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Nighttime Tropospheric Chemistry: Kinetics and Product Studies in the Reaction of 4-Alkyl- and 4-Alkoxytoluenes with NO_3 in Gas Phase

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Alkylbenzenes are important constituents of gasoline and industrial solvents and contribute to the formation of tropospheric ozone. The removal of these compounds from the troposphere is due to reaction with OH during the day and with NO_3 during the night. Five para-substituted toluenes are reacted with the nitrate radical in gas phase. Samples to be used for product analysis were preconcentrated and analyzed by GC-MSD analysis with the use of a reference curve. The yields of methanol, ethanol, and formaldehyde were determined by FTIR analysis of the reaction mixture in the chamber. Carbonyl compounds, benzyl alcohols, and nitroderivatives were formed. In the case of the alkoxytoluenes, products were also an alkanol, benzyl alcohols, and nitrophenols. Indirect rate constants measurements were performed by comparing by FTIR measurements the decay of the aromatic compound under investigation to that of a reference compound, with a known rate constant for the reaction with NO_3 added to the gas mixture. Wall loss constants were evaluated by FTIR. A Hammett correlation with $\rho = -4.3 \pm 0.6$; $r^2 = 0.87$ was obtained. This and the kinetic isotope effect of 1.5–1.8 suggest a reaction mechanism occurring via an addition–elimination pathway.

Introduction

The nitrate radical NO_3 is generated in the atmosphere by the reaction of NO_2 with O_3 and temporarily stored as N_2O_5 in the equilibrium rapidly established with NO_2:

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

$$NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M$$

Alkylbenzenes are important constituents of gasoline and industrial solvents and contribute to the formation of tropospheric ozone (*1*). The removal of these compounds from the troposphere is due to reaction with OH during the day and with NO_3 during the night (*2*).

The NO_3-initiated oxidation of aromatic hydrocarbons must be considered a minor sink for these species (*3*); however the high concentration of aromatics observed in urban areas demands a better knowledge of mechanisms and reaction products, in particular in regard to the possible formation of noxious compounds (e.g. nitroderivatives) (*4*).

Difficulty in sampling and analysis explains the limited number of product studies in atmospheric chemistry. The ring-retaining products in the reaction of aromatic compounds with OH have been extensively studied (*5*). Ring cleavage products in this reaction have been very recently elucidated (*6*). The reactions between the nitrate radical and aromatics received less attention until recently. Benzyl nitrates, aldehydes, benzyl alcohols, and nitroderivatives have been found as reaction products of methylarenes (*7*). Here we report on the kinetics and the product study concerning other 4-substituted toluenes, e.g. 4-ethyl-, 4-isopropyltoluene known to be constituents of gasoline, 4-*tert*-butyltoluene as a probe of reaction mechanism, and 4-methoxy- and 4-ethoxytoluene known as biomass burning products.

Experimental Section

Gas-Phase Reactions. The reactions were 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 connected to an FTIR spectrometer. N_2O_5 was synthesized in the chamber by mixing O_3 with an excess of NO_2**.** Subsequently the hydrocarbon was added, and the reaction was allowed to proceed until only insignificant amounts (<100 ppb) N_2O_5 remained. Typical initial concentrations were 20 ppmV N_2O_5, a few ppmV NO_2, and 20 ppmV of the hydrocarbon.

Samples to be used for product analysis were obtained by pumping known volumes of the reaction mixture through glass columns packed with 150 mg of coconut charcoal. The desorption was performed by extraction with 0.5 mL of dichloromethane under mechanical agitation for 1 h. The products were identified by GC-MSD analysis of the dichloromethane solution without further preconcentration, using a HP 5890 gas chromatograph with a 30 m capillary column (SPB5, 0.25 mm I.D.) interfaced with a quadrupolar detector (HP 5970), operating in Electron Impact mode at 70 eV. The yield was determined in triplicate with the use of a reference curve obtained using known amounts of each compound.

The yields of methanol, ethanol, and formaldehyde were determined by FTIR analysis of the reaction mixture in the chamber.

Kinetic Measurements. Indirect rate constants measurements were performed by comparing by FTIR measurements the decay of the aromatic compound under investigation to that of a reference compound, with a known rate constant for the reaction with NO_3 radicals, added to the gas mixture (*8*). Wall loss constants were evaluated by FTIR.

Results

Figures 1 and 2 show the results of the kinetic measurements of rate constants with the indirect method. The wall loss constants and the rate constants thus obtained are shown in Table 1. The rate constants of the reference compound anisole (*9*) and 1,3,5-trimethylbenzene (*10*) were literature data. The plot of log *k* for these 4-substituted toluenes and other obtained from the literature (*3*) vs Hammett's σ for the gas-phase reaction with NO_3 (nine compounds) gave (Figure 3) $\rho = -4.3 \pm 0.6$; $r^2 = 0.87$.

