH with:  $\bigcirc$  *para*-substituted benzoate:  $\triangle$  *para*-substituted phenols.

where a Hammett-type plot for the reactions of OH with *para*substituted phenol and *para*-substituted benzoate is presented. The selected coefficient rates considered in Fig. 8 are summarised in Tables 2 and 4.

As can be seen in Fig. 10, in the case of OH no saturation behaviour is observed and, moreover, all the second order rate constants can be interpreted by a single regression line indicating that OH might react with all the compounds through the same mechanism. Phenols and substituted benzoates are known to react with OH-radicals in the aqueous phase mainly by addition to the aromatic ring, where the observed rate constants are in the order of magnitude comprised between  $3.8 \times 10^9$  and  $2.6 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> for the reaction with 4-nitrophenol and 4-methoxyphenol, respectively.

The direct comparison of the two Hammett-plots in Fig. 9 shows clearly that for the reaction with the substituted benzoic acid, where the involved mechanism is an electron transfer, all the points can be interpreted by a single regression line. The influence of the substituents is proportional to the electronic effect of the substituents and the benzoic acid bearing an electronegative group has been shown to react more slowly with respect to the parental unsubstituted benzoic acid.

In the case of the *para*-substituted phenols two different behaviours of the regression line are evident (Fig. 9). For the phenols having an electron-donating group the slope of the regression line is close to zero, which indicates that for these compounds there is no evident electronic effect on the observed rate constants for the reaction with NO<sub>3</sub>. As shown in Fig. 9, the observed rate constants interpreted with the flat line can be explained with an H-abstraction mechanism (see Table 3). Thus, this indicates that during the reaction no "formal" charge is formed. However, in the H-abstraction reactions a small negative slope could be observed, <sup>56</sup> whereas, the electron

**Table 4** Rate constants for the reaction of OH with *para*-substituted benzoate ion at 298 K in aqueous phase and the substituent Brown parameter,  $\sigma_p^+$ 

Commenced	$l_{1}$ (1 $1^{-1}$ $-1$	D-f	_ +
Compound	$\kappa_{\rm 2nd}/1~{\rm mol}$ s	Rel.	$\sigma_p$
4-Nitrobenzoate ion	$2.6 \times 10^{9}$	17	0.79
4-Bromobenzoate ion	$3.2 \times 10^{9}$	52	0.15
4-Iodobenzoate ion	$2.5 \times 10^{9}$	53	0.14
4-Chlorobenzoate ion	$5.0 \times 10^{9}$	28	0.11
4-Fluorobenzoate ion	$3.6 \times 10^{9}$	52	-0.07
4-Methoxybenzoate ion	$8.0 \times 10^{9}$	54	-0.78
4-Hydroxybenzoate ion	$6.0 \times 10^{9}$	55	-0.92
4-Aminobenzoate ion	$8.2 \times 10^{9}$	52	-1.3

transfer is suggested to be the prevailing mechanism with the para-substituted phenols considered in the regression line.

#### **Environmental aspects** 4.

The NO<sub>3</sub> radical is recognised as playing an important role in night-time atmospheric chemistry. It has also been established that, since the industrial revolution, the tropospheric abundances of the precursors of NO<sub>3</sub>, *i.e.* NO<sub>2</sub> and O<sub>3</sub>, have been increasing as a result of anthropogenic activities. Thus, the abundance of NO<sub>3</sub> and its impact on the troposphere must also have increased.

Following the suggestion that NO<sub>3</sub> might react with hydrocarbons, the reactivity of NO3 towards naturally occurring and anthropogenic atmospheric trace gases has been investigated. Although aromatic compounds such as benzene or toluene react slowly with NO<sub>3</sub>, NO<sub>3</sub> has been shown to react rapidly with a variety of compounds and the results obtained in this work confirm the high reactivity of NO3 towards organic polar compounds such as substituted phenols.

Furthermore, it was observed under the experimental conditions applied in this work that phenols bearing an electron-donating group, such as hydroxyphenols, cresols and methoxyphenols, react with NO3 exclusively via H-abstraction with the formation of the corresponding substituted phenoxy radical and a molecule of HNO<sub>3</sub>. Hence, the gas phase conversion of aromatic compounds, such as benzene, toluene and anisole, which produces the corresponding phenols, might lead to an acidification of the tropospheric aqueous phase in the continental area as a consequence of the fast reaction of phenols with NO3 in aqueous solution. Deactivating substituents like -CN, -NO2 cause a decrease in the rate constants in aqueous solution in both mechanisms, in H-atom abstraction reactions as well as in electron-transfer reactions. Therefore these reactions might be of minor importance for tropospheric cloud and aerosol chemistry.

#### Summary and conclusions 5.

In this work, a number of rate constants for the reaction of NO3 with substituted phenols in aqueous solution were determined. The predominant number of kinetic parameters was determined for the first time and hence increases the kinetic database now available and can be used to implement existing models<sup>57,58</sup> for a better understanding of tropospheric multiphase chemistry. However, the potential user of the kinetic data and the correlations has to be aware of the uncertainties derived from rate constants obtained under conditions which may not be typical for the tropospheric aqueous phase throughout.

