J. Phys. Chem. A **2002,** *106,* 12045−12050

Reaction Kinetics of NO_2 with Resorcinol and 2,7-Naphthalenediol in the Aqueous Phase at Different pH

Lukas Gutzwiller,[†] Christian George,[‡] Elfriede Rössler,[†] and Markus Ammann*,[†]

Laboratory for Radio and Environmental Chemistry, Paul Scherrer Institute,
5232 Villigen, Switzerland, Laboratoire d'Application de la Chimie à l'Environnement (LACE),
CNRS-UCBL, 43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Received: June 5, 2002; In Final Form: October 7, 2002

The uptake coefficients of NO_2 on buffered solutions containing *m*-dihydroxy benzene (resorcinol) or 2,7-dihydroxynaphthalene ($Np(OH)_2$) were determined over the pH range from 3 to 11 using the wetted wall flow tube technique. The nominal reactant concentration was also varied by several orders of magnitude. Taking into account gas phase as well as liquid-phase diffusion, the uptake coefficients were interpreted using a simple model of stepwise deprotonation of these two weak bivalent acids. This model yields the rate constants for the reaction of NO_2 with the neutral, singly, and doubly deprotonated forms of both compounds. While the reaction of NO_2 with the neutral form is very slow (i.e., with rate constants of a few times 10^2 M^{-1} s^{-1}), the reaction of NO_2 with the deprotonated species is much faster (rate constants are reaching levels of several 10^6 M^{-1} s^{-1}). The rate constant of 3.8×10^8 M^{-1} s^{-1} for NO_2 with the doubly deprotonated resorcinol ion is in good agreement with the one found by Alfassi, the only reported literature value (Alfassi, Z. B.; Huie, R. E.; Neta, P. *J. Phys. Chem.* **1986**, *90*, 4156).

Introduction

In solution, nitrogen dioxide (NO_2) may undergo several types of reactions with organic substances,[2] e.g., hydrogen-atom abstraction from C−H bonds, addition to unsaturated bonds, oxygen-atom transfer, addition to free radicals, and electron transfer. One of the most prominent NO_2 electron transfer reactions is the one with phenoxide ions, which has been initially investigated by Alfassi[1] for methylphenols and hydroxybenzenes. Several authors have also studied the kinetics of reactions of NO_2 with phenol-derived biomolecules such as amino acids (e.g., glycyltyrosine),[3] as well as antioxidants such as ascorbate,[2,4] catechins,[5] and hydroxycinnamic acid derivatives.[6] With little exception, the above studies were carried out at only one pH,[2] although the reaction of phenols is expected to be strongly pH dependent due to their acidic nature. To apply these results to the natural environment or biological systems, it seems to be important to measure the kinetics over a larger range of pH. Both resorcinol and $Np(OH)_2$ might be formed in the atmospheric oxidation of benzene and naphthalene,[7] the latter being the most abundant polycyclic aromatic hydrocarbon (PAH) found in urban air.[8] Moreover, resorcinol has been identified in emissions from wood burning[9,10] and $Np(OH)_2$ in smog chamber experiments addressing naphthalene oxidation.[11,12]

The reactions of all the above-mentioned substances with NO_2 result in nitrite ions, the conjugated base of nitrous acid (HONO). In the atmosphere, HONO seems to be an important early morning precursor of OH radicals in the troposphere due to its photolysis by sunlight.[13] Field studies indicate that HONO is mainly formed heterogeneously from NO_2 on ground or airborne surfaces such as aerosol particles and cloud droplets. In a recent paper we have shown that semivolatile organic compounds contained in diesel exhaust are involved in the heterogeneous reduction of NO_2 to nitrite, the aqueous phase precursor of HONO.[14] To extrapolate those qualitative results to the atmosphere,[15] it is very important on one hand to quantify these semivolatile compounds in the atmosphere and to determine, on the other hand, their heterogeneous rate constant with respect to NO_2. Therefore, we report here uptake rate measurements of NO_2 into solutions of resorcinol and $Np(OH)_2$ in the pH range from 3 to 11 using the wetted wall flow tube technique.

Experimental Section

The uptake of NO_2 into aqueous resorcinol solutions was studied using the wetted wall flow tube (WWFT) technique which has been extensively described for this purpose by many authors.[16−20] The WWFT consists of a 50 cm long, vertically aligned, sand blasted glass tube of $2r = 1.2$ cm inner diameter (Figure 1). Using a peristaltic pump, the reagent solution was injected at the top of the WWFT and evenly distributed over the inside walls using an annular reservoir dispenser system, made from Teflon, which leads to a homogeneous film flowing downward on the inner walls of the flowtube. At the bottom of the tube, the reagent solution is pumped out for ion chromatographic analysis (Dionex AS11 column, gradient pump GP40, Detector CD20) with respect to nitrate and nitrite.