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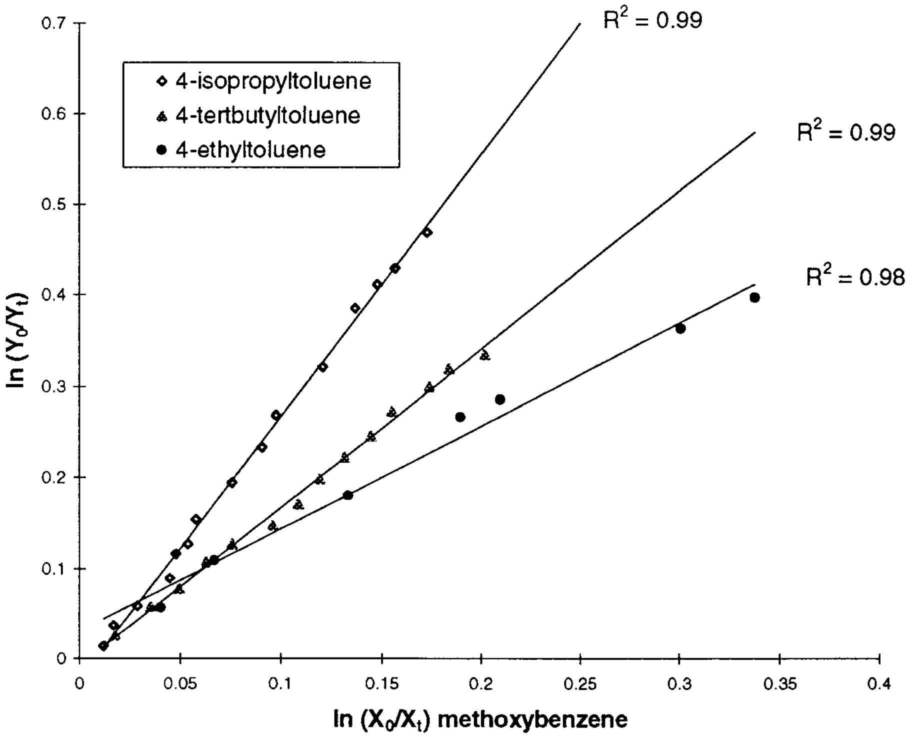


FIGURE 1. Kinetic measurements for 4-ethyltoluene 1, 4-isopropyltoluene 12, and 4-*tert*-butyltoluene 19.

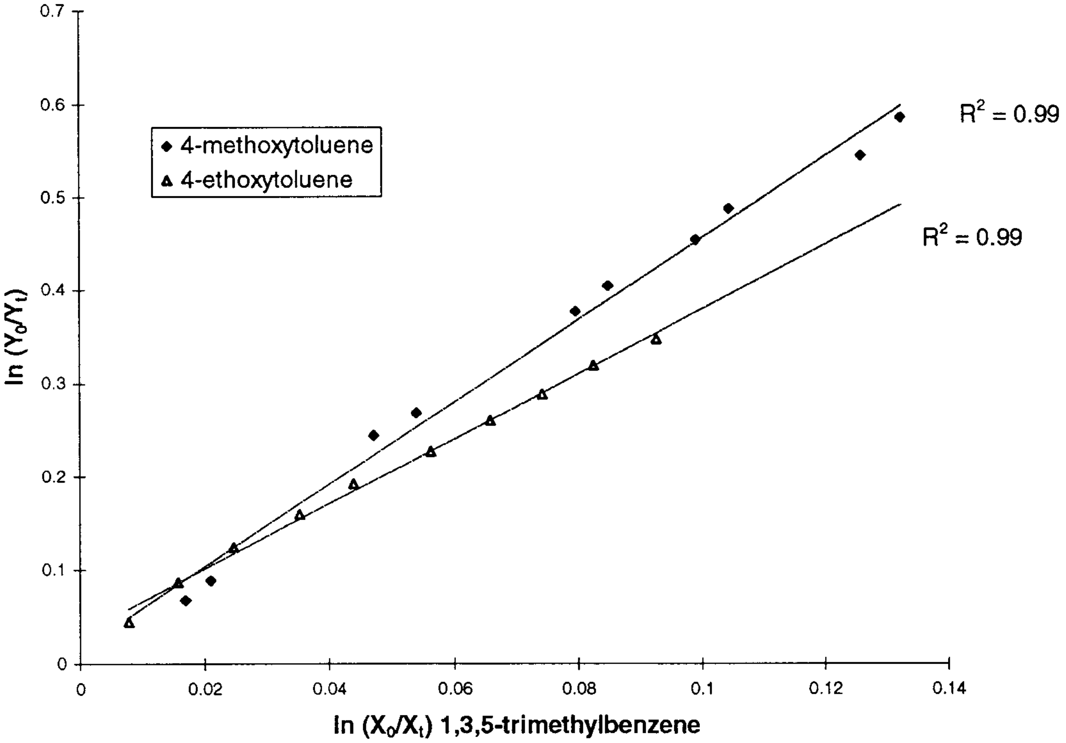


FIGURE 2. Kinetic measurements for 4-methoxytoluene 24 and 4-ethoxytoluene 28.

Product Studies. *4-Ethyltoluene **1**.* 4-Ethyltoluene **1** reacted with NO_3 giving products deriving from the reaction at the methyl group such as 4-ethylbenzaldehyde **2**, 4-ethylbenzyl alcohol **6**, and 4-ethyl benzyl nitrate **8** and products deriving from the reaction at the methylene group such as 4-methylacetophenone **3** and 1-(4-methylphenyl)ethan-1-ol **7**. Also 4-methylstyrene **4** and its oxidation product 4-methylbenzaldehyde **5** derived from the reaction at the methylene group. Compound **4** could be formed from the elimination of nitric acid from the intermediate secondary nitrate 1-(4- methylphenyl)ethan-1-nitrate **9**, probably during sampling. The two nitroderivatives **10** and **11** were also observed. Table 2 shows the quantitative results.