The reactivity of NO<sub>3</sub> turned out to be complex and hence complicated to model, as both thermochemical, molecular and structural effects appear to be important in determining the rate at which NO<sub>3</sub> reacts. Therefore, it is also important to study reactions which might not be directly relevant for tropospheric chemistry but lead to mechanistic insights.

The results presented here improved the knowledge on these reactions. For some compounds considered in this study it was possible to describe the observed rate constants in view of a single mechanism (H-ABS) acting during the oxidation process. For these compounds a correlation (eqn. (2)) was provided for the prediction of second-order rate constants for the reaction of NO3 with substituted phenols reacting by Habstraction mechanism. The correlation obtained here covers a lack in the literature and is in general agreement with previous studies.7 The contribution of the electron transfer on the rate coefficients for the reactions of  $NO_3$  with substituted phenols in aqueous solution was investigated and compared to former studies.<sup>47</sup> The model shows that for  $\Delta G_{\rm R} < -50 \text{ kJ mol}^{-1}$  the rate constants for the reaction with both anions as well as aromatic compounds including the substituted phenols become essentially independent of the Gibbs free energy of the reaction. This indicates electron transfer as the dominant mechanism. On the other hand for reactions with  $\Delta G_{\rm R} > -50 \text{ kJ mol}^{-1}$  the observed rate coefficients are not due to concerted electron transfer only.

Finally, it was observed that in ortho-substituted phenol steric effects plays a decisive role whereas electronic effects are responsible for the reactivity of *para*-substituted phenols.

#### References

- 1 H. B. Singh, Composition, Chemistry, and Climate of the Atmosphere, VNR, New York, 1995.
- B. J. Finlayson-Pitts and J. N. Pitts, Jr., Chemistry of the Upper 2 and Lower Atmosphere, Academic Press, San Diego, 2000.
- J. H. Seinfeld and S. N. Pandis, Atmospheric chemistry and physics, J. Wiley & Sons, Toronto, 1998. J. E. Stern, R. C. Flagan, D. Grosjean and J. H. Seinfeld, *Environ*.
- 4 Sci. Technol., 1987, 21, 1224.
- Eurotrac II CMD (Chemical Mechanism Development) Final Report 2003, eds. U. Schurath and K.-H. Naumann, Springer, Munich, 2003.
- J. U. White, J. Opt. Soc. Am., 1946, 42, 285.
- H. Herrmann and R. Zellner, Reactions of NO3-Radicals in Aqueous Solution in N-Centered Radicals, ed. Z. B. Alfassi, Wiley, New York, 1998, p. 291.
- Th. Umschlag, R. Zellner and H. Herrmann, *Phys. Chem. Chem. Phys.*, 2002, **4**, 2975. 8
- 9 P. Barzaghi and H. Herrmann, Phys. Chem. Chem. Phys., 2002, 4 3669
- 10 H. Herrmann, M. Exner, H.-W. Jacobi, G. Raabe, A. Reese and R. Zellner, Faraday Discuss., 1995, 100, 129.
- R. Bosque and J. Sales, J. Chem. Inf. Comput. Sci., 2003, 43, 637.
- O. Ito, S. Akiho and M. Iino, J. Phys. Chem., 1989, 93, 4079. 12
- 13 T. Del Giacco, E. Baiocchi and S. Steenken, J. Phys. Chem., 1993,
- 97. 5451.
- 14 G. F. Pedulli, M. Lucarini and P. Pedrielli, in Free Radicals in Biology and Environment, ed. F. Minisci, Nato ASI Series, Kluwer Academic Publishers, Dordrecht, 1997, p. 169.
- 15 K. A. Connors, Chemical Kinetics - The Study of the Reaction Rates in Solution, VCH Publishers Inc., New York, 1990.
- 16 H. Herrmann, Chem. Rev., 2003, 103, 4691.
- G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513. 17
- 18 M. Roder, L. Wojnarovits and G. Foldiak, Radiat. Phys. Chem., 1990, 36, 175.
- 19 E. J. Land and M. Ebert, Trans. Faraday Soc., 1967, 63, 1181.
- 20 N. Getoff and S. Solar, Radiat. Phys. Chem., 1986, 28, 443.
- R. S. Shetiya, K. N. Rao and J. Shankar, Indian J. Chem., Sect. A, 21 1976. 14. 575
- 22 M. Ye and R. H. Schuler, J. Liq. Chromatogr., 1990, 13, 3369.
- 23 O. S. Savel'eva, L. G. Shevchuk and N. A. Vysotskaya, Zh. Org. Khim., 1972, 8, 283
- J. Feitelson and E. Hayon, J. Phys. Chem., 1973, 77, 10. 24
- 25 P. O'Neill and S. Steenken, Ber. Bunsenges. Phys. Chem., 1977, 81, 550.
- B. Cercek and M. Ebert, Adv. Chem. Ser., 1968, 81, 210. 26
- 27 G. E. Adams, J. W. Boag, J. Currant and B. D. Michael, in Pulse
- Radiolysis, eds. M. Ebert, J. P. Keene, A. J. Swallow and J. H. Boxendale, Academic Press, New York, 1965, p. 131.
- 28 P. Neta and L. M. Dorfman, Adv. Chem. Ser., 1968, 81, 222.
- 29 G. W. Burton and K. U. Ingold, Acc. Chem. Res., 1986, 19, 194.
- 30 J. A. Howard and K. U. Ingold, Can. J. Chem., 1963, 41, 2800.
- 31 G. W. Burton and K. U. Ingold, J. Am. Chem. Soc., 1981, 103, 6472.
- G. W. Burton, T. Doba, E. L. Gabe, L. Hughes, F. L. Lee, L. Prasad and K. U. Ingold, J. Am. Chem. Soc., 1985, **107**, 7053. 32
- 33 H. A. Zahalka, B. Robillard, L. Hughes, J. Lusztyk, G. W. Button, E. G. Janzen, Y. Kotake and K. U. Ingold, J. Org. Chem., 1988, 53, 3739.
- J. A. Howard and J. C. Scaiano, in Radical Reaction Rates in 34 Liquids, ed. S. Fischer, Springer-Verlag, Berlin, 1984, vol. 13, Part d.
- 35 D. V. Avila, K. U. Ingold and J. Lusztyk, J. Am. Chem. Soc., 1993, 115, 466.
- 36 D. V. Avila, K. U. Ingold, J. Lusztyk, W. H. Green and D. R. Procopio, J. Am. Chem. Soc., 1995, 117, 2929.
- 37 L. Valmigli, J. T. Banks, K. U. Ingold and J. Lusztyk, J. Am. Chem. Soc., 1995, 117, 9966.

