Environ. Sci. Technol. **2001**, *35,* 1791−1797

Gas-Phase Reaction of Phenol with NO_3

EZIO BOLZACCHINI,[†]
MAURIZIO BRUSCHI,[†] JENS HJORTH,[‡]
SIMONE MEINARDI,[†] MARCO ORLANDI,[†]
BRUNO RINDONE,*[,†] AND
ELISA ROSENBOHM[‡]

Department of Environmental Sciences, University of Milano−Bicocca, Piazza della Scienza 1, I-20126 Milano, Italy, and Commission of the European Communities, Joint Research Centre, Environment Institute, 21020 Ispra (VA), Italy

The fast gas-phase reaction of NO_3 radicals with phenol was found to yield 2-nitrophenol as the only relevant nitration product. The yield of this product was high and independent of the concentration of NO_2 at the concentrations applied. In the presence of ozone, also significant amounts of 4-nitrophenol and *p*-benzoquinone were formed. The rate constant of the reaction between NO_3 radicals and phenol was determined to be 5.8×10^{-12} cm^3 molecule^{-1} s^{-1}. The selective formation of 2-nitrophenol (**2**) is suggested to derive from either the concerted keto−enol tautomerism in the reaction of a phenoxy radical with NO_2 or the concerted elimination of nitric acid from a cyclohexa-3,5-diene intermediate.

Introduction

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 (*1*). Phenols and nitrophenols may be emitted in the exhaust (*2*, *3*) as partial oxidation products of aromatic hydrocarbons.

Phenols can then subsequently be transformed into nitrophenols, which are known to be phytotoxic (*4*). The nitrate radical, NO_3, may be the promoter for these reactions. This radical is formed in the atmosphere by the reaction between O_3 and NO_2 (*5*):

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

NO_3 is recognized to play an important role in the nighttime tropospheric chemistry because of its fast reaction with other radicals and with several organic trace gases, in particular those of biogenic origin (*6*). The reactions of NO_3 radicals with phenol and cresols are fast both in the gas phase (0.4−1.4 $\times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) (*7*, *8*) and in the aqueous phase ($k = 1.8 \pm 0.3 \times 10^9$ M^{-1} s^{-1} at pH $= 0$ and $T = 298$ K) (*9*). Hence, these reactions are a sink (*10*) for NO_3, and nitrophenols may be formed by tropospheric gas-phase reactions or within the tropospheric aqueous phase.

We have recently demonstrated that isomer distribution in the reaction products and polar effects in the rate constants may help to elucidate some details of the reactions of the nitrate radical NO_3 with aromatic compounds in the gas phase (*11*). The reaction of phenol with NO_3 in gas phase to give mainly 2-nitrophenol has been recently reported (*7*), but the reasons for the exclusive ortho-regiochemistry are still uncertain. On the contrary, the reaction of phenol with NO_3 in liquid phase has been reported to give both 2- and 4-nitrophenol in organic solvents (*12*) and in water (*13*).

Understanding the mechanism of the nitration of phenol both in the gas phase and in the aqueous phase is important because nitrophenols are found in air and rainwater. These compounds have been found in rainwater in the microgram per liter range in the Rhein-Ruhr area in western Germany (*14*, *15*) and in clouds (*16*, *17*). However, only *o*-nitrophenol was found in Los Angeles rain (*18*). In urban Milano, only *p*-nitrophenol was found in rainwater in a summer campaign in 1998 (*19*). More recently, air samples were analyzed for nitrophenols, and the ratio of *o*-/*p*-nitrophenol was found to vary with the location of the sampling station and the season. In fact, in Milano *p*-nitrophenol was always found, and occasionally also *o*-nitrophenol was present (*20*). More *p*-nitrophenol is found in air sampled in an open space than in a tunnel in Wuppertal (*21*). Moreover, nitrophenols are known to be present in car exhaust (*22*), and an *o*-/*p*-nitrophenol ratio of 1.3 was measured in the exhaust. The finding of only some of the possible nitrophenols (3 isomers), dinitrophenols (6 isomers), nitrocresols (9 isomers), and dinitrocresols (16 isomers) may be used for the identification of sources and where tropospheric processing has occurred. Hence, studying the mechanism of the gas-phase nitration of phenol could complement recent studies on the aqueous-phase formation of nitrophenols (*23*) and could explain the different content in nitrophenols of air and rainwater samples.

Experimental Section

Gas-Phase Reactions. The reaction was studied in purified air at 760 Torr in a 480-L Teflon-coated 60 cm diameter cylindrical chamber equipped with a 81.2 m total beam path length White type mirror system coupled to a Bruker IFS 113V FT spectrometer for on-line infrared spectroscopy.

Concentrations of reactants and reaction products were monitored in situ by long path infrared spectroscopy. Experiments were performed at ambient pressure and temperature. Calibrations of the IR measurements were performed either by introducing known volumes of vapor at known pressures into the chamber or by evaporating known quantities of the compounds and transferring them with a stream of air into the chamber. Calibrated gas-phase spectra of *o*-nitrophenol and *p*-nitrophenol were obtained, while the dinitrophenols were found to have a too low volatility to be calibrated in the gas phase.

In the experiments to study yields of nitrophenols, N_2O_5 was synthesized in the chamber by mixing O_3 with an excess of NO_2**.** Subsequently, the phenol was added and the reaction was allowed to proceed until only insignificant amounts (<100 ppb) of N_2O_5 remained. Initial concentrations were 10−25 ppmV N_2O_5, 3−55 ppmV NO_2, and 15−30 ppmV of the organic compound. In some experiments, phenol and NO_2 were added first to the chamber and then ozone. The initial concentrations in this case were 11−51 ppmV NO_2, 22−31 ppmV phenol, and 16−70 ppmV ozone.

