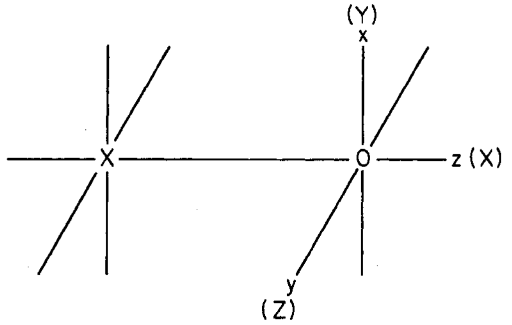

Figure 1. Axis system in C=O and N–O bonds: X = C, N.

atoms, as compared with the values for otherwise similar but non-hydrogen-bonded atoms.[7] The experimental data presented here corroborate the theoretical results (see also Figure 2 of ref 7).

In addition to the direct study of hydrogen bonding in the form of geometrical interpretation of the ^{17}O NQR data, the results presented here and in the previous paper facilitate the analysis of the electronic effects that are reflected in the ^{17}O NQR data. For example, the carbonyl group in 4(1*H*)-pyridinone is structurally similar to that in *p*-benzoquinone, but has a quite different quadrupole coupling constant, 8.33 vs. 11.51 MHz.[14] A large portion of the difference in the values of the quadrupole coupling constant is probably due to the effect of hydrogen bonding in 4(1*H*)-pyridinone, although the solid-state structure of this compound is not known. If we assume that the length of the hydrogen bond is the same as is found in 2(1*H*)-pyridinone (2.77 Å),[15] then we can estimate the effect of hydrogen bonding on the ^{17}O quadrupole coupling constant to be about 1.0 MHz. Because this still leaves a large difference of 2.2 MHz between the two oxygen sites, one can infer that there exists a significant difference in the electronic environment of the two carbonyl groups. The lower quadrupole coupling constant in 4(1*H*)-pyridinone suggests a much larger oxygen 2p$_\pi$ population.

In summary, we have presented ^{17}O NQR data for several hydrogen-bonded systems. The experimental data support the results of a previous theoretical study. The results demonstrate that hydrogen bonding in the solid state is amenable to study by ^{17}O NQR techniques. Secondly, the effects of hydrogen bonding upon the electric field gradient can be estimated, thus aiding in the further analysis of intramolecular electronic effects on the ^{17}O NQR data.

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Gas-Phase Hydroxyl Radical Reactions. Products and Pathways for the Reaction of OH with Aromatic Hydrocarbons[1]

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The reactions of OH with benzene, toluene, 1,4-dimethylbenzene, and 1,3,5-trimethylbenzene have been investigated in a discharge flow system at total pressures of 6–12 torr. In the presence of NO, NO_2, and O_2 the intermediate radicals are converted quantitatively to stable products from which two major reaction pathways are identified. Abstraction of a hydrogen atom from the methyl group by OH leads primarily to the corresponding aldehyde, and addition to the aromatic ring by OH gives primarily the corresponding phenols. Nitro substitution of the aromatics via the OH adduct competes with phenol formation; however, the amount depends on the ratio of NO_2/O_2. In the case for toluene, the ratio of rate constants, k_{NO_2}/k_{O_2}, for the two processes is $(4 \pm 2) \times 10^3$. The isomer distributions for OH addition to toluene were determined to be 0.806 ± 0.022 ortho, 0.051 ± 0.009 meta, 0.143 ± 0.019 para, and <0.008 ipso. The contributions of methyl attack (k_1) relative to total reaction ($k_1 + k_2$) are 0.15 ± 0.02 for toluene, 0.15 ± 0.02 for 1,4-dimethylbenzene, and 0.021 ± 0.006 for 1,3,5-trimethylbenzene.

Introduction

Aromatic hydrocarbons are important constituents of polluted urban atmospheres,[2–5] and the extent to which they contribute to photochemical smog is of considerable concern.[2,6–9] The kinetics of gas-phase OH–aromatic reactions have been the subject of several recent reports,[10–16] and it is clear that initial attack by OH is the major route for involvement of aromatic hydrocarbons in the chemistry of the troposphere.[2,11–18] Although the mechanisms of solution-phase OH–alkylbenzene reactions have been extensively investigated,[16,19] reactions in the gas phase, where ambiguities due to solvation or solvolysis are excluded, have not been studied in depth. Thus, products and

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[†] Deceased, May 1981.

