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Citation for published version:
Heal, MR, Harrison, MAJ & Cape, JN 2007, 'Aqueous-phase nitration of phenol by N2O5 and ClNO2', *Atmospheric Environment*, vol. 41, no. 17, pp. 3515-3520. https://doi.org/10.1016/j.atmosenv.2007.02.003

Digital Object Identifier (DOI):
10.1016/j.atmosenv.2007.02.003

Post-print of peer-reviewed article published by Elsevier.
Published article available at: http://dx.doi.org/10.1016/j.atmosenv.2007.02.003

Cite as:
Heal, M.R., Harrison, M.A.J. and Cape, J.N. (2007) Aqueous phase nitration of phenol by N_2O_5 and $ClNO_2$, *Atmospheric Environment* 41, 3515-3520.

Aqueous phase nitration of phenol by N_2O_5 and $ClNO_2$

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Keywords: Tropospheric chemistry; heterogeneous chemistry; nitrosation; nitronium ion.

Abstract

Nitrophenols are present in the atmospheric gas phase and in cloud and rainwater. Their formation via aqueous-phase reactions of phenol with the nitronium ion, NO_2^+, arising from N_2O_5 and $ClNO_2$ partitioning into the aqueous phase, has been proposed but not verified experimentally. Here we demonstrate for the first time that gaseous N_2O_5 and $ClNO_2$ partitioning into dilute aqueous

solutions of phenol yields 2- and 4-nitrophenol (and 4-nitrosophenol), but no dinitrophenol isomers. The rate of nitration does not vary significantly between 5 and 20 °C, presumably because of opposing temperature dependences in Henry's law partitioning and reaction rate coefficients. The rate coefficient for reaction of NO_2^+ with phenol could not be directly quantified but is evidently large enough for this reaction to compete effectively with the reaction between NO_2^+ and water and to provide a feasible route to nitrophenol production in the atmosphere.

Introduction

Nitrophenols have been identified in the atmospheric gas phase and in cloud and rain water (see Harrison et al. (2005a) for a recent review). The predominant nitro-aromatic species reported are 2- and 4-nitrophenol and 2,4-dinitrophenol. These compounds originate almost entirely from the oxidation and nitration of benzene and phenol emitted to the atmosphere rather than by direct primary emission of the nitrophenols themselves. Aside from the role of these compounds in understanding the atmospheric oxidation of monoaromatic species, the formation of nitrophenols is a concern because of their phytotoxicity at low concentrations.

Chemical box modelling has shown that nitration reactions in the aqueous phase can be an important route to atmospheric nitrophenol formation because of the favourable partitioning of phenol into the aqueous phase and the faster rates of reaction in the aqueous phase compared with the gas phase (Harrison *et al.*, 2005b). It is also likely that a proportion of the observed gas phase nitrophenol forms in the aqueous phase and partitions back into the gas phase. A number of atmospheric species have been verified experimentally to effect aqueous-phase nitration of phenol including the nitrate radical (NO_3) (Umschlag *et al.*, 2002), nitrogen dioxide (NO_2) (Barletta *et al.*,

2000), nitrous acid (HONO) (Vione *et al.*, 2004), and nitrate (NO_3^-) and nitrite (NO_2^-) ions in combination with UV irradiation (Vione *et al.*, 2003). Two other potential atmospheric nitration reagents, N_2O_5 and $ClNO_2$, have also been proposed (Harrison *et al.*, 2005a) but there have been no published studies investigating their nitrating capability with dilute aqueous solutions of phenol. N_2O_5 is an important atmospheric reservoir species for NO_x, particularly at night, and its reaction with sea-salt aerosols yields $ClNO_2$ (Behnke *et al.*, 1997). In both cases the nitration electrophile is assumed to be the nitronium ion, NO_2^+, which has been shown experimentally to be a hydrolysis product of the parent compounds (Horn *et al.*, 1994; Behnke *et al.*, 1997). Although the Henry's law solubilities of both N_2O_5 and $ClNO_2$ are low (values at 298 K of 2.1 M atm^{-1} for N_2O_5, and 0.024 and 0.048 M atm^{-1} for $ClNO_2$ (Sander, 1999)), their rapid solvation, and likely high reactivity of the resultant NO_2^+, increases substantially their effective solubility and likely importance as atmospheric nitrating reagents.

In this work, a flow of air containing N_2O_5 and $ClNO_2$ was bubbled through solutions of phenol and products analysed as a function of time. Product ratio and kinetic data are reported.