The rate constant of the reaction of the NO_3 radical with phenol was determined relative to that of its reaction with 2-methyl-2-butene. In these experiments, phenol and 2-methyl-2-butene were added first to the chamber, and then N_2O_5 was introduced by evaporating solid N_2O_5, prepared by the method of Schott and Davidson (*24*), and bringing it into the

---

* Corresponding author phone: +39 02 6448 2813; fax: +39 02 6448 2890; e-mail: Bruno.Rindone@unimib.it.

[†] University of Milano−Bicocca.

[‡] Environment Institute.

10.1021/es001290m CCC: $20.00

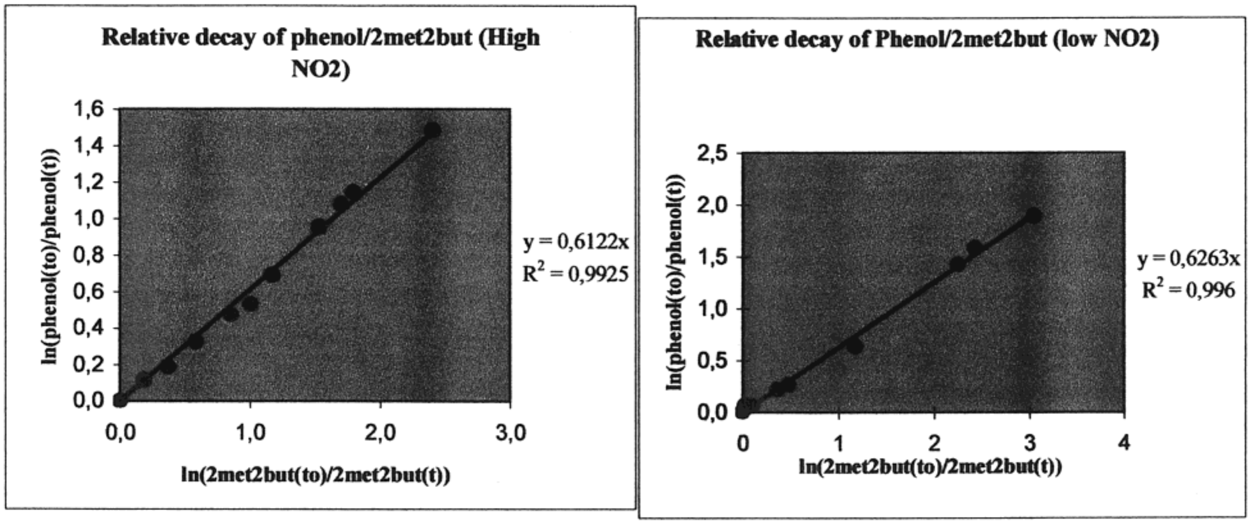


FIGURE 1. Plots of examples of observed decays of phenol vs 2-methyl-2-butene in the reaction with NO_3 radicals under conditions of high and low NO_2 concentrations.

chamber with a stream of air. In this case, the initial concentrations were 15−18 ppmV of 2-methyl-2-butene and 5−10 ppmV of phenol. N_2O_5 was in most experiments added several times during the experimental run in portions of a few ppmV. Initial NO_2 concentrations were 1−3 ppmV in these experiments. In other experiments, NO_2 was added to provide initial concentrations of 29−59 ppmV in order to test the influence of $[NO_2]$ on the observed rate constant.

Product Studies. The products were measured using two different analytical methods:

(i) FTIR analysis in the reaction chamber.

(ii) Samples to be used for subsequent product analysis were obtained by bubbling known volumes of the reaction mixture through a 5.3×10^{-4} M sodium hydrogen carbonate solution. The extraction was performed with 10 mL of dichloromethane after neutralization with sulfuric acid. HPLC with UV detection using a HPLC-DAD instrument (Waters 600E system controller and HP 1040 A diode array detector) was used to detect and quantify all the isomers monitoring the absorbance at 230 nm. The column that gave the best performance was a stainless steel column, 250 mm × 4.4 mm i.d., packed with 5-μm particles (100 Å) of silica-based C18 material, Kromasil (Superchrom). The number of theoretical plates for phenol was calculated to be about 100 000. The flow was 1 mL min^{-1}. We applied an isocratic gradient using a mixture of two different solutions: The first (solution A) was a mixture of an aqueous solution of KH_2PO_4 (5×10^{-3} M), phosphoric acid was added to adjust the pH to 4.5 (90 vol % of A) and CH_3CN (10 vol %). The second (solution B) was a mixture of an aqueous solution of KH_2PO_4 (5×10^{-3} M), phosphoric acid was added to adjust the pH at 4.5 (25 vol % of B) and CH_3CN (75 vol %). The two solutions in a volume ratio, A/B = 55/45, were filtered through 0.45-μm filters (Millipore, Bedford, MA) and degassed with helium during analysis. All reference compounds were purchased from Fluka or Aldrich.

Calculations. All calculations were performed using the ab initio Density Functional Theory (DFT) with the hybrid functional of Becke (*25*) and Lee et al. (*26*) and a flexible Gaussian basis of type 6-31G** (*27*).