*4-Isopropyltoluene **12**.* 4-Isopropyltoluene **12** was more reactive with NO_3 than both 4-methyl- and 4-ethyltoluene. Two reaction products deriving from the reaction at the benzylic primary position were 4-isopropylbenzaldehyde **13** and 4-isopropylbenzyl alcohol **14.** 4-Isopropenyltoluene **15** derived from the abstraction of the tertiary hydrogen atom in the isopropyl substituent and gave by further oxidation

TABLE 1. Wall Loss Constants and Rate Constants of the Reaction of 4-Substituted Toluenes with NO_3 at 298 K[a]

	wall loss constants (s^{-1})	reference compound (*3*)	$k_{substrate}/k_{reference}$	*k* (cm^3 $molecule^{-1}$ s^{-1})
4-ethyltoluene **1**	8.2×10^{-6}	1,3,5-trimethylbenzene	0.98	$7.71 \pm 1.10 \times 10^{-16}$
4-isopropyltoluene **12**	8.0×10^{-6}	methoxybenzene	2.94	$9.98 \pm 0.15 \times 10^{-16}$
4-*tert*- butyltoluene **19**	4.4×10^{-6}	methoxybenzene	1.78	$5.99 \pm 0.45 \times 10^{-16}$
4-methoxytoluene **24**	1.3×10^{-5}	1,3,5-trimethylbenzene	4.09	$3.12 \pm 0.54 \times 10^{-15}$
4-ethoxytoluene **28**	9.9×10^{-4}	1,3,5-trimethylbenzene	3.38	$2.67 \pm 0.53 \times 10^{-15}$

[a] Uncertainties are given as one standard deviation on experimental data and thus express random experimental error only.

TABLE 2. Percent Product Yields of the Gas Phase Reaction of NO_3 with Excess Substituted Toluenes in Air in the Presence of NO_2[a]

		reaction yield from the converted material (%)			
substrate	convn	carbonyls	alcohols	nitroderivatives	others
4-ethyltoluene **1**	67 ± 2	**2**: 16 ± 2 **3**: 17 ± 2 **5**: 13 ± 2	**6**: 3 ± 1 **7**: 2 ± 1	**10**: 5 ± 1 **11**: 6 ± 1	**4**: 4 ± 1 **8**: 3 ± 1
4-isopropyltoluene **12**	50 ± 3	**13**: 15 ± 1 **16**: 3 ± 1	**14**: 2 ± 1	**17** + **18**: 24 ± 1	**15**: 1 ± 1 formaldehyde: 30 ± 1
4-*tert*-butyltoluene **19**	54 ± 4	**20**: 32 ± 1	**21**: 16 ± 4	**22** + **23**: 42 ± 3	
4-methoxytoluene **24**	52 ± 2	**25**: 20 ± 1		**26**: 3 ± 1 **27**: 7 ± 1	methanol: 4 ± 2
4-ethoxytoluene **28**	59 ± 2	**29**: 11 ± 1 **31**: 3 ± 1		**30**: 1 ± 1	ethanol: 30 ± 10

[a]Yields are calculated on the amount of starting material converted and result from the integration of the gas chromatographic peaks in comparison with concentration/gas chromatographic plots for all the analytes.

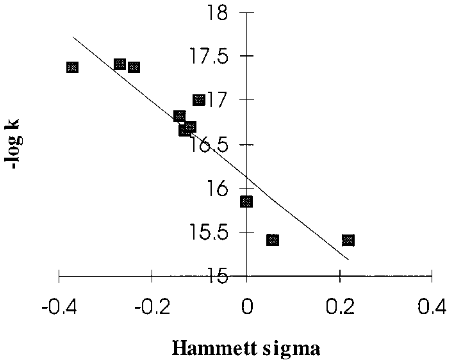
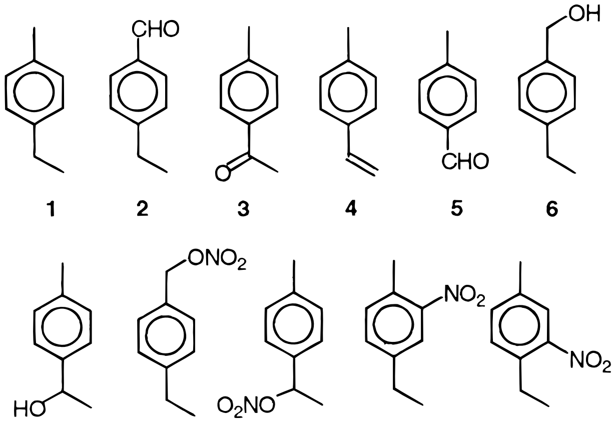


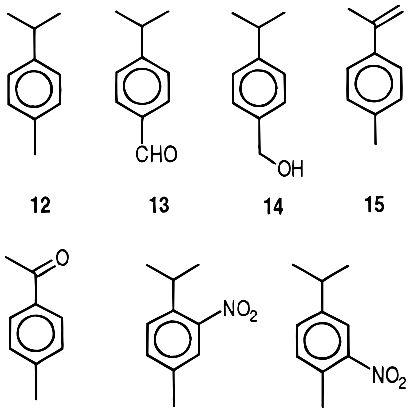
FIGURE 3. Hammett plot for the reaction of 4-substituted toluenes with NO_3.