Experimental

A continuous flow of N_2O_5 in air was prepared by mixing flows of 4.5% O_3 in O_2 (75 mL min^{-1}) and 1% NO_2 in air (750 mL min^{-1}) at the entrance of a cylindrical reaction chamber of 50 cm length and 9 cm diameter. (Gas residence time in chamber ~4 min). The $ClNO_2$ was prepared by passing the outlet flow containing N_2O_5 over a 4 M NaCl solution for 30 s. Characterisation of both gases was undertaken qualitatively via FTIR spectroscopy (http://webbook.nist.gov/chemistry) and quantitatively by bubbling the gas flow through deionised

water and determining the yield of NO_3^- (plus Cl^- for $ClNO_2$) by ion chromatography. A slight excess of NO_2 was the only impurity, and conversion of N_2O_5 to $ClNO_2$ was stoichiometric.

The gas flow containing the nitrating gas was continuously bubbled through a frit into the bottom of a reaction vessel (27 cm depth, 4.5 cm internal diameter) containing phenol solution in the concentration range 10^{-4}-10^{-1} M. Both the flask and the incoming gas flow were surrounded by thermostatted coolant. Experiments were conducted at 5 and 20 °C and at pH 6 and 10 (the latter obtained using dilute Na_2CO_3). A known quantity of 5-methyl-2-nitrophenol was present in the phenol solution as an internal standard for product quantification. The whole process was carried out in the dark to eliminate photolytic degradation of nitrating reagents.

Products were extracted from the aqueous phase after different reaction times using Strata D-L solid-phase extraction tubes, pre-treated with methanol and water, and eluted with ethyl acetate. The products were separated and quantified by GC-ECD (HP 5890) using a 30 m ZB5 capillary column (0.32 mm id, 1.0 μm phase thickness) and a temperature programme of 140 °C for 40 min followed by ramping at 30 °C min^{-1} to 230 °C for 5 min. Peak identity was also confirmed separately by GC-MS (HP 6890 with 5973 MSD).

Results and discussion

Products

In all experiments, 2- and 4-nitrophenol were the only nitrophenol products (Table 1). No 3-nitrophenol was observed. The absence of any dinitrophenol formation was confirmed for contact times in excess of 30 mins. Substantial proportions of 4-nitrosophenol were formed except at pH

10 with N_2O_5 as nitrating reagent. The observed product distributions did not vary with phenol concentration or duration of experiment. Neither did they vary with temperature. The product distributions reported in Table 1 are therefore averaged over these factors. 2-nitrophenol was the more abundant product of the two mononitrophenol isomers. Since 2-nitrophenol is the dominant product in experimental studies of gas phase nitration of phenol (Atkinson *et al.*, 1992; Bolzacchini *et al.*, 2001), any 4-nitrophenol measured in the atmosphere is presumed to result from condensed phase reactions, which these findings support.

For both nitrating reagents, considerably less 4-nitrosophenol was produced in the alkaline solution, indicating that nitration is more competitive than nitrosation at higher pH. Nitrosation reactions frequently accompany nitration reactions and are presumed to proceed in an analogous manner, but with NO^+ rather than NO_2^+ as the nucleophile. The nitrosation of phenol is thought to occur by reduction of NO_2^+ by phenol to generate NO^+ which itself attacks phenol (Sykes, 1986). The nitrosation occurs exclusively in the *para* position because NO^+ is a weaker electrophile than NO_2^+ and unable to overcome the steric hindrance at the *ortho* position caused by water molecules hydrogen-bonded to the hydroxyl group (Baer *et al.*, 1970). This mechanism also accounts for the pH dependence of the nitrosation. Phenol is a weak acid ($pK_a = 10$) so at high pH the phenoxide ion is several orders of magnitude more prevalent than at pH 6. The negative charge on the phenoxide ion increases the reactivity of the aromatic ring towards *ortho*/*para* NO_2^+ substitution to form nitrophenols compared with the alternative reduction of NO_2^+ to NO^+ and subsequent nitrosophenol formation.

Although it is possible for NO^+ to be generated via sequential reaction of NO_2-dimer (i.e. N_2O_4) with water (R1-2),

$$N_2O_4\ (g) + H_2O \rightarrow HNO_2\ (l) + NO_3^- + H^+ \qquad (R1)$$

$$HNO_2\ (l) + H^+ \rightarrow H_2O + NO^+ \qquad (R2)$$

this route is ruled out for the following reasons: nearly all incoming NO_2 was converted to N_2O_5 (and $ClNO_2$) upstream of the reaction vessel containing phenol, and calculations showed that <1% of the unconverted NO_2 would exist as N_2O_4; the IR spectra of N_2O_5 and $ClNO_2$ showed no evidence of N_2O_4; in separate experiments, passing only NO_2 through the phenol solution yielded no nitro- or nitrosophenols. All evidence therefore suggests that 4-nitrosophenol was produced by NO^+ formed by the reaction of NO_2^+ with the phenol present in the liquid rather than by NO^+ generated directly from N_2O_4.