Results

Rate Constant. The rate constant of the reaction of NO_3 radicals with phenol at 295 ± 2 K was investigated by the relative rate method, where the decay of phenol in an NO_3 radical containing atmosphere is compared to that of a reference compound that reacts with NO_3 radicals with a known rate constant. The reference compound was, in this case, 2-methyl-2-butene, and the rate constant k_1 for the reaction

$$NO_3 + \text{phenol} \rightarrow \text{products}$$

could then be calculated relative to the rate constant, k_2, for the reaction

$$NO_3 + \text{2-methyl-2-butene} \rightarrow \text{products}$$

from the relation

$$\ln\left\{\frac{\text{phenol}(t_0)}{\text{phenol}(t)}\right\} = \frac{k_1}{k_2}\ln\left\{\frac{\text{2-methyl-2-butene}(t_0)}{\text{2-methyl-2-butene}(t)}\right\}$$

The ratio k_1/k_2 was measured for relatively low and relatively high concentrations of NO_2, as discussed in the Experimental Section. The ratio k_1/k_2 was found to be 0.62 ± 0.12, which gives a k_1 value of $5.8 \pm 1.1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, using the value of 9.38×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for k_2 (*4*) and giving the uncertainty as one standard deviation on the experimental data. The rate constant was independent of the $[N_2O_5]/[NO_2]$ ratio (Figure 1), thus showing that the reaction of phenol takes place with NO_3 radicals and not with N_2O_5 or with NO_2. This value was slightly higher than that found at 296 ± 2 K (3.92 ± 0.25) (*5*) and at 298 ± 1 K (3.64 ± 0.14) (*28*). The reason for this difference is not obvious; wall losses are not a likely explanation since the loss of phenol in clean air in the cell was measured to be about 5% per hour and the reaction between NO_3 radicals and phenol under the conditions applied is completed within a much shorter time period. The initial concentrations of phenol applied and the amount of phenol that reacted in the present experiments were roughly 10 times higher than what was applied in the work of Atkinson et al. (*5*), and one might speculate about uptake of phenol on particles formed. Finally, of course, different analytical techniques were applied (IR spectroscopy vs GC-FID), and errors in one or the other method may also be an explanation for the different results.

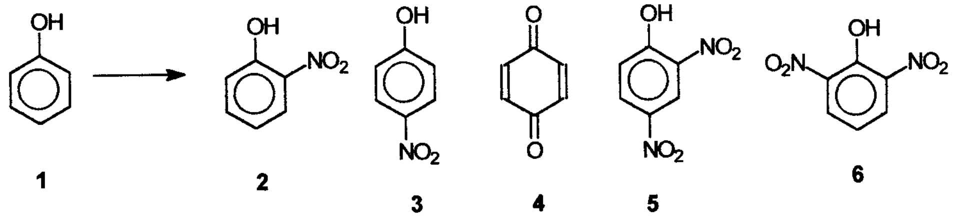
Products in Nitration of Phenol by Reaction with NO_3 Radicals. High yields of 2-nitrophenol (**2**) were found in the gas-phase nitration of phenol (**1**) initiated by NO_3 radicals. Table 1 shows yields obtained under different conditions and measured by FTIR. In particular, two experimental procedures were used:

TABLE 1. Gas-Phase Nitration of Phenol in Different Conditions[a]

exp	N_2O_5 start, ppm	NO_2 start, ppm	NO_2 after, ppm	NO_2 used, ppm	av NO_2, ppm	HNO_3 after, ppm	phenol start, ppm	conv phenol, ppm	2-nitrophenol, %	4-nitrophenol, %	ratio 2-/4-nitrophenol
1	12.2	39.1	40.4	23.1	39.8	7.2	14	5.6	29		
2	21.8	56.8	60.8	39.6	58.8	15.2	20	12.5	47		
3	22.5	21.7	20	46.7	20.8	14.7	25.7	10	38		
4	23.4	3.6	6.3	44.1	4.9	18.9	25.9	11.8	65	17	3.82
5	-	23.0	0.9	49.7	12.0	21.1	30.9	17.1	55	31	1.77
6	-	32.6	31.4	19.2	32	9.3	22.3	7.2	68	21	3.24
7	-	8.4	8.5	13.2	8.4	14.1	26.2	10.8	47	22	2.14
8	-	17.7	16.9	28.7	17.3	21.8	21.6	13.5	69	24	2.88
9	-	20.7	14.8	27	17.7	21.2	30.8	12	55	40	1.38

[a] The table shows initial and final experimental conditions. In experiments 1−4, phenol is added after the addition of ozone and NO_2 while in experiments 5−9 ozone is added last. Initial [N_2O_5] in experiments 1−4 is not measured directly but calculated from the difference between NO_2 added to the chamber and [NO_2] found after the reaction with ozone, assuming that all NO_2 has reacted to form N_2O_5. The estimated uncertainties on [NO_2], HNO_3, and [O_3] are 10% and on N_2O_5 and 2-nitrophenol are 20%. 4-Nitrophenol presents a particular problem as discussed in the text

SCHEME 1



(i) NO_3 radicals generated by the thermal dissociation of N_2O_5 in the presence of excess NO_2 were reacted with **1**. In this case (reactions 1−4), only **2** was found and 4-nitrophenol (**3**) was not observable by FTIR spectroscopy. At the NO_2 levels applied, no dependence of the yields in **2** on the average concentration of NO_2 during the experiments could be observed. No correction of the observed yields were made for losses of nitrophenols due to the reaction with NO_3, since this reaction is more than 100 times slower than the reaction of NO_3 radicals with phenol (*7*).