4-methylacetophenone **16** and formaldehyde. This latter compound was quantified observing the FTIR spectrum of the material in the reaction chamber. The nitroderivatives **17** and **18** were also found. Figure 4 shows the GLC-MS analysis.



1 2 3 4 5 6

7 8 9 10 11



12 13 14 15

HCHO

16 17 18

4-tert-Butyltoluene ***19.*** 4-*tert*-Butyltoluene **19** was less reactive than 4-isopropyltoluene but similar to 4-ethyl- and 4-methyltoluene. Reaction products were 4-*tert*-butylbenzaldehyde **20**, 4-*tert*-butylbenzyl alcohol **21**, and the two nitroderivatives **22** and **23**.

4-Methoxytoluene ***24.*** A different situation occurred with 4-methoxytoluene **24**. A major pathway involving the oxidation of the methyl group gave 4-methoxybenzaldehyde **25**. Minor products were those arising from the O-demethylation reaction, i.e. methanol and two nitrophenols **26** and **27**.

4-Ethoxytoluene ***28.*** 4-Ethoxytoluene **28** gave ethanol confirming the O-dealkylation reaction. Other reaction products were the aldehyde **29** and the nitropenol **30**. Also NO_3 attack on the ethyl substituent was observed since 4-methylphenyl acetate **31** was found as a reaction products. Considerable amounts of the nitroethers **32** (R = Me) and **33** (R = Et) were also formed in the reactions of 4-methoxy- and 4-ethoxytoluene.

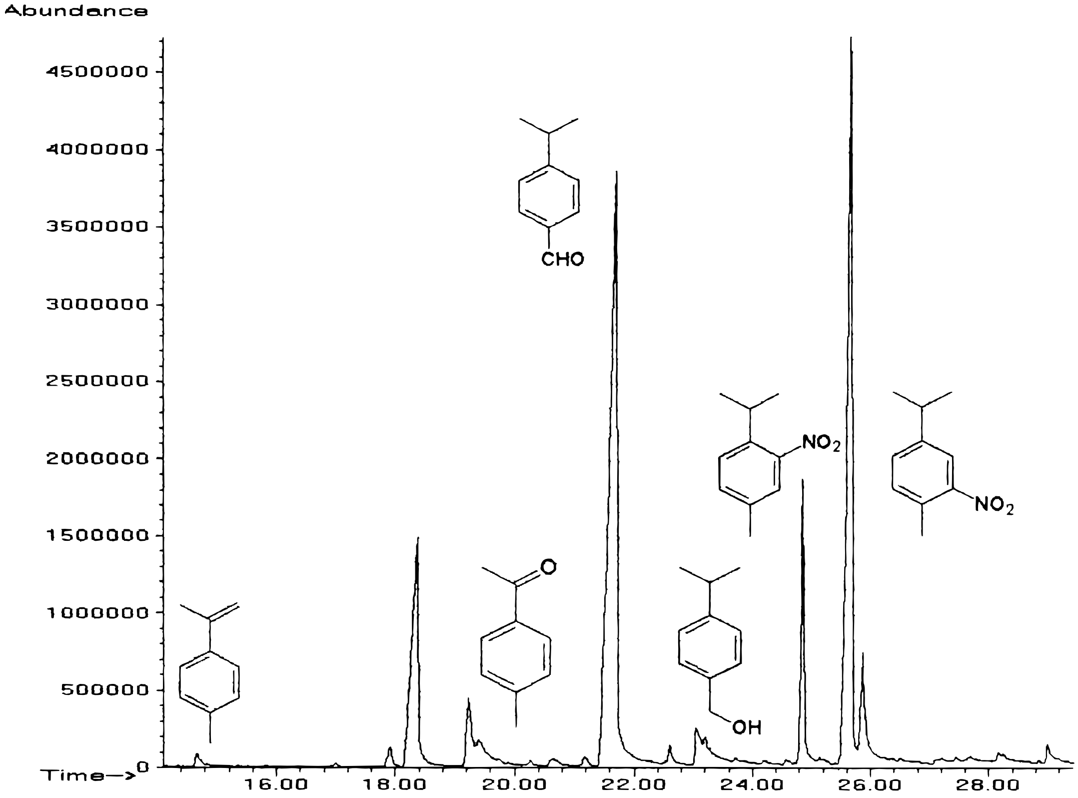
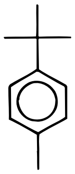


FIGURE 4. GLC-MS analysis of the reaction mixture from 4-isopropyltoluene **12**.



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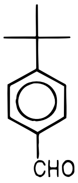

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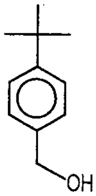

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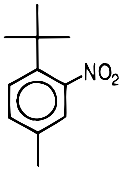

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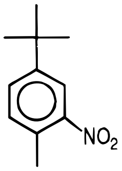

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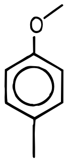

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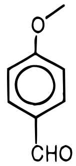

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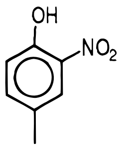

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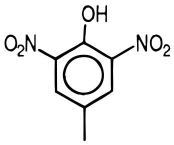
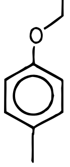


27

CH_3-OH

The occurrence of mononitroderivatives in the reactions of 4-alkyltoluenes with NO_3 is of particular interest. Hence, some control experiments were performed in order to ascertain whether these compounds were formed in the reaction chamber or during the trapping procedure. The results showed that nitroderivatives of aromatic hydrocarbons form essentially in the gas phase in the reaction chamber and not mainly in the carbon trap. On the contrary, mononitro-4-alkoxytoluenes **32** and **33** were formed mainly during the sampling procedure.