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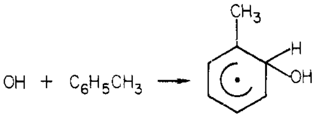
precise mechanisms of the gas-phase reactions remain undetermined; however, identifying them is essential for determining the fate of aromatics in the environment and for developing accurate chemical models of urban airsheds.

Given these considerations, we have undertaken to determine the products of the gas-phase reaction of OH with benzene, toluene, *p*-xylene, and 1,3,5-trimethylbenzene.

Our results show that two major reaction pathways are available. Shown for the case of toluene, these are benzylic hydrogen atom abstraction (reaction 1) and radical ad-

$$OH + C_6H_5CH_3 \rightarrow H_2O + C_6H_5CH_2\cdot \qquad (1)$$

dition to the aromatic ring (reaction 2). For each of the



(2)

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hydrocarbons studied, we have determined the relative incidence of reactions 1 and 2 by product analyses. Our data are in close agreement with relative rate constants determined by kinetic experiments.[15] The intramolecular selectivity of ring addition to toluene by OH is also reported and discussed in terms of formation of an intermediate OH–toluene π complex. Finally, we consider the environmental implications of our findings.

Experimental Section

Materials. The benzene and toluene used were Mallinckrodt Analytical Reagent grade. 1,4-Dimethylbenzene (99%) and 1,3,5-trimethylbenzene (99+%, Gold Label) were from Aldrich Chemical Co. Benzene, toluene, and 1,4-dimethylbenzene were purified by reaction with concentrated H_2SO_4, phase separation, three aqueous washings, drying with $MgSO_4$, and fractional distillation. 1,3,5-Trimethylbenzene was fractionally distilled before use. Argon, H_2, and O_2 were supplied by Liquid Carbonics, and NO_2 (0.54% in He) was supplied by Linde.

Apparatus. The flow system used in the studies was constructed of 2.5-cm i.d. Pyrex tubing. O-ring joints and stopcocks with Viton O-rings were used throughout. A Scintillonics Model HV15A microwave generator was used to dissociate hydrogen. Pressures of gaseous reactants were measured with a Validyne Model DP7 transducer. The linear flow rate was 1×10^3 cm s^{-1} throughout the experiments.

GLPC analyses were performed with a Hewlett-Packard Model 5700A chromatograph equipped with a flame-ionization detector. A Finnigan Model 3200 tandem GC–MS was used for product identification. HPLC analyses were performed with a Waters Associates system consisting of two Model 6000A pumps, a Model 660 solvent programmer, and a U6K injector. A Schoeffel Instrument Corp. Model GM770 variable wavelength detector was used.

Methods. Reaction Conditions. Aromatic hydrocarbons were added by syringe at constant rates as low as 0.17 cm^3 min^{-1} using a syringe pump. Hydrogen atoms were generated by passing a dilute mixture of H_2 in Ar through the microwave discharge. Typical reactant pressures (torr) were as follows: H_2, 0.2; Ar, 5; hydrocarbon, 0.1; NO_2, 1×10^{-3}–5×10^{-3}; He, 0.2–1; O_2, 1–10. Total pressures thus ranged from 6 to 15 torr. All reactions were conducted at ambient temperature, 25 ± 3 °C.

Product Analysis. Products were sampled by condensation in the reaction stream in a cold trap (−78 or −196 °C) or by pulling a fraction of the gas stream through a short column of solid-phase absorbant. Control experiments demonstrated that the condensation traps collected only ~10% of the organic material passing through the system. For this reason, mass balances could not be obtained. Other experiments showed, however, that condensable species were trapped nonselectively, i.e., that product ratios in the condensed material were equivalent to ratios in the gas stream. Control experiments to test the efficiency of the gas sampling system using Chromosorb G, AW/DMCS, 100/120 mesh (Applied Science), showed that products were not quantitatively trapped on the Chromosorb G column, the more volatile materials being pulled through the column to the sampling pump. When Tenax GC adsorbant was used to sample the reaction products, the results were quantitative provided collection times were short. By using an internal standard to measure the decrease of toluene, it was possible to determine yields of products relative to the decrease in reactant.