- P. Franchi, M. Lucarini, G. F. Pedulli, L. Valmigli and B. J. 38 Lunelli, J. Am. Chem. Soc., 1999, 121, 507.
- 39 R. M. Borges dos Santos and J. A. Martinho Simoes, J. Phys. Chem. Ref. Data, 1998, 27, 707.
- M. Jonsson, J. Lind, T. E. Eriksen and G. Merenyi, J. Chem. Soc., 40 Perkin Trans. 2, 1993, 1567.
- 41 G. Raabe, Dissertation, University of Essen, 1996.
- 42 M. G. Evans and M. Polanyi, Trans. Faraday Soc., 1938, 34, 11.
- C. Hansch, A. Leo and R. W. Taft, Chem. Rev., 1991, 91, 165. 43
- J. Lind, X. Shen, T. E. Eriksen and G. Merenyi, J. Am. Chem. 44 Soc., 1990, 112, 479.
- 45 F. G. Bordwell and J. P. Cheng, J. Am. Chem. Soc., 1991, 113, 1736.
- M. T. Tribble and J. G. Traynham, *J. Am. Chem. Soc.*, 1969, **91**, 379. H. Herrmann, *Habilitation Thesis*, University of Essen, 1997. 46
- 47
- 48 R. W. Taft, in Separation of Polar, Steric and Resonance Effects in Reactivity in Steric Effects in Organic Chemistry, ed. M. S. Newman, J. Wiley & Sons, New York, 1956, p. 556.

- 49 P. Sykes, in A Guidebook to Mechanism in Organic Chemistry, Longman, Harlow, 1986, p. 375. M. V. Smoluchowski, Z. Phys. Chem., 1917, **92**, 129.
- 50
- A. J. Elliot, D. R. McCracken, G. V. Buxton and N. D. Wood, J. Chem. Soc., Faraday Trans., 1990, 86, 1539.
   M. Anbar, D. Meyerstein and P. Neta, J. Phys. Chem., 1966, 70, 51 52
- 2660 53
- M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isot.*, 1967, **18**, 493. P. O'Neill, S. Steenken and D. Schulte-Frohlinde, *J. Phys. Chem.*, 54
- 1977, 81, 31. 55 R. F. Anderson, K. B. Patel and M. R. L. Stratford, J. Chem. Soc.,
- 56
- K. F. Anderson, K. B. Pater and M. K. L. Strauord, J. Chem. Soc., Faraday Trans. 1, 1987, 83, 3177.
  F. R. Mayo and C. Walling, Chem. Rev., 1950, 46, 191.
  B. Ervens, J. Williams, G. V. Buxton, G. A. Salmon, M. Bydder,
  F. J. Dentener, C. George, P. Mirabel, R. Wolke and
  H. Herrmann, J. Geophys. Res., 2003, 118, 4426. 57
- See: http://www.tropos.de/CHEMIE/multimod/CAPRAM/capram. 58 html.