

MULTIPHASE NITRATION OF PHENOL IN TROPOSPHERE

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Emissions of benzene and toluene from traffic or industry (1) result in the formation of phenol or cresols and ring fragmentation products (2). Phenols are known to be formed in the atmosphere by the OH-initiated atmospheric oxidation of aromatic hydrocarbons and a number of product studies reported in the literature show that their yields can be relatively high (e.g. as high as 19% in the case of p-xylene, subsequent to the uptake by cloud droplets (2)).

Phenolic material is then transformed into nitrophenols (3). In fact, nitrophenols have been found in rainwater in the $\mu\text{g L}^{-1}$ range in the Rhein-Ruhr area in western Germany (4) and in urban Los Angeles rain (5). Dinitrophenols are suggested to constitute particulate matter.

The phytotoxicity of nitro- and dinitrophenols is well documented (6) and strongly depends on the position of the nitro group(s) relative to the phenolic moiety (7).

Aromatic nitroderivatives may either be directly emitted from anthropogenic sources, they may be formed by tropospheric gas phase reactions and finally they may be formed within the tropospheric aqueous phase. These processes may be driven by reactions of the nitrate radical with dissolved aromatics or by the reaction of the nitronium cation (NO_2^+) formed from the dissociation of its gas phase precursor N_2O_5 on aqueous surfaces within the troposphere. In this study were considered three different nitrating agents:

Reaction products are shown in Scheme 1. The quantitative analysis of the reaction products is reported in Table 1.

Scheme 1

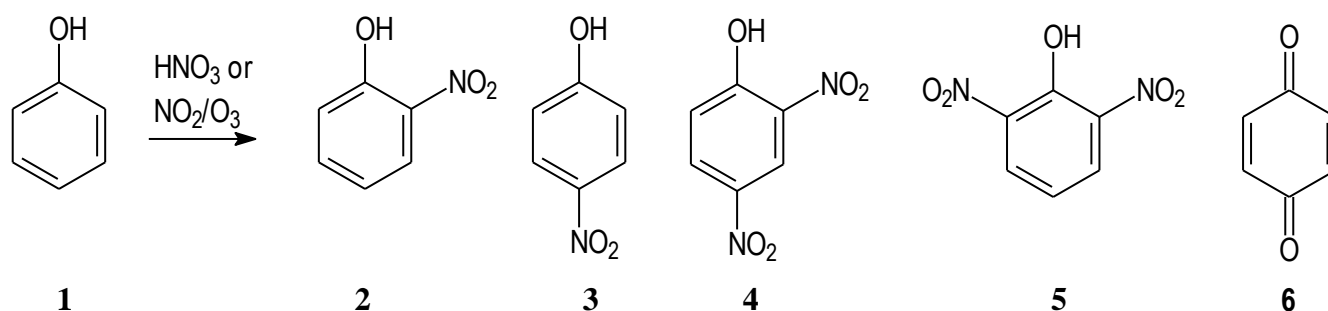


Table 1

reagent	solvent	Conversion (%)	Reaction products	isomer ratio <i>ortho:para</i> (%) ^a
HNO ₃ 65 % ^b	H ₂ O	65	2:26.5; 3:32.5; 6: 6	0.82
HNO ₃ /H ₂ SO ₄ ^c	H ₂ O	98	2:28.1; 3:57.5; 6: 6.4	0.47
NO ₂ /O ₃ ^d	CHCl ₃	72	2:33; 3:30; 4:5.3; 6:3.7	0.72
NO ₂ /O ₃ ^d	CH ₂ Cl ₂ ^e	58	2:26.5; 3: 28.5; 6:3	0.82
NO ₂ /O ₃ ^d	THF	97	2:37.6; 3:57.4; 6:2	0.85
NO ₂ /O ₃ ^d	CH ₃ NO ₂	24	2:12.4; 3:11	1.08
NO ₂ /O ₃ ^d	CH ₃ CN	87	2:45.4; 3:36.1; 4:2.5; 5:1.6; 6:1.4	1.22
CAN/hv	CH ₃ CN	100	2:41; 3: 49; 6:9	0.85

^aNo *m*-nitro phenol was detected. ^{b,c}Reactions were carried out at a temperature between 0 and 4°C. ^dAll reactions were carried out for the substrate (1 mmol) in solvent (30 mL) containing nitrogen dioxide and ozone at 0°C. ^eMilder condition due to the high reactivity in this solvent.

Phenol **1** is converted into a mixture of mono- and poly-nitrophenols in very high yields by the conventional electrophilic nitration reaction where NO₂⁺ is the reagent (8). Scheme 1 reports the reaction products obtained. Under these conditions, *para*-nitrophenol **3** is slightly preferred to *ortho*-nitrophenol **2** (*Ortho/para* ratio 0.72-0.79). 2,4- **4**, 2,6-dinitrophenol **5** and *p*-benzoquinone **6** are also formed.

The nitration via the *kyodai* method (9) generates NO₃ in liquid phase via the reaction of ozone with nitrogen dioxide. The reactions were carried out in different solvent at 0°C and stopped after 1 minute in order to obtain essentially the mono-nitration products.