Product distributions from both condensed- and gas-phase sampling methods were carefully compared to rule out the possibility of interference caused by side reactions occurring in the cold trap.[27]

Products were identified by GC–MS and by comparing GLPC retention times with authentic samples. Toluene and its reaction products were analyzed by using a 2.5 m × 0.5 mm i.d. stainless-steel column packed with 4% tri-2-cresyl phosphate on 100/120 mesh Chromosorb G AW/DMCS and a 1.8 m × 1.0 mm glass column packed with 10% OV-17 on 80/100 mesh Chromosorb W. Benzene and its reaction products were analyzed with the same OV-17 column. The tricresyl phosphate column was also used for analysis of 1,4-dimethylbenzene and 1,3,5-trimethylbenzene reactions. Products of the latter reaction were also analyzed by HPLC using a μ-Bondapak C_{18}

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(27) In some instances products indicative of ionic (as opposed to free radical) reactions were found in the cold traps. In general, these side reactions could be eliminated by sampling at −78 °C rather than −196 °C and by working at low pressures (≤ 5×10^{-3} torr) of added NO_2.

TABLE I: Distribution of Individual Products as a Function of $[NO_2]$ Added for Reaction of OH with Toluene plus 9.7×10^{16} Molecules cm^{-3} O_2[a]

$10^{-14}\cdot[NO_2]$, molecule cm^{-3}	individual product as % of total									
	C_6H_5CHO	C_6H_5-CH_2OH	3-NO_2C_6-H_4CH_3	2-HOC_6-H_4CH_3	4-HOC_6-H_4CH_3	3-HOC_6-H_4CH_3	total HOC_6-H_4CH_3	CH_3C_6-H_3O_2	R_1[b]	R_2[c]
0.71	12.5	4.0	36.6	37.6	5.69	3.6	46.9		16.5	2.2
1.04	12.5	4.8	36.9	35.3	6.03	4.04	45.4	0.46	17.3	5.7
1.39	12.4	4.4	45.3	27.0	5.5	4.5	37.0	0.9	16.7	2.0
1.75	8.16	9.52	53.2	19.6	4.72	4.1	28.4	0.69	17.7	1.3

[a] Total pressure = 8.18 torr. [b] $R_1 = (C_6H_5CHO + C_6H_5CH_2OH)/(\text{total products})$. [c] $R_2 = (\text{total products}/C_6H_5CH_3) \times 10^4$.

column with 30% CH_3OH/H_2O as the mobile phase. GLPC and HPLC response factors were obtained for all products. In the experiments to correlate the conversion of toluene with the total products, Porapak QS columns were used. This column separates toluene, benzene (standard), and the reaction products, although it does not resolve the individual products. This simplified the analysis but required additional runs on the tricresyl phosphate column to ensure that the trapping procedure did not modify the reaction products or their distribution. The Porapak QS column was also used to measure the low molecular weight products.

Results. Hydroxyl radicals were generated by the discharge flow method from hydrogen atoms and NO_2 (*reaction 3*). This method has been used extensively[28-34] for

$$H\cdot + NO_2 \rightarrow HO\cdot + NO \qquad (3)$$

determination of OH reaction kinetics and is known to be reliable. In our system, an aromatic hydrocarbon and molecular oxygen are added 10 cm downstream from the point of addition of NO_2. For the linear flow velocity (1.0×10^3 cm s^{-1}) and concentrations of NO_2 and hydrogen atoms ($[H\cdot] \approx 10^{13}$ particles cm^{-3})[35] used in our system, reaction 3 ($k_3 = 1.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1})[36] has gone to completion at this point. Providing that the concentration of NO_2 added is greater than or equal to the concentration of H atoms, the products observed will have resulted entirely from reaction of OH with the aromatic hydrocarbon in the presence of O_2, NO, and NO_2. The hydrocarbon concentration was generally kept 100–1000 times larger than the concentration of OH to minimize secondary reactions.