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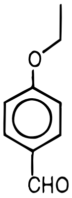

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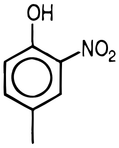
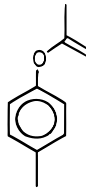


30

CH_3CH_2OH



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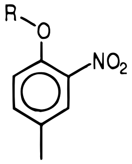


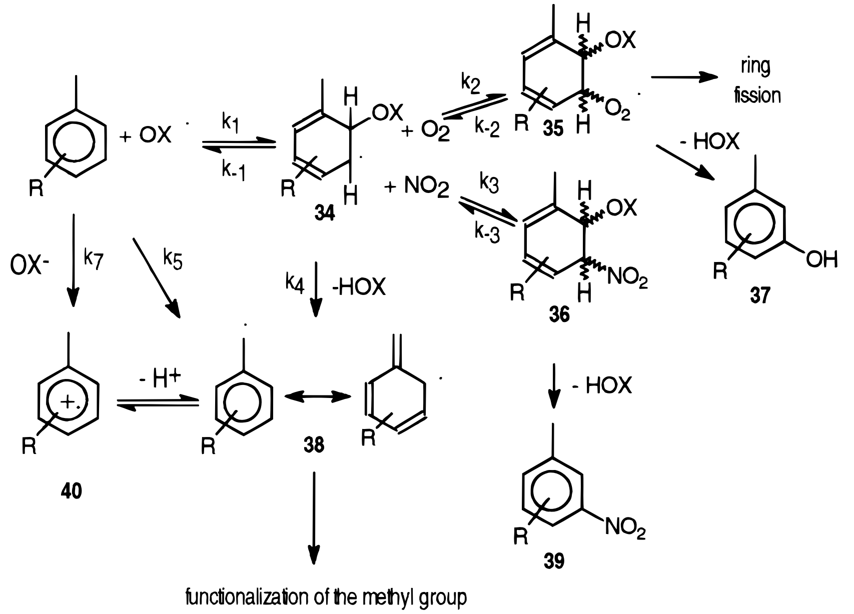
32 R = Me

33 R = Et

Discussion

The Rate-Determining Step. Scheme 1 shows a general description of the reactivity of substituted toluenes with OH (X = H) and NO_3 (X = NO_2). A competition between the addition channel (ADD) represented by the equilibrium constant $K = k_1/k_{-1}$, the H-abstraction reaction (H-ABS) represented by the rate constant k_5, and the electron transfer (ET) represented by the rate constant k_7 is likely to occur in both cases. However, the ET mechanism has been never suggested in gas phase. The intermediate benzyl radical **38** is formed directly (i) by H-ABS, (ii) by elimination of HOX from the adduct **34** in the ADD mechanism, and (iii) by deprotonation of the cation radical **40** in the ET mechanism. Hence, products deriving from the functionalization of the methyl group such as aldehydes, and benzyl alcohols, benzyl nitrates are not diagnostic of the occurrence of one particular mechanism. A sharp predominance (≈90%) of the ADD mechanism has been shown in the reaction of OH with toluene and substituted toluenes (*11*), and this explains the formation of phenols **37** and ring fission products via the reversible reaction with dioxygen **35** (X = H) and of nitroderivatives **39** via the adduct with NO_2 **36** (X = H) (*12*). The phenol/ring fission ratio is probably related to the stereochemistry of the adduct **35**, having two stereogenic carbons.

SCHEME 1



The occurrence of either the ADD or the H-ABS mechanism in the gas-phase reaction of NO_3 with substituted toluenes is under discussion. Three experimental facts can be used for distinguishing ADD, H-ABS, ET in the reaction of NO_3: (i) positional selectivity, (ii) kinetic isotope effects (k_{ie}), and (iii) the Hammett correlation.

(1) H-ABS. The H-ABS mechanism involves the rate-determining cleavage of a carbon−hydrogen bond in the methyl group. A low Hammett ρ value and a primary (k_{ie}) is expected from this reaction, in analogy with other reactions occurring via the formation of the benzyl radical via a rate-determining H-ABS. In fact, with electrophilic radicals such as bromine atoms from *N*-bromosuccinimide a ρ of -1.46 was obtained in liquid phase. Using molecular bromine in solution a $\rho = -1.07$ resulted (*13*). Here the kinetic isotope effect was respectively $k_{ie} = 4.86-5.11$ and $4.59-5.15$ (*14*). The gas-and the liquid-phase radical chlorination of substituted toluenes had lower k_{ie} (1.99−2.09) and ρ values (−0.76) as expected in an exothermic reaction with very low activation energy ($\approx$1 kcal mol^{-1}). The endothermic bromination had 7 kcal mol^{-1} activation energy (*15*) in accord with the Hammond postulate (*16*) which states that exothermic radical reactions are likely to have reactant-like transition states. Hence, they will have low values of primary k_{ie}. However, the H-ABS mechanism in the reaction of NO_3 with alkylaromatics had to be checked by comparison with the radical bromination. In both reactions only benzylic hydrogens are abstracted, whereas in the radical chlorination also hydrogens other than benzylic are abstracted (*17*). Moreover, the reaction of NO_3 with toluene has been calculated to be exothermic (*18*).