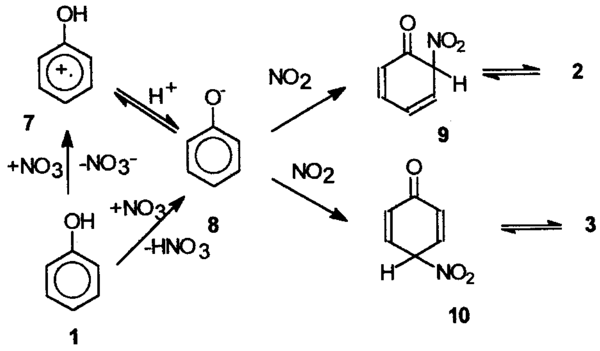
(ii) A different situation was observed when **1** reacted with NO_3 radicals in the presence of ozone. In this case (reactions 5−9), significant amounts of **3** were observed.

The predominant formation of **2** in some conditions was confirmed by off-line analytical procedures. These analyses showed that, besides **2** and **3**, also minor amounts of 2,4-dinitrophenol (**5**) and 2,6-dinitrophenol (**6**) were present in molar yields of 1−3% each. In all the experiments, *p*-benzoquinone (**4**) was also found present in molar yields of 3−6% (Scheme 1). A comparison between the on-line FTIR analysis of **2** and the off-line HPLC analysis showed that the latter underestimates the amount of **2** by more than 20%. The loss of **2** in the off-line analysis may be due to losses in the sampling line or to oxidative degradation of **2** in alkaline solution.

Discussion

Regarding the quality of the experimental data on the yields of nitrophenols, it should be mentioned that the experience from the present and other experimental studies indicate that 2-nitrophenol tends to remain in the gas phase under the experimental condions applied and thus can be measured accurately by IR spectroscopy. However, we have found that 4-nitrophenol, which has higher melting and boiling points than 2-nitrophenol, has a stronger tendency to stick on particles, and thus on-line IR spectroscopy may not be the best way of measuring this compound. An inspection of the data in Table 1 does not suggest any evident influence on initial concentrations on the product yields.