The gas-phase products of the reaction of OH with toluene were found to be benzaldehyde (C_6H_5CHO), benzyl alcohol ($C_6H_5CH_2OH$), 3-nitrotoluene (3-$NO_2C_6H_4CH_3$), isomeric cresols (2-, 3-, 4-$HOC_6H_4CH_3$), and 2-methyl-1,4-benzoquinone ($CH_3C_6H_3O_2$). Phenol, benzoic acid, benzyl nitrate, and α-, 2-, and 4-nitrotoluene were searched for but not found. We set 1% of the total reaction products as an upper limit for the formation of each of these products. Low molecular weight products were searched for, but only glyoxal was detected under conditions where H atoms were totally converted to OH. It accounted for ~0.6 mol % of the total products. In cases where insufficient NO_2 was used to titrate the H atoms, acetyaldehyde, methylglyoxal, and formaldehyde were also detected to the extent of ~1 mol % along with as much as 3 mol % benzene. Also, the cases where H atoms were not titrated, there was roughly a 2-fold increase of the products resulting from OH attack on the benzylic hydrogens of toluene. The fact that ring cleavage products are readily detected when H atoms are present, even though they are not major products, substantiates the ability of the analytical method to detect cleavage products. Thus, the fact that essentially no cleavage products are observed under conditions where H atoms have been completely converted to OH rules out ring cleavage as a significant reaction pathway under these conditions. To further ensure that we were detecting all of the reaction products, we carried the reaction to high conversion and compared the yield of products with the consumed toluene. For the analysis benzene was used as an internal standard. Although benzene is less reactive than toluene, it is not inert, and it is necessary to account for its consumption in determining the conversion and yield. The conversion was determined by the expression

$$\text{conversion} = (T_0/B_0) - (T/B)(B/B_0)(T_0/B_0)^{-1}$$

where T_0 and T are initial and final toluene concentrations and B_0 and B are initial and final benzene concentrations. The yield of products based on the initial toluene was determined from

$$\text{yield} = \frac{\sum\text{products}}{T}\,\frac{(T/B)(B/B_0)}{(T_0/B_0)}$$

In these experiments the toluene pressure was 1×10^{-2} torr to ensure a high conversion. The initial ratio of toluene to benzene was ~20/1. For six runs the average conversion of toluene was 11.2%, and the yield of products based on initial toluene was 10.8%. The yield based on converted toluene computed for the individual runs was 93 ± 15%. Thus, the reported products account for the consumed toluene within the limits of experimental precision of the data, although the maximum possible unaccounted reacted toluene could be as high as 22%.

Product analyses were obtained with hydrocarbons other than toluene. Reaction of OH with benzene yielded phenol and nitrobenzene. The reaction with 1,4-dimethylbenzene gave 4-$CH_3C_6H_4CHO$, 4-$CH_3C_6H_4CH_2OH$, 2-HO-1,4-$(CH_3)_2C_6H_3$, and 2-NO_2-1,4-$(CH_3)_2C_6H_3$. Finally, the products of reaction of OH with 1,3,5-trimethylbenzene were 3,5-$(CH_3)_2C_6H_3CHO$, 3,5-$(CH_3)_2C_6H_3CH_2OH$, and 2-HO-1,3-5-$(CH_3)_3C_6H_2$.

For each hydrocarbon, product distributions were studied quantitatively as a function of $[O_2]$, $[NO_2]$, and total pressure. These experiments were studied in greatest detail for the case of toluene. Product distributions for this reaction at constant $[O_2]$ and various $[NO_2]$ are given in Table I. Table II gives distributions at constant $[NO_2]$

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TABLE II: Distribution of Individual Products as a Function of $[O_2]$ Added and of Total Pressure for Reaction of OH with Toluene Using 1.39×10^{14} Molecules cm^{-3} Added NO_2