The residence time of the solution in the flow tube was between 30 and 50 s, depending on the liquid flow (see Table 1). The maximum liquid surface area established in these experiments was 188 cm^2. Nitrogen dioxide in synthetic air, from a certified cylinder (10 ppm, Carbagas), was diluted with the carrier gas (see Table 1) using mass flow controllers. Before injection into the WWFT, the reactant gas passed a denuder coated with sodium carbonate in order to remove trace species such as HONO and HNO_3 and was also prehumidified to about

---

* Corresponding author. Markus Ammann, OFLA 106, Paul Scherrer Insitute, 5232 Villigen, Switzerland. Phone: ++41 56 310 4049. Fax: ++41 56 310 4435. E-mail: markus.ammann@psi.ch.

[†] Paul Scherrer Institute.

[‡] Laboratoire d'Application de la Chimie à l'Environnement (LACE).

10.1021/jp026240d CCC: $22.00

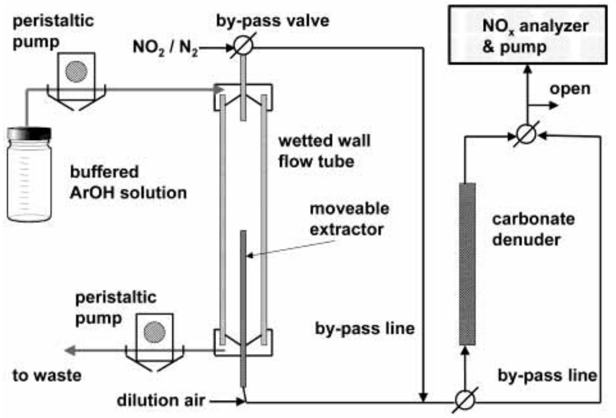

Figure 1. Experimental setup of the wetted wall flow tube (WWFT), see text for details.

TABLE 1: Experimental Wetted Wall Flow Tube Parameters

	resorcinol	2,7-dihydroxynaphthalene
gas flow/dilution after WWFT (sccm)	350/350	300/300
liquid flow (mL/min)	0.5	0.3
residence time (s)	30±5	50±5
carrier gas	nitrogen	synthetic air
buffer, above or below pH 6	phosphate or H_2SO_4	KOH or H_2SO_4

60% relative humidity (at ambient temperature). After interaction with the liquid film, the reacted gas at 100% relative humidity was extracted using a moveable outlet (made from Teflon). Before analyzing the gas with respect to NO_2 by means of a NO_x chemiluminescence analyzer (Monitorlabs, ML9841), the extracted gas was diluted by adding the same amount of carrier gas (doubling the total flow) so that the resulting gas stream had a relative humidity of 50%. This dilution procedure was chosen in order to minimize the quenching effect by water in the chemiluminescence detector, which is known to occur at very high relative humidity and which may lead to up to 20% lower NO_2 values. Moreover, a T-connector open to the atmosphere was placed in front of the NO_x analyzer so that the entire flow system was slightly above atmospheric pressure.

The decay of NO_2 was followed by extracting the reacted gas at five different tube positions corresponding to 15, 20, 25, 30, and 35 cm gas/liquid interaction lengths, leading to contact times between 14 and 70 s. The first 15 cm were not used for the analysis because the laminar flow profile may not be fully established within the first few cm of tube length and because this length is required for the relative humidity to reach 100%. After that "injection zone", the gas flows are well established and the vapor pressure is in equilibrium with the liquid film, allowing kinetic measurements to be made under reproducible conditions.

In reference experiments, the WWFT was bypassed so that the NO_2 inlet concentration could be measured. In other control experiments, a carbonate denuder was set up between the WWFT and the NO_x analyzer. In that case, any change in nitrogen oxide concentrations would be related to gaseous HONO formation in the WWFT. As anticipated from the acidic constant of HONO, $pK_a^{HONO} = 3.5$, no HONO was detected in the gas phase for the experiments at pH 6 or above, because all nitrite ions remain in the liquid film. However, in experiments with a liquid film at pH below 6, the NO_2 signal decreased by about 5 and 10% in the case of resorcinol at pH 4.6 and 2.6, respectively, when the carbonate denuder was positioned in front of the NO_x analyzer. This decrease in the NO_2 signal was attributed to the partitioning of nitrite into the gas phase as HONO which was then trapped by the carbonate denuder, lowering the NO_2 signal compared to the case where both gases reached the NO_x analyzer. Moreover, for resorcinol at pH 2.6, about one-third of the total NO_2 lost appeared as NO, possibly due to secondary processes involving HONO, which were not systematically investigated further. No significant change in the NO_x signal due to HONO was observed for 2,7-dihydroxynaphthalene ($Np(OH)_2$) down to a pH of 3. In the present study, the uptake coefficients were derived using the "real" NO_2 concentration, i.e., when the carbonate denuder was in place and any HONO interferences removed.