SCHEME 2

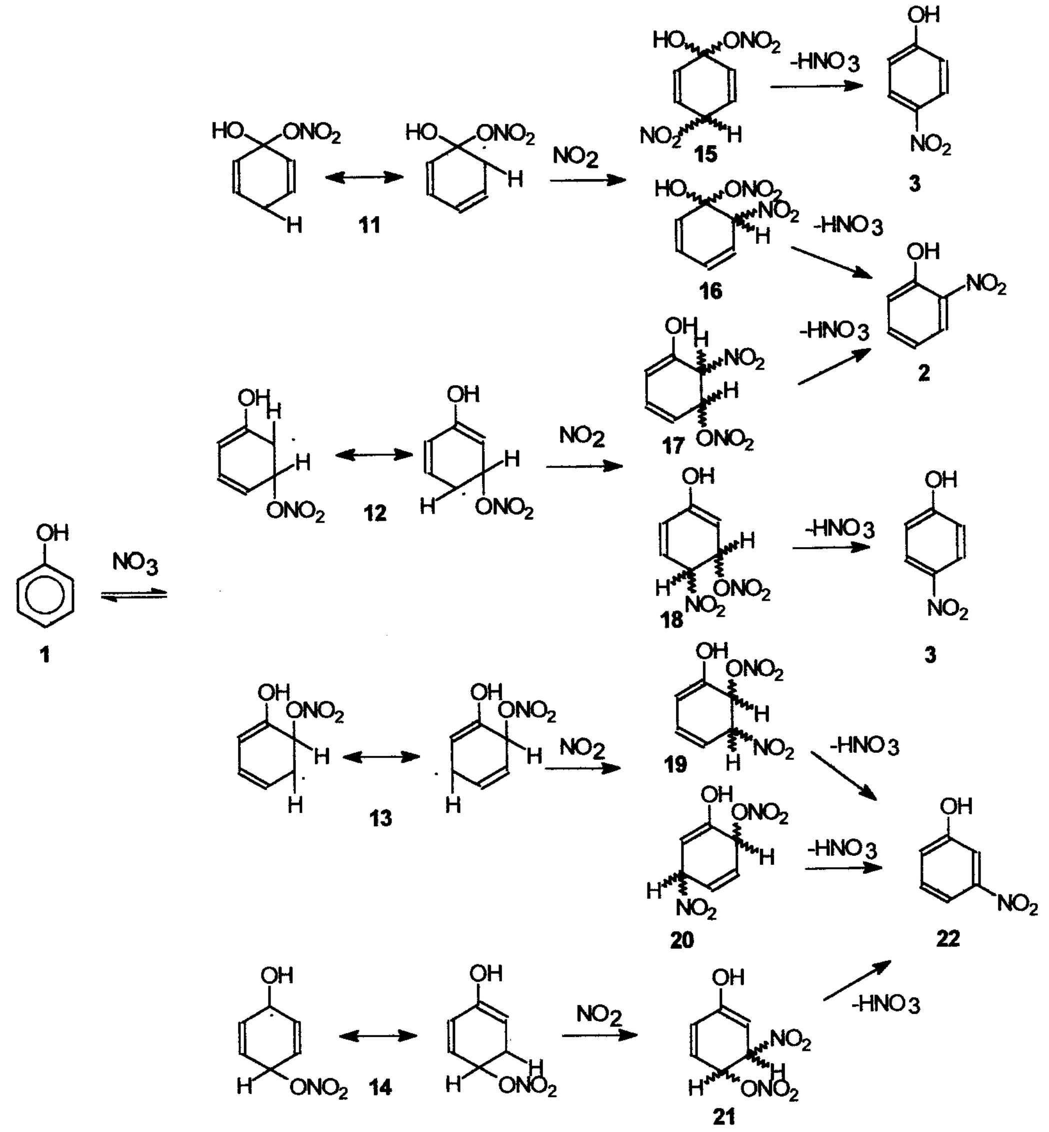


Phenols are known to react with NO_3 in aqueous acidic conditions via a single electron transfer (SET) (*29*) giving a cation radical such as **7**, which is in prototropic equilibrium with the phenoxy radical (**8**) and a nitrate anion (Scheme 2). Reaction of **8** with NO_2 should give both **2** and **3** via tautomers **9** and **10**. This behavior is also observed in the reaction of NO_3 with electron-rich aromatics (*30*). Hence, the intermediate formation of **8** explains the observed selectivity for the orthonitration only if, in gas phase, reaction **9** ⇒ **2** is much faster than reaction **10** ⇒ **3**. This may be due to the concerted keto−enol tautomerism **9** ⇒ **2**. The phenoxy radical **8** may also derive from the direct hydrogen abstraction from the phenolic hydroxyl (H-ABS).

A third possibility is that **1** reacts with NO_3 via an addition−elimination mechanism such as that depicted in Scheme 3 (*31*). Here, four regioisomeric adducts **11**−**14** are formed with an equilibrium reaction in the ADD mechanism. These will then add NO_2 to give diastereoisomeric cyclohexadienes **15**−**21**. Final elimination of HNO_3 will form **2** and **4** from the ipso adduct (**11**) or the meta adduct (**12**); 3-nitrophenol (**22**) from the ortho adduct (**13**) or the para adduct (**14**).

To better understand the mechanism involved in these reactions, structural and energetic data for the possible reaction intermediates were investigated theoretically. Ge-

SCHEME 3



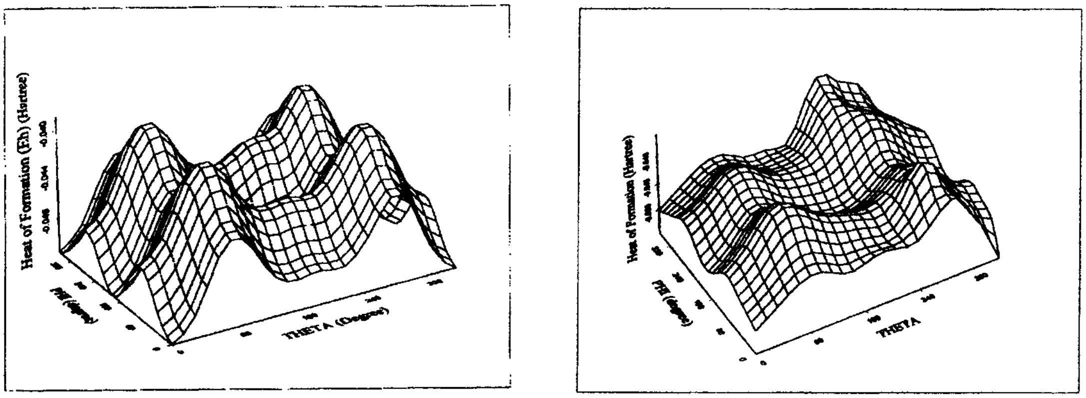
ometry optimizations and energy determinations performed at UB3LYP/6-31G** level of theory of the molecules participating to reactions in Scheme 3, showed that hydrogen abstraction to give a phenoxy radical **8** is exothermic by 14.94 kcal/mol. The SET mechanism is believed not to be possible in gas phase.

Concerning the ADD mechanism, the regiochemistry of the adduct under equilibrium condition may influence the distribution of reaction products. Since energy differences among different adducts (ipso, ortho, meta, and para) is supposed to be small, and in the same order of magnitude of conformational energies, an analysis of potential energy surfaces (PES) in order to locate all possible stable conformations is needed. Analysis of the PES was performed for the rotation around C−O and O−N bonds [C1−C2−O2−N1 $= \theta$; C1−C2−O1−H1 $= \varphi$] (Scheme 4) using the semiempirical PM3 Hamiltonian in the unrestricted formalism (UHF/PM3)]. For each point of the PESs all other degrees of freedom were fully optimized (Figure 2).

The stable conformers obtained from the PES analysis were re-optimized at UB3LYP/6-31G** level of theory. The energies of the first reaction shown in Scheme 3 computed at this level are shown in Table 2. One of the ortho conformers is the most stable ($\Delta E = -10.0$ kcal/mol). For this conformer the distance O3−H1 (1.857 Å) and the angle O3−H1−O1 (154.76°) (Scheme 4) are consistent with the formation of an intramolecular seven-membered ring hydrogen bond between O3 and H1. The energy of the hydrogen bond can be roughly estimated equal to −3.14 kcal/mol from the difference between the energy of this conformer (conformation **13-2** in Table 2) and the conformation **13-3** in which the hydrogen bond is not present.