10^{-16}. $[O_2]$, molecule cm^{-3}	total press., torr	individual product as % of total									
		C_6H_5-CHO	C_6H_5-CH_2OH	3-NO_2C_6-H_4CH_3	2-HOC_6-H_4CH_3	3-HOC_6-H_4CH_3	4-HOC_6-H_4CH_3	total HOC_6-H_4CH_3	2-CH_3C_6-H_3O_2	R_1[a]	R_2[b]
3.2	6.8	6.6	6.2	44.8	35.2	3.8	3.5	42.5	<0.5	12.8	9.4
6.5	7.8	7.4	5.0	42.0	34.6	6.3	4.5	45.4	<0.5	12.4	6.4
9.7	8.8	8.5	3.7	44.3	30.7	5.5	4.7	40.9	2.5	12.2	15.7
13.0	9.8	10.1	3.3	49.9	25.8	5.3	5.3	36.4	<0.5	13.4	2.5
14.6	10.3	11.0	2.6	47.6	27.0	5.8	5.9	38.7	<0.5	13.6	2.2
16.2	10.8	8.5	3.8	44.3	29.2	6.5	6.5	42.0	1.1	12.3	1.8
19.2	11.8	12.4	4.4	45.3	27.0	5.5	4.5	37.0	0.9	16.7	2.0

[a] $R_1 = (C_6H_5CHO + C_6H_5CH_2OH)/(\text{total products})$. [b] $R_2 = (\text{total products}/C_6H_5CH_3) \times 10^4$.

TABLE III: Products and Rate-Constant Ratios ($k_1/(k_1 + k_2)$) for Reactions of OH with Various Hydrocarbons in the Presence of NO_2 and O_2[a]

hydrocarbon	products	$k_1/(k_1 + k_2)$ this work	$k_1/(k_1 + k_2)$ ref 15
benzene	C_6H_5OH, $C_6H_5NO_2$	<0.05[b]	0.05 (0.01-0.13)[c]
toluene	C_6H_5CHO,[d] $C_6H_5CH_2OH$,[d] $CH_3C_6H_3O_2$,[e] 3-$NO_2C_6H_4CH_3$, 2-, 3-, and 4-$HOC_6H_4CH_3$	0.15 ± 0.02	0.16 (0.11-0.23)
1,4-dimethylbenzene	4-$CH_3C_6H_4CHO$,[d] 4-$CH_3C_6H_4CH_2OH$,[d] 2-HO-1,4-$(CH_3)_2C_6H_3$, 2-NO_2-1,4-$(CH_3)_2C_6H_3$	0.15 ± 0.02	0.07 (0.04-0.14)
1,3,5-trimethylbenzene	3,5-$(CH_3)_2C_6H_3CHO$,[d] 3,5-$(CH_3)_2C_6H_3CH_2OH$,[d] 2-HO-1,3,5-$(CH_3)_3C_6H_2$	0.021 ± 0.006	0.02 (0.01-0.04)

[a] Reaction conditions employed were similar in all cases to those reported in Tables I and II for toluene. [b] Represents fraction of total reaction proceeding by ring hydrogen atom abstraction. [c] Values in parentheses represent the reported range. [d] Products derived from benzylic hydrogen atom abstraction. [e] Minor product.

as a function of $[O_2]$ and total pressure.

Discussion

As Tables I and II show, the individual product yields vary with reaction conditions, but the ratio (C_6H_5CHO + $C_6H_5CH_2OH$)/(total products) is independent of NO_2, O_2, and total pressure. A mechanism that accounts for this and for the observed products of all of the OH–aromatic reactions is given (for the case of toluene) by reactions (1–12). Reactions 4–9 are analogous to the known reactions

$$C_6H_5CH_2\cdot + O_2 \rightarrow C_6H_5CH_2O_2\cdot \quad (4)$$

$$C_6H_5CH_2O_2\cdot + NO \rightarrow C_6H_5CH_2O\cdot + NO_2 \quad (5)$$

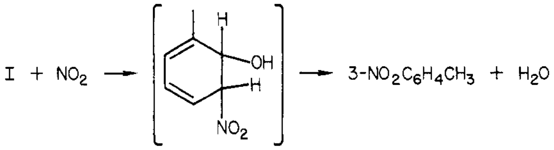
$$2C_6H_5CH_2O_2\cdot \rightarrow C_6H_5CHO + C_6H_5CH_2OH + O_2 \quad (6)$$