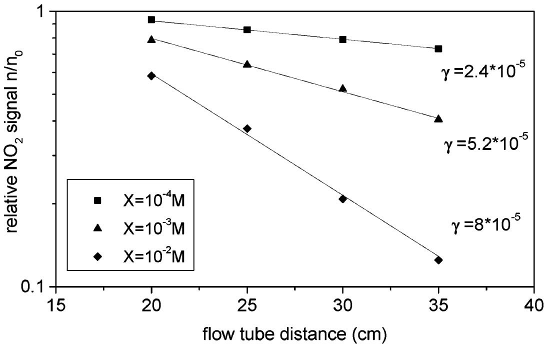

Figure 2. Relative NO_2 signal (n/n_0), on a logarithmic scale, as a function of exposed flow tube length, i.e., extractor position, and for three different resorcinol concentrations at 80 ppb NO_2. The value of n_0 corresponds to the NO_2 signal at 15 cm exposed length. The uptake coefficient γ can be calculated from the decay of the NO_2 signal using the CKD equation.

Aqueous solutions (milliQ water) of resorcinol or 2,7-dihydroxynaphthalene were prepared using reagent grade chemicals in the concentration range of 10^{-4} to 1 M and 5×10^{-5} to 10^{-3} M, respectively. Using a pH-meter (Schott CG 817, Orion Electrode 8103), the various pH values of the $Np(OH)_2$ solutions were adjusted between pH 6 and 11 with KOH. Since the resorcinol solutions were observed to degrade with time when exposed to laboratory air, they were prepared in a glovebag under N_2 in order to avoid any oxidation of resorcinol prior to the experiment. The size of the glovebag did not allow the use of the pH-meter so that the pH values between 6 and 11 were set using phosphate buffers according to Küster and Thiel.[21] The low pH-solutions for both reactants (below pH 6) were prepared using sulfuric acid.

Results

The determination of uptake coefficients γ was based on the relative NO_2 concentration decays as a function of extractor position, respectively, reaction time (Figure 2). The concentration, n, of a trace species undergoing a first order wall reaction in a cylindrical flow reactor, when limited by gas-phase diffusion, can be described by a solution of the differential equations for transport and diffusion as given by Cooney et al.[22] (further called CKD equation):

$$n/n_0 = B_1 \exp(-\Lambda_1^{\,2} z^*) + B_2 \exp(-\Lambda_2^{\,2} z^*) + ... \quad (1)$$

where n_0 is the initial NO_2 concentration and z^* a dimensionless reaction length. The eigenvalues Λ_n are available from Murphy and Fahey;[16] they depend on the uptake coefficient γ and gas-phase diffusion coefficients D_{gas}. The gas-phase diffusion coefficient D_{gas} for NO_2 in air under standard conditions, derived using the Lennard-Jones potentials, were taken from Massman[23]

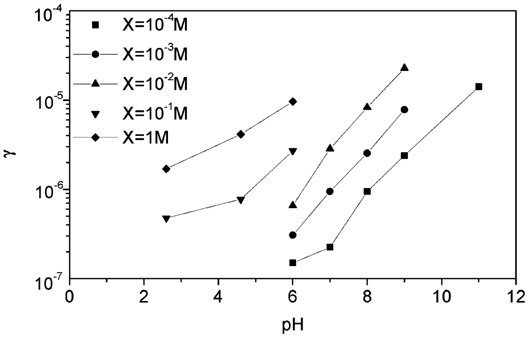

Figure 3. The uptake coefficient γ as a function of pH and for three different resorcinol concentrations. The presented uptake coefficients correspond to the average of three values obtained in the range of 80 to 100 ppb NO_2.

and calculated for $T = 295$ K, assuming an ideal gas (for which D_{gas} depends on T^2). The uptake coefficients were evaluated by fitting the CKD equation to the experimental data, with γ as an adjustable parameter.

Figure 3 shows the uptake coefficients γ of NO_2 on resorcinol containing solutions as a function of pH. The corresponding experiments were performed at NO_2 concentrations between 50 and 90 pbb, where N_2O_4 is negligible, and accordingly no NO_2 gas-phase concentration dependence was observed within this small range of concentration. At 1600 ppb NO_2 concentration the uptake coefficient γ was about two times smaller than at 80 ppb, eventually due to surface saturation. Reported experiments were systematically performed only in the lower concentration range (from 50 to 90 ppb), and since no concentration dependence was observed in this range, the values for γ were averaged when all other parameters remained constant. The values of the uptake coefficients are contained in the range from 4×10^{-7} to 2×10^{-5} for the whole set of experiments. The uptake coefficient for the blank experiment using the buffer solution without reagent was a few times 10^{-7} corresponding to the detection limit. As expected, the uptake of NO_2 on the solutions containing resorcinol and $Np(OH)_2$ increased as a function of pH as well as reactant concentration, since more deprotonated species are available at higher pH.