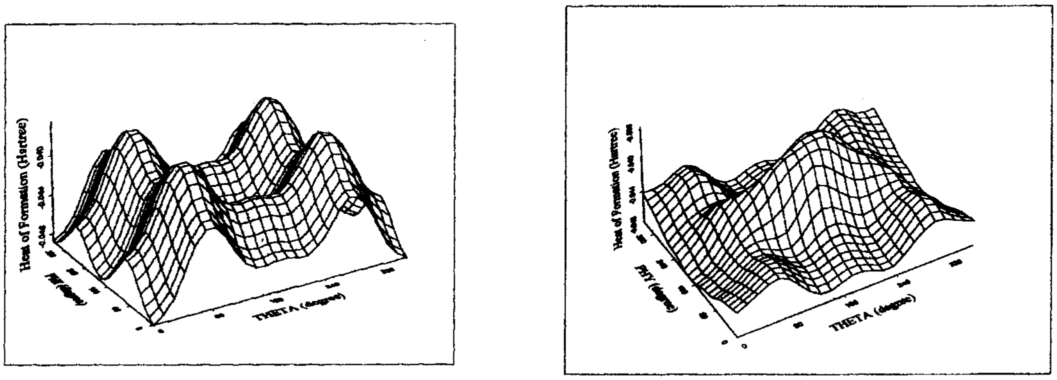
Contrary to what has been suggested earlier (*10*), ipso-hydroxynitratocyclohexadienyl adduct is less stable than the ortho adduct by 8.67 (conformation **11-1**) and 4.50 kcal/mol (conformation **11-2**). Hence, if the stability of ortho adduct is governing the regiochemistry, 3-nitrophenol (**22**) should be formed.

The stability of the intermediate adduct had been used to understand the preferential formation of 2-methylphenol in the hydroxylation of toluene with OH in gas phase (*28*). However, with **1** the stability of the adduct was unable to explain the ortho regiochemistry in the gas-phase nitration. Hence, some other factor should be central for the regioselectivity. A model reaction could be useful for the identification of this additional effect. The combined action of ozonized oxygen and nitrogen dioxide in organic (Kyodai nitration) to yield ortho and para nitration of phenol was used for this purpose. The reactant in the Kyodai nitration is the NO_3 radical. The reaction was suggested by us to occur through



PES of the *para* NO_3-adduct

PES of the *ortho* NO_3-adduct.



PES of the *meta* NO_3-adduct

PES of the *ipso* NO_3-adduct.

FIGURE 2. Potential energy surfaces.

the formation of a charge-transfer complex (CTC) **23** that evolves to adducts **11**−**14** (Scheme 5) (*12*).

The Kyodai nitration of phenols was demonstrated to be a radical process by the low sensitivity to the electronic contribution of the nuclear substituent, as shown by the low Hammett ρ value of $= -0.72$ using Hammett's σ of the substituent. A fast formation of a CTC followed by recombination to give radical adducts such as **11**−**14** in the case of **1** could explain this behavior. A similar mechanism should occur in the gas-phase nitration of phenols with NO_3 in the presence of NO_2. Here in fact the available rate constants are 5.8×10^{-12} for phenol and 10.7×10^{-12} for *p*-cresol (*7*). These numbers suggest a Hammett ρ value smaller than that found in the Kyodai nitration (nearly 0), thus suggesting that a similar radical mechanism has to be occurring for the two groups of aromatic substrates.

However, in gas-phase experiments where only **2** was found, some effect directing the reaction toward the ortho regiochemistry in the nitration reaction should be operating. The exclusive ortho regiochemistry is the result of a selective reaction of NO_2 at the position ortho to the phenolic hydrogen.

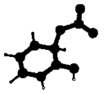
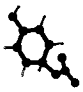
Hence, the reaction could occur via the intermediate formation of a phenoxy radical (**8**) if the keto−enol tautomerism **9** $\Rightarrow$ **2** is concerted. Alternatively, the exclusive formation of **2** may be understood if the ipso adduct (**11**) or the meta adduct (**12**), although not the most stable adducts, are the intermediates in this reaction. In fact, **2** cannot derive from **13** or **14**.

Formation of **11** or **12** is not the only condition to understand the regioselectivity. In fact, **11** will react with NO_2 to give an equilibrium mixture (*33*) of the two mesoforms of 1,4-cyclohexadienes (**15**), thus leading to both **2** and **3**, to a diastereoisomeric mixture of the four isomeric of 1,3-cyclohexadienes (**16**), and to **12**, thus leading to **2**. **12** will react with NO_2 to give a diastereoisomeric mixture of the four isomeric of 1,3-cyclohexadienes (**17**), thus leading to **2** and to a diastereoisomeric mixture of the four isomeric of 1,3-cyclohexadienes (**18**), thus leading to **3**. Hence, together with the regioselective addition of NO_2, also a regioselective loss of nitric acid from one of the adducts is necessary to understand the reasons for the preferred regioselective ortho nitration of phenol.

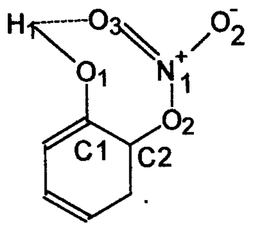
The first point is to understand the reason of the preferred formation of adduct **11**. In the CTC, the $NO_3^{\bullet-}$ fragment is likely to be hydrogen bonded to the positive oxygen in the $[C_6H_5OH]^{\bullet+}$ fragment. Hence, a concerted collapse of the CTC to form selectively **11** under kinetic control (Scheme 6) could drive the reaction toward the ortho regiochemistry. Moreover, the fact that the yield of **2** is independent from the concentration of NO_2 suggests again that the collapse of the CTC to **11**−**14** is rate-determining and that the reaction between the adducts and NO_2 are much faster than the corresponding reactions with O_2 at the NO_2 concentrations applied in this study.

