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Short communication

Aqueous-phase nitration of phenol by N_2O_5 and $ClNO_2$

Mathew R. Heal[a,*], Mark A.J. Harrison[a,1], J. Neil Cape[b]

[a] *School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*
[b] *Centre for Ecology & Hydrology, Edinburgh Research Station, Bush Estate, Penicuik, Midlothian EH26 0QB, UK*

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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.

Keywords: Tropospheric chemistry; Heterogeneous chemistry; Nitrosation; Nitronium ion

1. Introduction

Nitrophenols have been identified in the atmospheric gas phase and in cloud and rainwater (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

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[*] Corresponding author. Tel.: +44 131 6504764; fax: +44 131 6506453.
E-mail address: m.heal@ed.ac.uk (M.R. Heal).

[1] Current address: Met Office, FitzRoy Road, Exeter EX1 3PB, UK.

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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.

2. 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 i.d., 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).

3. Results and discussion

3.1. 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 min. 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

Table 1
Observed product distributions (mean ± 1 S.D. 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