Nitrosophenols are not generally reported in the atmospheric aqueous phase, although it is not clear the extent to which they have been specific target analytes in field measurements. The observation of 4-nitrosophenol in this work is in accord with Vione *et al.* (2004) who likewise observed 4-nitrososphenol alongside 2- and 4-nitrophenol in experiments with nitrous acid as a nitrating agent for phenol in aqueous solution. Since 4-nitrosophenol is susceptible to oxidation it is assumed that 4-nitrosophenol formed in atmospheric water ultimately undergoes oxidation to 4-nitrophenol by agents such as $O_2/O_3/HO_2^-$ etc. This reinforces the importance of the aqueous phase for 4-nitrophenol formation and is in accord with the observation that 4-nitrophenol is the dominant mononitrophenol isomer in the atmosphere.

Kinetics

The rate of total product formation in experiments using the most dilute phenol solutions (10^{-4} M) showed pseudo-first order reaction kinetics (Figure 1, top left) indicating that reaction under these conditions was limited by the amount of phenol present. In contrast, product formation was linear

with time at the highest phenol concentration (0.1 M) (Figure 1, bottom right), indicating that reaction was zero order with respect to phenol and limited by the rate of introduction of nitrating gas into the system. The same kinetic profiles were observed for each of the nitrophenol products individually.

The kinetic scheme shown in Figure 2 was postulated to describe the overall nitration process. The figure shows N_2O_5 as the nitrating reagent but dissociation of $ClNO_2$ to yield NO_2^+ (and Cl^-) is assumed to occur analogously. In these experiments, NO_2^+ is generated continuously by phase transfer of N_2O_5 from the gas to liquid surface (Henry's Law partitioning), mixing of N_2O_5 between surface and bulk, and dissociation of N_2O_5 into NO_2^+ (and NO_3^- or Cl^-). The overall rate of NO_2^+ production in solution for a given set of experimental conditions can be assigned a constant flux, F. The resulting NO_2^+ can react with either phenol (R3), with bimolecular rate coefficient, k_2, or with water (R4), with pseudo-first order rate coefficient k_w.

$$NO_2^+ + \text{phenol} \rightarrow \text{product} \qquad \text{(R3)}$$

$$NO_2^+ (+ H_2O) \rightarrow NO_3^- + 2H^+ \qquad \text{(R4)}$$

This scheme leads to the following kinetic equation describing NO_2^+ concentration in solution,

$$\frac{d[NO_2]}{dt} = F - k_w[NO_2^+] - k_2[NO_2^+][\text{phenol}] \qquad \text{Eq.1}$$

The parameter-fitting routine of the FACSIMILE software (http://www.mcpa-software.com/) was used to fit this kinetic scheme to the experimental data obtained at all four phenol concentrations simultaneously (for a given pH and nitrating reagent); thus, for example, a single fit used all the experimental data shown in Figure 1. The fitting parameters were F, k_2 and k_w. Since there was no significant difference in kinetics with temperature (for given other conditions), data at both 5 and

20 °C were used simultaneously. The lack of temperature dependence is likely the consequence of opposing factors: a negative temperature dependence in Henry's Law partitioning and a positive temperature dependence in reaction rates.

It was not possible explicitly to fit all three parameters independently because the kinetic scheme is sensitive only to the ratio of the rate coefficients, k_2/k_w. The value of this ratio obtained by fitting is insensitive to the value chosen for k_w over a few orders of magnitude. The fitted values obtained for F and k_2/k_w are shown in Table 2, and the set of modelled kinetic profiles obtained for the data in Figure 1 shown by the solid curves. The model fits to the data agree closely.

The values of the ratio k_2/k_w in Table 2 are consistent with the expectation that aromatic rings, particularly substituted rings, are more effective nucleophiles than water. Furthermore, the ratios of rate coefficients derived here for reaction between NO_2^+ and phenol or water are lower than the rate coefficient ratio of 1×10^4 M^{-1} derived by Johnson and Margerum (1991) for reaction between NO_2^+ and Cl^- or water, again consistent with the expectation that NO_2^+ is less reactive towards phenol than Cl^- because of the formal attracting charges in the latter case.