Concerning the product-determining steps, it should be noted that in the gas-phase elimination reaction may occur only via the E2 mechanism, and this requires a strict stereochemical relationship among the two groups to be eliminated (H^+ and NO_3^-). As shown in Scheme 6, only the cis and trans form of the 1-hydroxy-1-nitrato-2-nitro-3,5-cyclohexadienes **(16)** may undergo a concerted elimination

TABLE 2. Energy (kcal mol^{-1}) of the Reaction NO_3 + Phenol → Radical Adducts 11–14

	Conformation 1	Conformation 2	Conformation 3
Ipso adduct **11**			
Angle θ	-1.34	130.04	-129.95
Angle ϕ	114.45	-120.81	120.84
ΔE B3lyp	-1.31	-5.48	-5.48
Ortho adduct **13**			
Angle θ	1.93	149.87	-140.07
Angle ϕ	178.59	10.77	172.31
ΔE B3lyp	-4.41	-10.0	-6.22
Meta adduct **12**			
Angle θ	-0.011	143.19	
Angle ϕ	-3.50	-3.09	
ΔE B3lyp	-2.71	-4.84	
Para adduct **14**			
Angle θ		143.69	
Angle ϕ	-2.65	-1.39	
ΔE B3lyp	-4.07	-6.48	

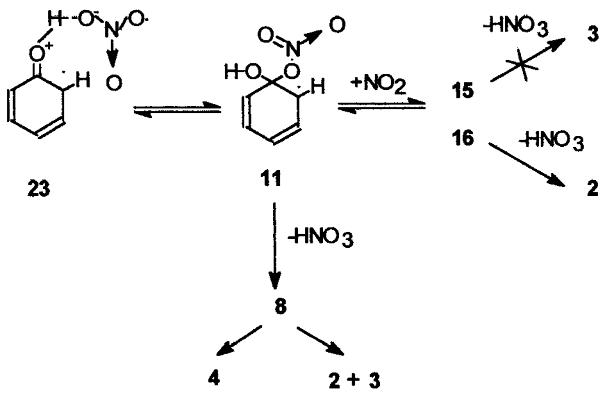
SCHEME 4



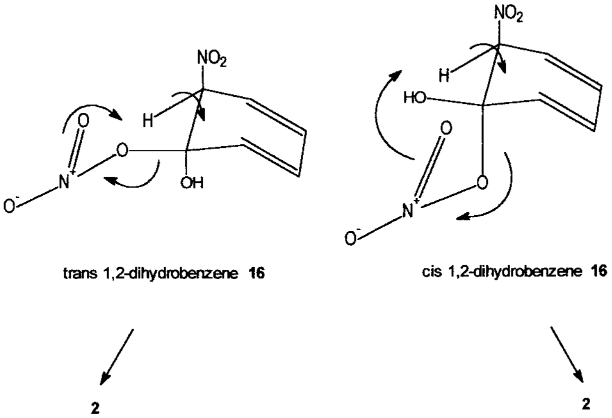
C2-C1-O1-H1 = φ

C1-C2-O2-N1 = θ

SCHEME 5



SCHEME 6



of nitric acid in a E2-type elimination reaction, and this will give selectively **2**. The conclusion is that the initial CTC formation, its collapse to **11**, and the subsequent addition of NO_2 are equilibrium reactions Hence, the irreversible loss of nitric acid will drive the reaction toward **2**. In conclusion, the selective formation of **2** is suggested to derive from either the concerted keto–enol tautomerism in the reaction of a phenoxy radical with NO_2 or in the concerted elimination of nitric acid from a 1,2-dihydrobenzene intermediate.

In the experiments where some ozone was present when **1** was introduced in the reaction chamber (reactions 4–9), both nitrophenols were formed. We do not see any evident reason for this behavior. A hypothetical explanation could be that ozone assists in the abstraction of a hydrogen atom or a proton from the 4-position in the intermediate **10** and thus facilitates the formation of the nitrophenols. Alternatively, if the ADD mechanism is occurring, ozone could inhibit the concerted recombination of the two fragments in the CTC (Scheme 3). Another possibility is that, for some reason, under the conditions of the experiments where ozone is present, less 4-nitrophenol is adsorbed on particles and thus the compound can be observed in the gas phase.

Atmospheric Implications

The reaction of NO_3 radicals with phenol and cresols are fast ($0.4-1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) and thus a potentially important atmospheric sink for these at nighttime and a potentially relevant source of the corresponding nitroderivatives. A high yield of nitrophenol is found, which does not show an evident dependence on the NO_2 concentration under the experimental conditions applied. If this insensitivity to [NO_x] will be valid also at typical atmospheric levels, and thus if equally high yields will be found under ambient conditions, cannot be determined from the present experimental results but will require further studies (e.g., in large simulation chambers).

Chamber studies indicate that **2** will be the main nitration product of the gas-phase reactions of phenol with NO_3 and with OH radicals. This, combined with information about the selectivity of aqueous-phase nitration reactions with respect to the formation of isomers, may allow us to draw conclusions about the origin of nitrophenols in the environment (e.g., in rainwater) based on the ratio between isomers. In fact, the ratio 2-nitrophenol/4-nitrophenol of 1.5 has been found in engine exhaust (*22*). Moreover, this ratio both in air and in rain samples has been found to be highly variable (*18, 20, 21*). The different physicochemical characteristics of these isomeric nitrophenols may play a role in their atmospheric behaviors. The influence of ozone on the yield of the 4-nitrophenol isomer is mechanistically interesting but is not likely to be relevant under atmospheric conditions, where ozone concentrations are typically 2–3 orders of magnitude lower than in the laboratory experiments.

Acknowledgments

Financial support of this work from the European Community for Scientific Research (ENV4-CT97-0411) is gratefully acknowledged. We thank also the Italian CNR for financial support.