The uptake of a gas species into a liquid is characterized by the four consecutive processes of (a) mass transfer to the liquid surface (characterized by the gas diffusion coefficient D_{gas}), (b) mass accommodation (characterized by the mass accommodation coefficient α), (c) diffusion in the liquid phase (characterized by the diffusion coefficient D_{liq}), and (d) the liquid-phase reaction. Gas-phase diffusion is accounted for by the CKD equation. We assume that $\alpha \gg \gamma$ under all conditions considered here, and that the surface concentration of NO_2^{aq} at the 15 cm position of the extraction tube is in equilibrium with the gas-phase concentration. For slow liquid-phase reactions, the liquid-phase diffusion can be neglected. In this case, the loss rate of NO_2 from the gas phase is given by

$$\frac{d[{NO_2}^{gas}]}{dt} = \gamma\frac{\bar{c}}{4}\frac{S}{V}[NO_2^{gas}] = k^{II}X[NO_2^{gas}]H_{NO2} = k^{II}X[NO_2^{aq}] \tag{2}$$

where $[NO_2^{gas}]$ and $[NO_2^{aq}]$ are the NO_2 concentrations in the gas and liquid phase, respectively, X is the excess reactant concentration (in our case the hydroxy substituted aromatics), k^{II} the second-order rate constant in the liquid phase, H_{NO2} is the Henry's law constant for NO_2, $\bar{c}$ the mean thermal molecular speed (37 000 cm s^{-1} for NO_2 at 298 K) and $S/V = 2/r = 3.33 cm^{-1}$ is the surface-to-volume ratio of the flow tube. In this case, the pseudo first-order rate constant k^I in the aqueous phase is obtained from eq 2:

$$k^I = k^{II}X = \frac{\gamma}{H_{NO2}}\frac{\bar{c}}{4}\frac{S}{V}$$

or

$$\gamma = \left(\frac{4V}{\bar{c}SH_{NO2}}\right)k^{II}X \tag{3}$$

If, however, the liquid-phase reactions are becoming fast enough compared to the diffusion of NO_2 in the solution, then the reaction will not take place across the entire liquid film but rather in a surface layer, meaning that the uptake becomes diffusion limited; accordingly, a concentration gradient builds up from the film's surface to the inner tube walls. In such a situation, bulk kinetics equations cannot be applied and one has to consider the solution of the mixed diffusion-reaction equations. The approximate distance within the liquid over which the reaction is taking place can be expressed by the so-called diffuso-reactive length $l = \sqrt{D_{liq}/k^I}$,[24] where D_{liq} is the liquid-phase diffusion coefficient equal to 1.85×10^{-5} cm^2 s^{-1} for NO_2.[25] This length can be compared to the thickness d of the reaction medium, i.e., of the reactant film in the WWFT, which, based on geometrical considerations, is given by $d = F_{liq}/\tau_{den}S_{den}$, where F_{liq} is the flow of the reactant solution through the denuder, τ_{den} is the residence time of the film in the denuder and $S = 186$ cm^2 the denuder surface. For an average residence time of 40 s, this thickness becomes 2.2×10^{-3} cm, leading to an upper limit of $k^I = k^{II}X = D_{liq}/l^2 \leq D_{liq}/d^2 = 1.85 \times 10^{-5}/(2.2 \times 10^{-3})^2 = 3.8$ s^{-1}, above which the reaction is diffusion limited. Accordingly, if the reaction is fast corresponding to $k^I > 3.8$ s^{-1}, the liquid-phase diffusion has to be taken into account when plotting γ as a function of k^I and eq 2 takes the form

$$\gamma = \frac{H_{NO2}RT\sqrt{k^I D_{NO2}}}{\bar{c}/4} \tag{4}$$

where R and T are the gas constant and the temperature, respectively.[24] Resolved for k^I, this yields

$$k^I = k^{II}X = \left[\frac{\gamma\frac{\bar{c}}{4}}{H_{NO2}RT}\right]^2\frac{1}{D_{NO2}} \tag{5}$$

or

$$\gamma = \left(\frac{4H_{NO2}RT}{\bar{c}}\right)\sqrt{k^{II}XD_{NO2}} \tag{6}$$

To check whether the present reaction takes place only in the top surface layer of the film or homogeneously over the whole bulk of the film, γ was fitted in two ways according to the two extreme possibilities described above, i.e., as a function of the concentration (linear dependence of eq 3) or as a function of the square root of the concentration (as given by eq 6). This fitting procedure was performed over a reagent concentration range covering 4 orders of magnitude at pH 6 (see Figure 4).