In reality, the k_2 rate coefficient represents the combined reaction of NO_2^+ with both phenol and phenoxide anion, and the k_w rate coefficient represents the combined reaction of NO_2^+ with both H_2O and OH^-. The contribution of each pair of reactions to their overall reaction cannot be explicitly quantified. However, the rate of product formation at the different pH values gives insight into the relative effects of basicity on reaction of NO_2^+ with "phenol" (the product route) or with "water" (non-product route). When phenol rather than NO_2^+ is the limiting reactant, product formation has an effective first-order rate coefficient Fk_2/k_w. For both N_2O_5 and $ClNO_2$ as nitrating

reagent, the Fk_2/k_w data are greater at pH 10 than at pH 6, indicating that reaction of NO_2^+ with phenoxide is more significant to the NO_2^+ + "phenol" reaction than the reaction of NO_2^+ with OH^- is to the NO_2^+ + "water" reaction. On the other hand, under the same limiting conditions, the product formation rate coefficient, at a given pH, does not differ much between N_2O_5 or $ClNO_2$ as the source of the nitrating electrophile.

There is no previous published investigation of the rate coefficient, k_2, for reaction between phenol and NO_2^+. There has also only been one published value for the rate coefficient for reaction between NO_2^+ with water (Behnke *et al.*, 1997), which was determined indirectly. These workers derived a value of 15.1 M^{-1} for the ratio of the rate coefficients for reaction of NO_2^+ with Cl^- or with water (with the latter expressed in pseudo-first order dimension), and used modelling to try and constrain values for the two rate coefficients individually. They derived $k_w = 4.9 \times 10^9$ s^{-1}. Subsequent literature consistently refers back to the Behnke et al. (1997) ratio of rate coefficients for NO_2^+ reaction with Cl^- or H_2O as the source for k_w, although Frenzel et al. (1998) (same group) derived a slightly modified value of $k_w = 1.7 \times 10^9$ s^{-1}. Applying this latter value of k_w to the ratio of rate coefficients determined in this work gives the estimates for the rate coefficient for NO_2^+ with phenol in the final column of Table 2. Clearly these values (~10^{12} M^{-1} s^{-1}) are unfeasibly large when compared with a maximum value of ~10^{10} M^{-1} s^{-1} that can be estimated for a diffusion-limited rate coefficient in water at 298 K (Atkins, 2006). The value of k_w derived by Benhke et al. (1997) is therefore called into question. In fact, the value of 15.1 M^{-1} reported by Benhke et al. (1997) for the ratio of rate coefficients for reaction of NO_2^+ with Cl^- or with H_2O is orders of magnitude smaller than the value of 1×10^4 M^{-1} reported by Johnson and Margerum (1991), a discrepancy that Behnke et al. (1997) could not resolve. The Behnke et al. (1997) ratio also appears small in comparison with the expected relative nucleophilic reactivities of Cl^- and H_2O.

An interpretation of the above is that the true k_w for the pseudo-first order reaction between NO_2^+ and H_2O is smaller than the ~10^9 s^{-1} quoted above. This would make the value for k_2 smaller by the same factor. The deduction of a lower k_w is also entirely consistent with the expectation from nucleophile/electrophile arguments discussed above that the rate coefficient for reaction between NO_2^+ and phenol lies between that for reaction with Cl^- and H_2O. (As an aside, our data are also consistent with the view of Behnke et al. (1997) that the ratio of NO_2^+ rate coefficient with OH^- or H_2O cannot be as large as estimated by Johnson and Margerum (1991) otherwise the former rate coefficient would dominate reaction at pH 6 as well as pH 10).

Regardless of the uncertainty in deriving an absolute value for the rate coefficient of NO_2^+ with phenol, it is evident that this rate coefficient is sufficiently competitive against other loss processes for NO_2^+ in aqueous solution (i.e. reaction with H_2O and/or OH^-) readily to yield observable nitrophenol products.

Conclusions

The capacity for N_2O_5 and $ClNO_2$ to yield 2- and 4-nitrophenol and 4-nitrosophenol from a dilute aqueous solution of phenol has been demonstrated. There is no dinitrophenol production under these conditions. The overall nitration process has no observed temperature dependence between 5 and 20 °C. Although the rate coefficient for reaction between NO_2^+ and phenol could not be directly quantified, it is evidently large enough for this reaction to compete effectively with the reaction between NO_2^+ and water. The findings demonstrate that N_2O_5 and $ClNO_2$ are viable nitrating agents for nitrophenol production in the atmosphere aqueous phase.

Acknowledgements

MAJH was supported by a studentship from the UK EPSRC and CASE funding from the NERC Centre for Ecology & Hydrology.

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Table 1. Observed product distributions (mean ± 1 sd of triplicates) for different nitration reagents and aqueous pH.