(2) ET. The liquid-phase oxidation of toluene with Co(III) acetate occurring via ET concerted with deprotonation has the higher ρ value of $= -2.4$ and the primary k_{ie} of 3.7 (*19*).

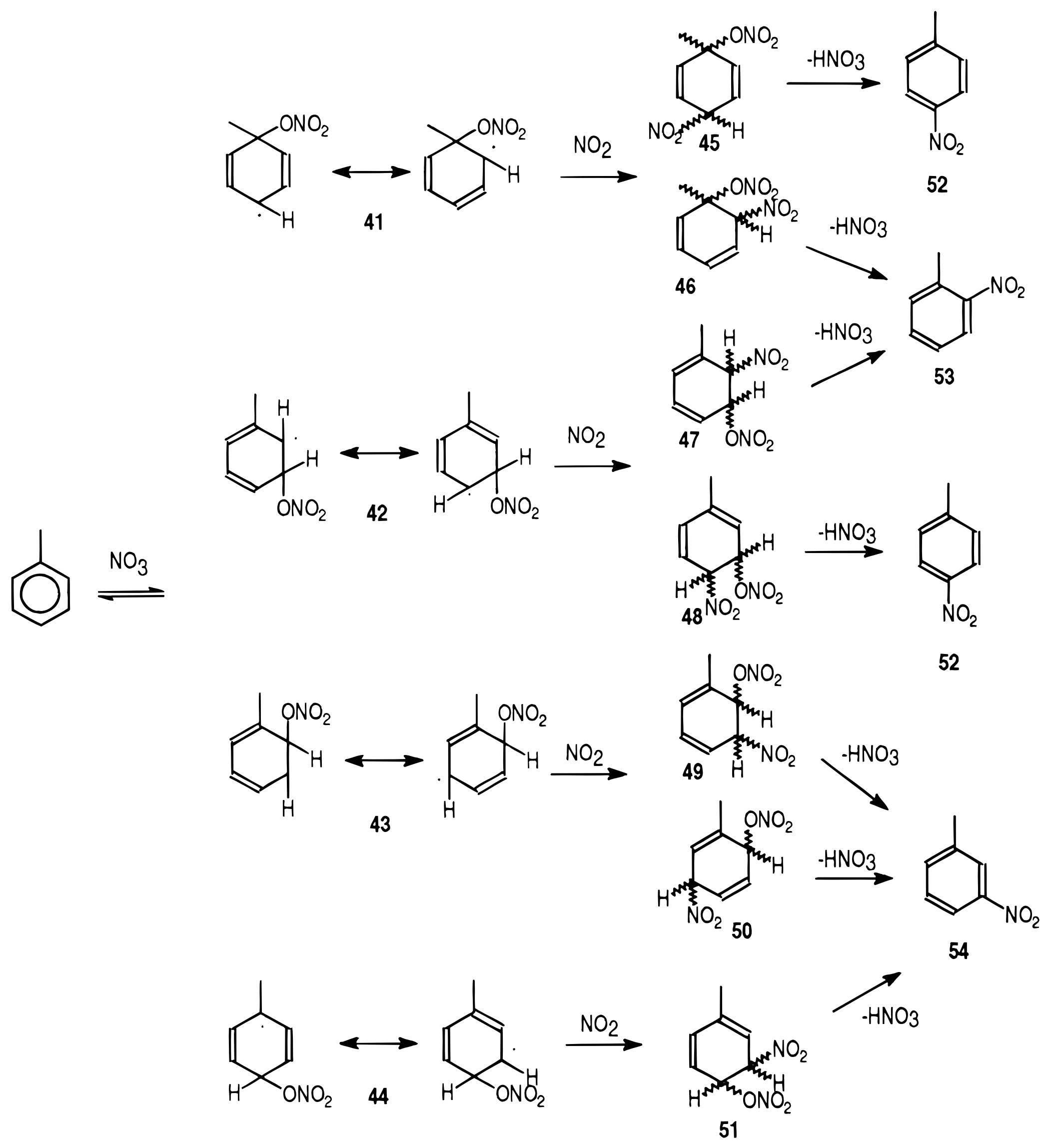
(3) ADD. A different behavior was observed in the liquid-phase reaction of NO_3 with several toluenes substituted with electron withdrawing groups. Here, the ADD mechanism in acetonitrile was suggested by a ρ value of -3.2 (*20*). More recently, a reinvestigation of this reaction led to the conclusion that an inner-sphere ET mechanism was always occurring via an intermediate NO_3-aromatic complex. This gave NO_3^- and the cation radical **40** which underwent fast deprotonation to the benzyl radical **38**. This mechanism resulted in $k_{ie} = 1.6$ (*21*). The ADD channel was shown to compete with ET in a recent study on the reaction of several aromatics with NO_3 in water (*22*).