To perform such a fit over 4 orders of magnitude of reactant concentration, a log−log plot had to be chosen in which both the linear and the square root dependence appear as straight

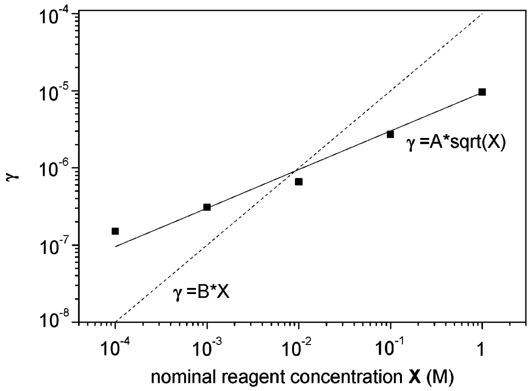

Figure 4. Assessment of liquid-phase diffusion limitation: the uptake coefficient γ is plotted as a function of resorcinol concentration at pH 6, and fitted according to eq 3 (not diffusion limited, dotted line) and eq 6 (diffusion limited, solid line). Note that due to the log−log scale the slope of both fitting lines is fixed and differs by a factor of 2.

lines. The slopes of both lines are fixed, and only their offset can be varied by means of the parameters *A* and *B*, respectively:

$$\log(A\sqrt{X}) = \log(A) + (1/2)\log(X) \text{ and } \log(BX) = \log(B) + \log(X)$$

As can be seen from the above algebraic relations, their slopes differ by a factor of 2. Figure 4 clearly evidences that the slope of the square root dependence, corresponding to the diffusion-limited regime, is in good agreement with the experimental data over the whole range of reagent concentration X. We thus conclude that the kinetics of the present experiments need to be corrected for liquid-phase diffusion.

Discussion

In addition to the disproportionation reaction, i.e.,

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \quad (7)$$

the next three reactions have to be considered:

$$NO_2 + Ar(OH)_2 \rightarrow \text{products} \quad (8)$$

$$NO_2 + ArOHO^- \rightarrow NO_2^- + ArOHO^\bullet \quad (9)$$

$$NO_2 + ArO^-O^- \rightarrow NO_2^- + ArO^\bullet O^- \quad (10)$$

where $Ar(OH)_2$ is the undissociated form of resorcinol and $Np(OH)_2$, respectively, $ArOHO^-$ is the singly deprotonated form, and ArO^-O^- is the doubly deprotonated form. Similarly, $ArOHO^\bullet$ and $ArO^\bullet O^-$ are the corresponding radicals on the product side. Knowing the values of pK_{a1} and pK_{a2} for both acids, the relative amount θ_1 and θ_2 of the singly and doubly dissociated species at a certain pH can be calculated using the Henderson−Hasselbalch formula:[26]

$$\theta_1 = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} = \frac{1}{1 + 10^{(pK_{a1}-pH)} + 10^{(pH-pK_{a2})}} \quad (11)$$

and

$$\theta_2 = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} = \frac{1}{1 + 10^{(pK_{a2}-pH)} + 10^{(pK_{a1}+pK_{a2}-2pH)}} \quad (12)$$

The second deprotonation is treated likewise so that the pH dependence of k^I can be written as

$$k^I = k^{II}X = [(1 - \theta_1 - \theta_2)k_1 + \theta_1 k_2 + \theta_2 k_3]X \quad (13)$$

where k_1, k_2, and k_3 correspond to reactions 8, 9, and 10, respectively; $\theta_1 X$ and $\theta_2 X$ are the actual concentrations of $ArOHO^-$ and ArO^-O^-, where *X* is the nominal concentration of $Ar(OH)_2$. Combining eq 5 and eq 13 yields a relationship between the experimentally determined value of k^{II} and the unknown rate constants k_1, k_2 and k_3 as a function of pH and nominal reactant concentration *X*. This relationship is given by

$$k^{II} = \left(\frac{\gamma\frac{\bar{c}}{4}}{H_{NO2}RT}\right)^2 \frac{1}{D_{NO2}X} = [(1 - \theta_1 - \theta_2)k_1 + \theta_1 k_2 + \theta_2 k_3] \quad (14)$$