Different results were obtained using a different source of the nitrate radical in liquid phase, e. g. the photolysis of cerium(IV) ammonium nitrate (CAN) under a nitrogen atmosphere. Using

acetonitrile as the solvent a ortho to para ratio 0.85 was obtained. This ratio was slightly lower than that obtained with the *kyodai* system in the same solvent. A much lower conversion was obtained in water, and the ortho nitration product was sharply preferred to the para isomer.

Kinetic studies on the aqueous radical nitration of phenol were carried by generating $\text{NO}_3\cdot$ radicals via photolysis of pH 0 of peroxodisulphate solutions containing nitrate anions (NO_3^-) using an excimer laser at $\lambda = 248$ nm (active medium: KrF). All experiments are carried out under pseudo-first order conditions. The rate constants shown in Table 2 were obtained. A study of temperature dependence of the rate constant of the reaction of phenol with $\text{NO}_3\cdot$ in the T-range of $288 \text{ K} \leq T \leq 328 \text{ K}$ gave the results shown in Table 2.

As can be seen from the derived rate constants the reaction of the $\text{NO}_3\cdot$ radical with phenol and its nitration products proceeds very fast. So these reactions might be of importance for tropospheric cloud and aerosol chemistry. At daytime the degradation of the aromatics compounds may predominantly expire via the reaction of OH radicals with them. At night, however the reaction of the $\text{NO}_3\cdot$ radical with these compounds might be an additional pathway in the nitration of aromatic compounds in aqueous solution beside the nitration of aromatics by the nitronium cation (NO_2^+).

Table 2

compound	$k_{2nd} / \text{L mol}^{-1} \text{s}^{-1}$	$k(T)$	Activation parameters
Phenol, 1	$(1.8 \pm 0.3) \times 10^9$	$(1.4 \pm 0.2) \exp [-(2050 \pm 480)/T]$	$\Delta H^\ddagger = 14.5 \pm 3.4 \text{ kJ mol}^{-1}$ $\Delta S^\ddagger = -20.7 \pm 3.0 \text{ J mol}^{-1} \text{K}^{-1}$ $\Delta G^\ddagger = 20.7 \pm 7.8 \text{ kJ mol}^{-1}$ $E_a = 17 \pm 4 \text{ kJ mol}^{-1}$
4-nitrophenol, 3	$(7.1 \pm 0.4) \times 10^8$		
2,4-dinitrophenol, 4	$(5.3 \pm 0.6) \times 10^8$		

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References

1. Piccot, S. D., Watson, J. J., Jones, J. W. *J. Geophys. Res.*, **1992**, 97D, 9897-9912; Finlayson-Pitts, B. J., Pitts, Jr J. N. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, Wiley, New York., **1988**.

2. Atkinson, R. J. *Phys. Chem. Ref. Data, Monograph 2*, **1991**, 20, 459-507.
3. Bolzacchini, E., Umschlag, Th., Herrmann, H., Meinardi, S., Rindone, B., *Kinetic and Product Study of the Reaction of the NO₃· Radical with Phenol, Benzoic Acid and their Nitration Products in Aqueous Solution*, 6th FECS Conference on Chemistry and the Environment, Copenhagen, Denmark 26-28 August, 1998.
4. Levsen, K., Behnert, S., Priess, B., Svoboda, M., Winkeler, H. D., Zietlow, J., **1990**, *Chemosphere*, 21, 1037-1061; Mussmann, P., Levsen, K., Radeck, W., *Fresenius Journal of Analytical Chemistry*, 1994, **348**, 654-659; Geißler, A., Schöler, H. F., *Vom Wasser*, **1993**, 80, 357; Geißler, A., Schöler, H. F., *Wat. Res.*, **1994**, 28, 2047.
5. Kawamura, K., Kaplan, I. R., *Organic Compounds in Rainwater*, **1991**, in Hansen, L. D., Eatough, D. J., *Organic Chemistry of the Atmosphere*, 1991, CRC Press, Boca Raton, 233.
6. Von Oettingen, W. F., *Nitro compounds and related phenolic insecticides in Handbook of Pesticide Toxicology*, **1991**, Academic Press, New York 1191; Shea, P. J., Weber, J. B., Overcash, M. R., **1983 Res. Rev.**, , 87, 1; Schafer, W. E., Schönherr, *Ecotox. Environ. Safe.*, **1985**, 10, 239.
7. Barletta, B., Belloli, R., Bolzacchini, E., Meinardi, S., Orlandi, M., Rindone, B., *Toxic nitrophenols from the liquid phase nitration of phenols Eurotrac-2 Symposium*, Garmisch 23-27 march **1998**.
8. Olah, G. A., Malhotra, R., Narang S. C. *Nitration: Methods and Mechanism*, **1989**, VCH Publishers Inc., New York, p 201-204.
9. Suzuki, H., Nonoyama, N., Tomaru, J., Mori, T., **1996**, *Zh.Org.Khim.* 32, 265-268; Suzuki, H., Nonoyama, N., **1997**, *J.Chem.Soc.Perkin Trans.1*, 2965-2971; Suzuki, H., Mori, T., **1997**, *J.Org.Chem*, 62, 6498-6502.