The negative ρ value obtained in the kinetic experiments with NO_3 reported in this paper ($\rho = -4.3 \pm 0.6$; $r^2 = 0.87$) indicates an electrophilic attack involving a polar transition state (*23*). The analogous reaction of aromatic compounds with OH in gas phase has been reported to follow the general description by the Hammett equation (*24*). In our hands a similar calculation with the available rate constants of the reaction of 4-substituted toluenes with OH shows a $\rho = -2.3 \pm 0.2$; $r^2 = 0.96$ (*25*). This negative ρ value is then the result of the predominant rate-determining addition of OH involving a polar transition state (*11*). Hence, the similarity of the ρ values in the reactions of OH and NO_3 suggests the predominant rate-determining addition of NO_3 to 4-substituted toluenes. The more negative ρ value with NO_3 is the result of its major electrophilicity over OH. The kinetic isotope effect value which was found (*26*) to be 1.5−1.8 in the reaction of toluene and xylenes with NO_3, slightly higher than that of 0.98−1.13 found for the reaction of toluene with OH (*2*) could be the result of the concerted loss of nitric acid from the adduct **34** to form the benzyl radical **38**.

The Product-Determining Steps. Concerning the product-determining steps, the reversible addition reaction of NO_3 to the aromatic has four different regiochemistries **41**−**44** in the case of 4-substituted toluenes (Scheme 2). The position of the equilibrium in the formation of adducts in the reaction of OH with toluene has been recently calculated using an ab initio approach and the ortho adduct has been shown to be the most stable (*27*). This explains the predominance of the formation of o- over p-cresol in this reaction (*28*). Preliminary semiempirical calculations in the formations of the adducts in the reaction of NO_3 with toluene show a similar stability of the ortho-, meta-, and para-adducts but a lower stability for the ipso-adduct (*29*). A refinement of this calculation using an ab initio method shows that this exothermic reaction gives the ortho adduct from toluene as the most stable adduct (*18*).

Alkyl-substituted nitrotoluenes may have their origin in the reaction chamber in the reaction of the NO_3-adducts (**41**−**44,** shown in Scheme 2 for toluene) with NO_2 to form diastereoisomeric dihydrobenzenes **45**−**51** that eliminate nitric acid to give the nitroderivatives **52**−**54**. This reaction has been shown to be fast (*30*). The finding of high amounts

SCHEME 2

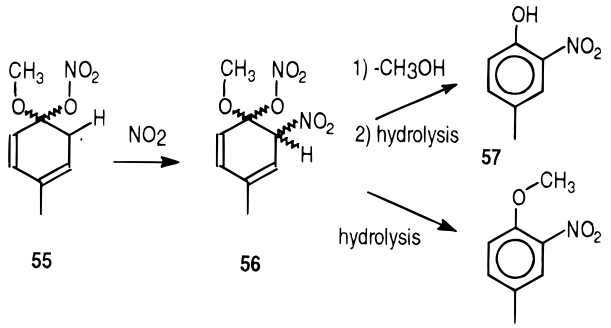


of *m*-nitrotoluene **54** from toluene using sampling procedures which should not enrich samples in one particular isomer (*7*) is an indication of a radical nitration (*31*). This again suggests the importance of the ADD mechanism and is explained by the prevailing equilibrium amount of the ortho adduct **43**. In fact should these nitrotoluenes derive exclusively from the chain-terminating reaction of benzyl radical **38** (Scheme 1) only the para **52** and the ortho isomer **53** should be formed.

Also the O-dealkylation reaction observed with 4-methoxy- **24** and 4-ethoxytoluene **28** is an indication of the occurrence of the ADD mechanism. In particular, the oxidative O-dealkylation reaction leading to nitrophenols and nitrophenyl ethers may be explained to occur via the "ipso" adduct **55** formed by initial addition of NO_3. This adduct, which has been suggested also in the case of the reaction of phenol with NO_3 (*32*), will then react with NO_2 to give a diastereoisomeric intermediate **56** that may react further via elimination reactions to form (i) the nitrophenol **57** and (ii) a nitrophenyl ether **58** (Scheme 3).

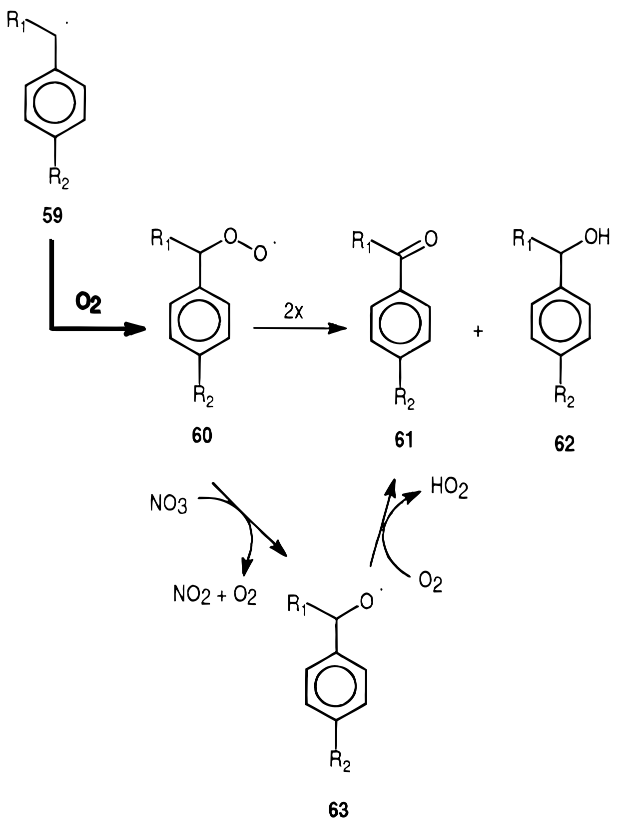
Alcohols and carbonyls formed in this reaction derive from the intermediate benzyl radical **59** formed in all the mechanistic alternatives (Scheme 4). This will be transformed into a peroxy radical **60** which will disproportionate to carbonyls **61** and alcohols **62**. Alternatively, peroxy radicals **60** may react with NO_3 to form alkoxy radicals **63** and then carbonyl compounds **61**. The observed predominant formation of carbonyls over benzyl alcohols with 4-alkyltoluenes suggests a major role for this latter pathway.