and allows fitting the experimental data using the three rate constants k_1, k_2 and k_3 as parameters. This expression, derived under the assumption of an uptake rate affected by aqueous diffusion, allows fitting the experimental uptake coefficients using the three rate constants k_1, k_2, and k_3 as parameters. Figures 5a and 5b show the experimental as well as the fitted values (least-squares fit) of k^{II} as a function of pH for resorcinol and $Np(OH)_2$, respectively. Thanks to the normalization with respect to the nominal reactant concentration *X* (see denominator on left side of eq 14), the values of k^{II} essentially coincide for a given pH, which was not the case when plotting γ as a function of pH (Figure 3). For both substances, k_1 and k_3 are practically determined by γ at extreme pH values around pH 3 and 11, respectively, so that the entire intermediate range of γ, where most data points are available (the number of points *np* is given in Table 2), is used to determine k_2. Moreover, using the previously reported value of $k_3 = 3.8 \times 10^8$ M^{-1} s^{-1} for resorcinol[1] at pH 12 as input into the kinetic model yields a very good fit for k^{II} above pH 9. Table 2 summarizes the results obtained by a least-squares fitting procedure in which the values of k_2 at a given pH were weighted by θ_1. In fact, since the values of k^{II} cover a range of 5 orders of magnitude, they had to be divided by a weighing factor before determining the least-squares fit. The use of θ_1 as a weighing factor yields reasonable results, i.e., a homogeneous distribution of the relative errors over the whole range of k^{II}.

In the case of resorcinol, the two pK_a values are quite similar; therefore, the second-order rate constant k^{II} in the transition regime of pH 9 to 11 is smooth. In the case of $Np(OH)_2$, however, a clear step function for k^{II} is apparent, indicating that the two values of pK_a are further apart than in the case of resorcinol. The only literature value of pK_{a1} for $Np(OH)_2$ was assessed using UV−vis spectroscopy more than forty years ago and amounts to 9.37.[28,29] Moreover, only a value for pK_{a1} but not for pK_{a2} is given in these studies, which might be due to the interference experienced when the two ionizing groups lie within 3 pK_a units of one another.[26] Applying the same technique to determine the values of pK_a in our lab did not yield a conclusive result. Using the above value of 9.37 did not allow reproducing the step function for k^{II}, therefore two different

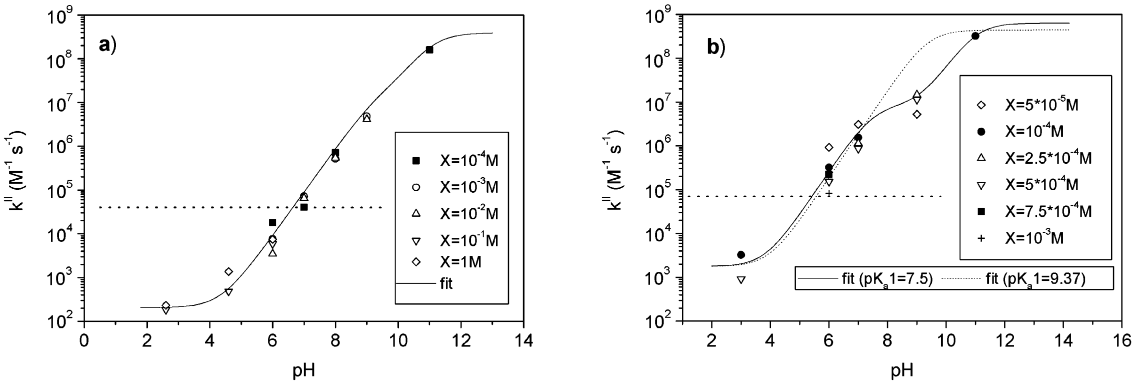

Figure 5. Overall second-order rate constant k^{II} as a function of pH according to eq 14 for resorcinol (a) and $Np(OH)_2$ (b). The experimental data points are obtained from the uptake coefficients corrected for liquid-phase diffusion (left side of eq 14). The fit is calculated using the rate constants k_1 to k_3 as fit parameters according to the right side of eq 14. The horizontal dotted line corresponds to k^{II}, above which the overall reaction becomes diffusion-limited in the case of the *lowest* nominal reactant concentration corresponding to 10^{-4} M and 5×10^{-5} M for resorcinol and $Np(OH)_2$, respectively.

TABLE 2: Second Order Rate Constants Obtained by a Least-Square Fitting Procedure

	pK_{a1}	pK_{a2}	k_1 (M^{-1} s^{-1})	k_2 (M^{-1} s^{-1})	*np*	k_3 (M^{-1} s^{-1})
resorcinol	9.31 [27]	11.1 [27]	205 ± 24	$(1.3 \pm 0.2) \times 10^7$	14	3.8×10^8 [1]
$Np(OH)_2$; scenario I	9.37 [28]	undef.[a]	$(1.8 \pm 1.1) \times 10^3$	$(4.4 \pm 0.7) \times 10^8$	13	undef.[a]
$Np(OH)_2$; scenario II	7.5	11	$(1.8 \pm 1.1) \times 10^3$	$(8.4 \pm 2.7) \cdot 10^6$	13	6.3×10^8

[a] In scenario I, pK_{a2} and k_3 are redundant, since the experimentally observed two step deprotonation cannot be fitted appropriately.