Reagent	pH	2-nitrophenol / %	4-nitrophenol / %	4-nitrosophenol / %
N_2O_5	6	14 ± 5	6 ± 5	80 ± 7
N_2O_5	10	61 ± 10	39 ± 10	0
$ClNO_2$	6	10 ± 5	10 ± 7	80 ± 12
$ClNO_2$	10	32 ± 13	19 ± 2	49 ± 14

Table 2. Results of FACSIMILE fits to experimental kinetic profiles. Data at 5 and 20 °C were combined. Values for F and k_2/k_w are independently determined. Values for k_2 are calculated from k_2/k_w using $k_w = 1.7 \times 10^9$ s^{-1} (see text).

Reagent	pH	Fk_2/k_w / s^{-1}	F / M s^{-1}	k_2/k_w / M^{-1}	k_2 / M^{-1} s^{-1}
N_2O_5	6	1.5×10^{-3}	4.6×10^{-6}	330	0.6×10^{12}
N_2O_5	10	3.8×10^{-3}	2.5×10^{-6}	1500	2.5×10^{12}
$ClNO_2$	6	2.1×10^{-3}	3.3×10^{-6}	640	1×10^{12}
$ClNO_2$	10	4.5×10^{-3}	9.9×10^{-6}	450	0.8×10^{12}

Figure 1. Total product concentration with time for nitration with N_2O_5, at pH 10, of phenol solutions of concentration 10^{-4} M (top left), 10^{-3} M (top right) , 10^{-2} M (bottom left) and 10^{-1} M (bottom right). Open and closed symbols are experimental data obtained at 5 and 20 ^{0}C, respectively. Error bars (± 1 sd of triplicates) are shown for illustration on two sets of data only. The solid lines are kinetic model fits to all data simultaneously (see text).

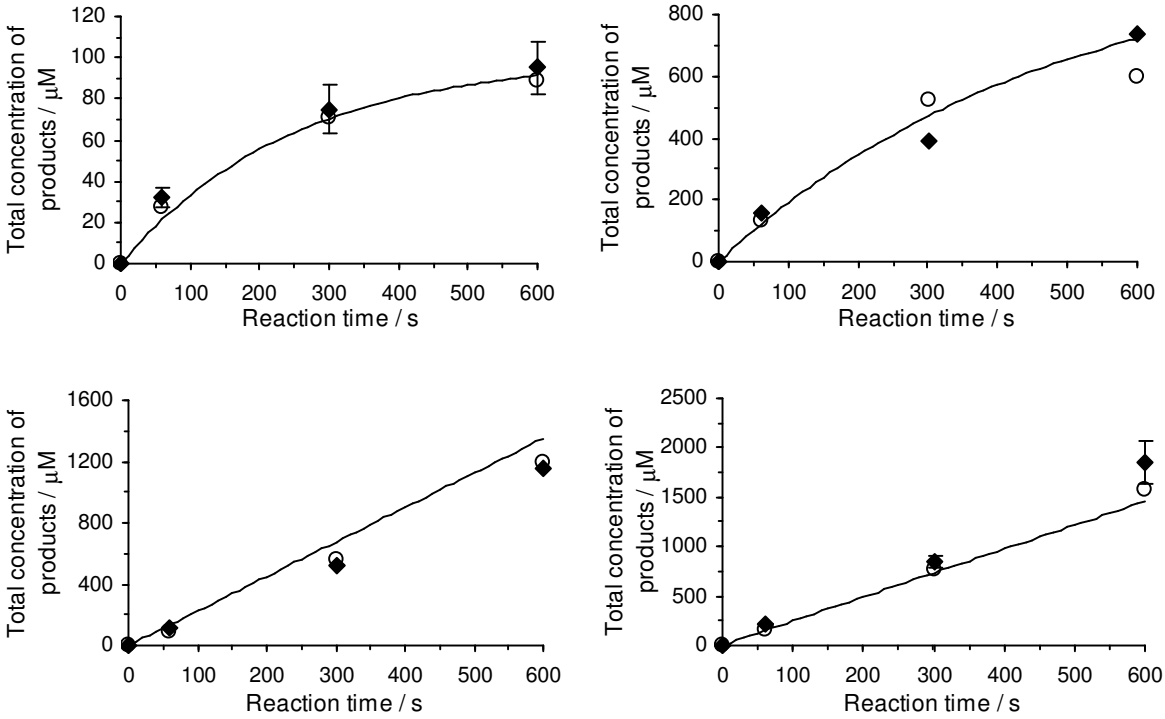

Figure 2: Schematic illustrating the phase transfer of N_2O_5 followed by dissociation to NO_2^+ which can then react with either water or with phenol (PH) to yield nitrated products (NP).