SCHEME 3



The nature of the carbonyl compounds from 4-alkyltoluenes is likely to be controlled by two factors: (i) the stability of the corresponding benzyl radical and (ii) the regiochemistry of the attack of NO_3. The physicochemical characteristics of the carbonyls obtained are so similar that one could expect similar trapping and elution efficiency. This allows to compare

SCHEME 4



reaction yields in order to obtain information about branching ratios. In fact, in the reaction of 4-ethyltoluene **1**, the ratio between the yields of compounds **3** + **4** + **5** (arising from the reaction at the methylene group) and **2** + **6** + **8** (arising from the reaction at the methyl group) is 1.5:1. This is also due to the different stability of the corresponding benzyl radicals **64** and **65** (Scheme 5) obtained in the loss of one hydrogen atom from the initial adduct. However, this is not the major factor, since the benzylic hydrogen abstraction has the following order of reactivity (*33*): tertiary = 6.8−260 > secondary = 3.2−50 > primary = 1.

In the reaction of 4-isopropyltoluene **12**, compounds **15** + **16** derive from the fragmentation of the intermediate tertiary radical **69**, whereas the aldehyde **13** and the alcohol **14** derive from the primary radical **68**. Hence in this case the ratio between the products formed by the tertiary **69** vs the primary radical **68** is 1:3.7. This implies that the pathway leading to the primary radical **68** is more important than that leading to the tertiary radical **69** via the adduct **67**. This is probably due to the fact that the equilibrium concentration of the adducts **66** and **67** is strongly influenced by steric factors. In fact, attack of NO_3 could occur either ortho to the bulky isopropyl group to generate the adduct **66** or ortho to the methyl group to generate the adduct **67**. The equilibrium concentration of the latter, more stable, should be higher that of the former, less stable. Consequently, a higher amount of the primary radical **68** over the tertiary radical **69** is formed. A preliminary calculation of the difference in heat of formation of adducts **66** and **67** using a semiempirical AM1 approach showed that adduct **66** is 0.71 kcal mol^{-1} more stable that adduct **67** (*18*).

In conclusion, the reactions of NO_3 radicals with aromatic hydrocarbons are relatively slow and thus believed to be of little importance as a sink for these in ambient air. Carbonyls and nitroderivatives are main reaction products. However, the finding of nitroderivatives and nitrophenols in rainwater in polluted areas (*34*) is of particular interest because of the toxicity of these compounds, and it needs to be established if their formation is taking place at a significant rate in the atmospheric gas phase or in the aqueous atmospheric phase. Some preliminary observations (*35*) suggest that inspection of the isomeric distribution could throw light on this point because of the radical nature of the gas-phase process and the electrophilic mechanism of the aqueous reaction. These two pathways lead to different isomer distributions.

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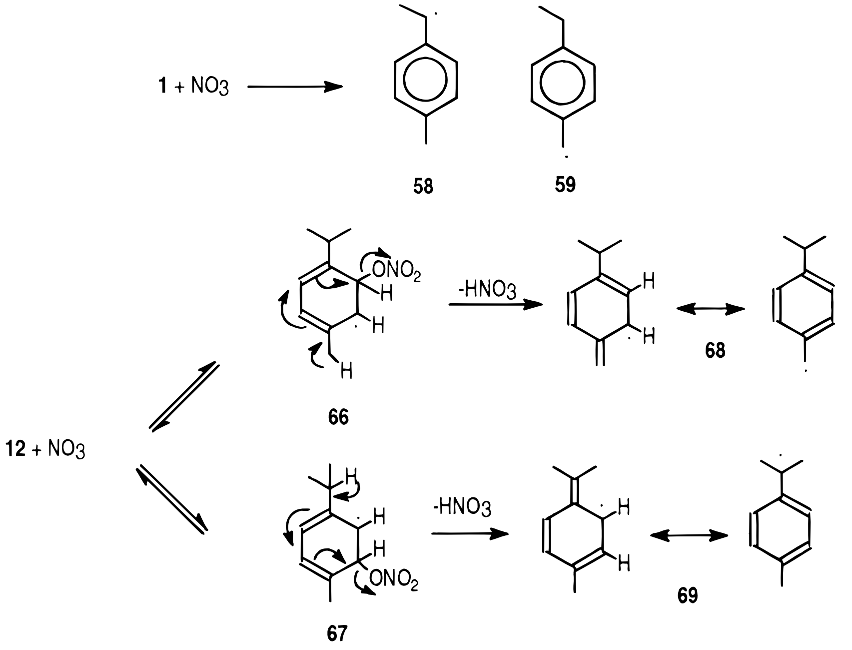
SCHEME 5



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