fitting procedures were tested, referred to as scenario I and II in Table 2. In the first one, the literature value of pK_{a1} was taken as input and pK_{a2} was adjusted; and in the second procedure, both values of pK_a were adjusted. To get a reasonable fit for scenario I, k_2 has to be chosen so large that reaction 10 involving the doubly deprotonated species becomes redundant, i.e., pK_{a2} and k_3 are not needed to get a good fit (they do not improve the fit). Applying the second procedure, a good fit was obtained by setting $pK_{a1} = 7.5$ and $pK_{a2} = 11$. It has to be noted that the depth of the step occurring around pH 8 is mainly given by the difference of pK_{a1} and pK_{a2} rather than their absolute values. Comparing the results of both procedures reveals that k_2 obtained in the first procedure, in which pK_{a2} and k_3 are undefined, is of the same order of magnitude (10^8 $M^{-1}s^{-1}$) as k_3 obtained in the second procedure, which better captures the bivalent acid nature of $Np(OH)_2$.

The reactivity of both substances, resorcinol and $Np(OH)_2$, seems to be similar since k_2 and k_3 in the case of $Np(OH)_2$ (second procedure) are only a factor of 2 larger than the ones for resorcinol. Moreover, the value of k_2 for the singly deprotonated $Np(OH)_2$ is in excellent agreement with the rate constant $k_2 = 8.6 \times 10^6$ M^{-1} s^{-1} of a functionally similar species, the phenoxide ion.[1] Regarding k_1, however, the value of k_1 for $Np(OH)_2$ is a factor of 9 larger than for resorcinol, which may also be attributed to the larger error at low pH where the detection limit is reached.

The hypothesis of diffusion limitation can now be verified numerically by applying the condition $k^I = k^{II}X > 3.8$ s^{-1} (see Results section) to the data in Figure 5. The horizontal dotted line shows the limit above which the overall reaction becomes diffusion-limited in case of the *lowest* investigated nominal reactant concentration X. In the case of 10^{-4} M nominal resorcinol concentration, only one point lies below this limit, and in the case of 5×10^{-5} M $Np(OH)_2$, none. Close to the detection limit, i.e., below pH 7, the uptake coefficients were obtained using large enough nominal reactant concentrations so that the reactions were diffusion-limited despite the low values of k^{II}. For product analysis, the effluent from the WWFT was sampled and analyzed, after storing in a freezer for a few days, for its nitrite content by ion chromatography. For both resorcinol and $Np(OH)_2$, this analysis showed almost a one-to-one correspondence of the measured nitrite and the expected nitrite due to NO_2 loss from the gas phase. The slight deficiency of measured nitrite can be explained by the relatively large and variable nitrate background: it is known that nitrite may be oxidized to nitrate in the freezing process of a solution.[30] Since the amount of products formed was very low compared to the reactant concentration in the liquid phase, further reactions of NO_2 with $ArOHO^•$ and $ArO^•O^•$ were not considered. For $Np(OH)_2$, however, an increased uptake of NO_2 was observed when N_2 was used as carrier gas instead of synthetic air. This might indicate that, in the second case, some of the $AOHO^-$ and ArO^-O^- ions may have reacted with O_2 instead of NO_2.

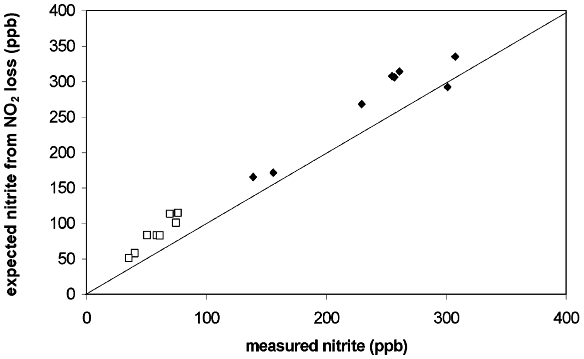

Figure 6. Product analysis: correlation between measured nitrite and the expected amount of nitrite if all the NO_2 lost from the gas-phase reacted to nitrite in the liquid-phase according to eqs 7 to 10. Diamonds and open squares correspond to resorcinol and $Np(OH)_2$, respectively.

Conclusions

Using the wetted wall flow tube technique, the liquid-phase kinetics of two weak bivalent acids, resorcinol and $Np(OH)_2$, with NO_2 were investigated over the pH range 3 to 11 and for nominal reactant concentrations varying over four (resorcinol) and two ($Np(OH)_2$) orders of magnitude. These substances serve as model compounds for the understanding of NO_2 reduction to nitrite, the liquid phase precursor of atmospheric nitrous acid. The results were interpreted using a simple model taking into account the stepwise deprotonation of these two weak bivalent organic acids. From the six determined rate constants, only one can be compared to a literature value with which it is in good agreement. The present results might serve as input into atmospheric box models aiming at assessing the importance of heterogeneous HONO formation due to semi-volatile organic compounds as postulated in one of our recent studies.[14] As shown in a modeling approach by Lahoutifard et al.,[15] under moderate acidic conditions (i.e., pH above 4), the type of reactions presented in this paper may be responsible for more than 75% of the total HONO/NO_2^- production rate in the aqueous phase. Such pH values are found in fog or cloud droplets, or in aerosol particles affected by neutralizing agents (ammonia, dust). On the other hand, the reactions presented here may become insignificant in very acidic droplets or particles such as those often encountered in heavily polluted environments.