Literature Cited

(1) Atkinson, R. *J. Phys. Chem. Ref. Data* **1994**, *Monogr. No. 2*.
(2) *Unregulated Motor Vehicle Exhaust Gas Components*; Volkswagen AG Report; 1989.
(3) Tremp, J.; Mattrel, P.; Fingler, S.; Giger, W. *Water Air Soil Pollut.* **1993**, *68*, 113−123.
(4) (a) Shea, P. J.; Weber, J. B.; Overcash, M. R. *Residue Rev.* **1983**, *87*, 1. (b) Schafer, W. E.; Schönherr. *Ecotoxicol. Environ. Saf.* **1985**, *10*, 239.
(5) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Academic Press: New York, 2000.
(6) Atkinson, R. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459−507.
(7) Atkinson, R.; Aschmann, S. M.; Arey, J. *Environ. Sci. Technol.* **1992**, *26*, 1397−1403.
(8) Bolzacchini, E.; Hjorth, J.; Meinardi, S.; Orlandi, M.; Rindone, B.; Rosenbohm, E., *Eurotrac-2 Symposium Chemical Mechanism Determination Subproject*, Karlsruhe, September 23−25, 1998.
(9) Bolzacchini, E.; Umschlag, Th.; Herrmann, H.; Meinardi, S.; Rindone, B. *6th FECS Conference on Chemistry and the Environment*, Copenhagen, Denmark, August 26−28, 1998.
(10) Colville, R. N.; Chularton, T. W.; Gallager, M.-W.; Wicks, A. J.;, Downer, R. M.; Tyler, B. J.; Storeton West, K. J.; Fowler, D.; Cape, J. N.; Dollard, G. J.; Davis, T. J.; Jones, B. M. R.; Penkett, S. A.; Bendy, B. J.; Burgess, R. A. *Atmos. Environ.* **1994**, *28*, 397.
(11) Bolzacchini, E.; Meinardi, S.; Orlandi, M.; Rindone, B.; Hjorth, J.; Restelli, G. *Environ. Sci. Technol.* **1999**, *33*, 461−468.
(12) Barletta, B.; Bolzacchini, E.; Meinardi, S.; Orlandi, M.; Rindone, B**.** *Environ. Sci. Technol.* **2000**, *34*, 2224−2230.
(13) Palm, W.-U.; Behnke, W.; Zetzsch, C. Presented at the EC Workshop “Chemical Mechanisms of Atmospheric Processes”, Copenhagen, 1998.
(14) Levsen, K.; Behnert, S.; Priess, B.; Svoboda, M.; Winkeler, H. D.; Zietlow, J. *Chemosphere* **1990**, *21*, 1037−1061.
(15) Lüttke, J.; Levsen, K.; Scheer, V.; Wünsch, G.; Cape, J. N.; Hargreaves, K. J.; Storeton-West, R. L.; Acker, K.; Wieprecht, W.; Jones, B. V. *Atmos. Environ.* **1997**, *16*, 2637−2648.
(16) Geissler, A.; Schöler, H. F. *Vom Wasser* **1993**, *80*, 357.
(17) Geissler, A.; Schöler, H. F. *Water Res.* **1994**, *28*, 2047.
(18) Kawamura, K.; Kaplan, I. R. Organic Compounds in Rainwater. In *Organic Chemistry of the Atmosphere*; Hansen, L. D., Eatough, D. J., Eds.; CRC Press: Boca Raton, 1991; p 233.
(19) Belloli, R.; Barletta, B.; Bolzacchini, E.; Meinardi, S.; Orlandi, M.; Rindone, B. *J. Chromatogr. A* **1999**, *846*, 277−281.
(20) Belloli, R.; Bolzacchini, E.; Clerici, L.; Rindone, B.; Sesana, G.; Librando, V. *Atmos. Environ.* (submitted for publication).
(21) Kurtenbach, R. Personal communication.
(22) Tremp, J.; Mattrel, P.; Fingler, S.; Giger, W. *Water, Air, Soil Pollut.* **1993**, *68*, 113−123.
(23) Uptake and Nitration of Aromatic Compounds in the Tropospheric Aqueous Phase, EC Contract Research No. ENV4-CT97-0411, Final Report.
(24) Schott, G., Davidson, N. *J. Am. Chem. Soc.* **1958**, *80*, 1841−1853.
(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(27) Frisch, M. J.; Trucks, G. W.; Schlege, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, G.; Pople, J. A. *Gaussian ‘94;* Gaussian, Inc.: Pittsburgh, PA, 1995.
(28) Atkinson, R. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459−407.
(29) Atkinson, R.; Aschmann, S. M.; Winer, A. M. *Environ. Sci Technol.* **1987**, *21*, 1123−1125.
(30) Del Giacco, T.; Baciocchi, E.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 5451−5456.
(31) Herrmann, H.; Zellner, R. Reactions of NO_3 in Aqueous Solution. In *Chemistry of N-Centered Radicals*; Alfassi, Z., Ed.; Wiley: New York, 1998; pp 291−343.
(32) Ito, O.; Akhido, S.; Iino, M. *J. Org. Chem.* **1989**, *54*, 2436−2440.
(33) (a)Andino, J. M.; Smith, J. N.; Flagan, R. C.; Goddard, W. A., III; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 10967−10980. (b) Lay, T. H.; Bozzelli, J. W.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 6543−6554.
(34) Bohn, B.; Zetzsch, C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5097−5107.

Received for review May 23, 2000. Revised manuscript received October 27, 2000. Accepted December 11, 2000.

ES001290M