Acknowledgment. We thank the Federal Office for Education and Science for their funding within NITROCAT (EVK2-CT-1999-00025), an EC project under the fifth Framework Program. We also thank the “Direction des Relations Internationales du CNRS, DRI” for providing funds for the collaboration with Ch. George.

References and Notes

(1) Alfassi, Z. B.; Huie, R. E.; Neta, P. *J. Phys. Chem.* **1986**, *90*, 4156.

(2) Huie, R. E. *Toxicology* **1994**, *89*, 193.

(3) Prütz, W. A.; Monig, H.; Butler, J.; Land, E. J. *Arch. Biochem. Biophys.* **1985**, *243*, 125.

(4) Forni, L. G.; Mora-Arellano, V. O.; Packer, J. E.; Willson, R. L. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1.

(5) Miao, J. L.; Wang, W. F.; Pan, J. X.; Lu, C. Y.; Li, R. Q.; Yao, S. D. *Radiat. Phys. Chem.* **2001**, *60*, 163.

(6) Zhan, Z.; Yao, S.; Lin, W.; Wang, W. F.; Jin, Y.; Lin, N. *Free Radical Res.* **1998**, *29*, 13.

(7) Olariu, R. I.; Barnes, I.; Becker, K. H.; Klotz, B. *Int. J. Chem. Kinet.* **2000**, *32*, 696.

(8) Arey, J.; Atkinson, R.; Zielinska, B.; McElroy, P. A. *Environ. Sci. Technol.* **1989**, *23*, 321.

(9) Fine, P. M.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **2001**, *35*, 2665.

(10) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1998**, *32*, 13.

(11) Lane, D. A.; Fielder, S. S.; Townsend, S. J. *Polycyclic Aromat. Comput.* **1999**, *14*, 129.

(12) Lane, D. A., personal communication.

(13) Lammel, G.; Cape, J. N. *Chem. Soc. Rev.* **1996**, 361.

(14) Gutzwiller, L.; Arens, F.; Baltensperger, U.; Gäggeler, H. W.; Ammann, M. *Environ. Sci. Technol.* **2002**, *36*, 677.

(15) Lahoutifard, N.; Ammann, M.; Gutzwiller, L.; Ervens, B.; George, C. *Atmos. Chem. Phys.* **2002**, *2*, 1.

(16) Murphy, D. M.; Fahey, D. W. *Anal. Chem.* **1987**, *59*, 2753.

(17) Scheer, V.; Frenzel, A.; Behnke, W.; Zetzsch, C.; Magi, L.; George, C.; Mirabel, P. *J. Phys. Chem. A* **1997**, *101*, 9359.

(18) Hanson, D. R. *J. Phys. Chem.* **1995**, *99*, 13059.

(19) Fickert, S.; Helleis, F.; Adams, J. W.; Moortgat, G. K.; Crowley, J. N. *J. Phys. Chem. A* **1998**, *102*, 10689.

(20) Danckwerts, P. V. *Gas−Liquid Reactions*; McGraw-Hill: New York, 1970.

(21) Küster, F. W.; Thiel, A.; Fischbeck, K. *Logarithmische Rechentafeln*; Walter de Gruyter & Co: Berlin, 1962.

(22) Cooney, D. O.; Shin Seung, K.; Davis, E. J. *Chem. Eng. Sci.* **1974**, *29*, 1731.

(23) Massman, W. J. *Atmos. Environ.* **1998**, *32*, 1111.

(24) Hanson, D. R.; Ravishankara, A. R.; Solomon, S. *J. Geophys. Res.* **1994**, *99*, 3615.

(25) Chameides, W. L. *J. Geophys. Res.* **1984**, *89*, 4739.

(26) Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants*; Chapman and Hall: London and New York, 1984.

(27) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 79th ed.; CRC Press: Boca Raton, 1998.

(28) Arnal, N.; Deumié, M.; Viallet, P. *J. Chim. Phys. PCB* **1961**, *66*, 421.

(29) Hercules, D. M.; Rogers, L. B. *Spectrochim. Acta* **1959**, 393.

(30) Takenaka, N.; Daimon, T.; Ueda, A.; Sato, K.; Kitano, M.; Bandow, H.; Maeda, Y. *J. Atmos. Chem.* **1998**, *29*, 135.