$$C_6H_5CH_2O\cdot + O_2 \rightarrow C_6H_5CHO + HO_2\cdot \quad (7)$$

$$C_6H_5CH_2O\cdot + NO \rightarrow C_6H_5CHO + HNO \quad (8)$$

$$C_6H_5CH_2O\cdot + NO_2 \rightarrow C_6H_5CHO + HNO_2 \quad (9)$$

$$I + O_2 \rightarrow HOC_6H_4CH_3 + HO_2\cdot \quad (10)$$



(11)

$$HO_2\cdot + NO \rightarrow HO\cdot + NO_2 \quad (12)$$

of methyl,[37] methylperoxy,[38,39] and methoxy[40,41] radicals. Reaction 10 closely resembles the reaction of cyclohexadienyl radicals with O_2.[42] Reaction 11[43] and similar addition–elimination reactions[44,45] have been observed in solution. Reaction 12 has been the subject of numerous recent investigations.[46–49]

According to the proposed mechanism, C_6H_5CHO and $C_6H_5CH_2OH$ result ultimately from benzylic hydrogen atom abstraction (reaction 1), whereas 3-nitrotoluene and cresols result from ring addition (reaction 2). Thus the ratio of abstraction products to total products should be a constant governed by the ratio $k_1/(k_1 + k_2)$. We have run the HO–toluene reaction a total of 20 times, and for all runs the average value of (C_6H_5CHO + $C_6H_5CH_2OH$)/(total products) was 0.15 ± 0.02. This is in excellent agreement with the value of $k_1/(k_1 + k_2) = 0.16 \pm ^{0.07}_{0.05}$ obtained by Perry et al.[15] from the temperature dependence of the apparent OH rate constant obtained by flash photolysis–resonance fluorescence technique. Values of $k_1/(k_1 + k_2)$ were calculated for the other hydrocarbons used in our study. As Table III shows, our values of $k_1/(k_1 + k_2)$ agree in all cases with those of Perry et al. within the limits of experimental uncertainty.

Over the pressure range of our experiments, we have found no evidence of a pressure effect. Therefore, we believe that the reversible decomposition of the hot OH–aromatic adducts is not occurring in our system. This is supported by earlier work of Davis et al.[12] For the case of toluene, these workers found that at 298 K and 5–15 torr of He bath gas, the value of $(k_1 + k_2)$ was ~0.8 of the

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TABLE IV: Reactivity and Positional Selectivity of Ring Addition to Toluene by Various Species

species	phase	k_{add}, cm^3 molecule^{-1} s^{-1}	100 × fraction of ring addition			ref	
			2 position	3 position	4 position	k_{add}	products
OH	gas	5.4×10^{-12}	80.6	5.1	14.3	15	this work
OH	soln ($PhCH_3$)		59	6	35		26
OH	soln (H_2O)	4.8×10^{-12}	55	15	29.5	19	24
O(^{3}P)	gas	2.3×10^{-13}	60	15	18	51	50

high-pressure value. Since our results were obtained with a mixture of Ar and O_2 as bath gas rather than He, our value of $k_1/(k_1 + k_2)$ is expected to be essentially at the high-pressure limit. Variations in $k_1/(k_1 + k_2)$ over the pressure range 6–15 torr should be well within the ±13% standard deviation observed for our experiments with toluene. Reaction k_2 for the dimethyl- and trimethylbenzenes should be even less susceptible to reversibility than it is for toluene, and k_2 occurs to the exclusion of other reactions for the case of benzene. We therefore conclude that the reverse of reaction 2 is unimportant at the temperature and pressures used in our experiments.

The relative rates of OH attack at each ring position for toluene, $k_2(\text{o})/k_2$, $k_2(\text{m})/k_2$, and $k_2(\text{p})/k_2$, i.e., the portions of reaction 2 that proceed by OH attack at each position, can be calculated. To derive these relative rate constants, we use the measured product ratios for 3-nitrotoluene and the isomeric cresols and the following relations:

$$k_2(\text{m})/k_2 = (\text{3-HOC}_6\text{H}_4\text{CH}_3)(\text{total cresols} + \text{3-NO}_2\text{C}_6\text{H}_4\text{CH}_3)^{-1} \quad (13)$$

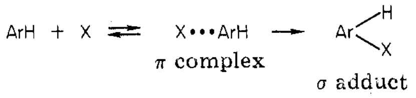
$$k_2(\text{o})/k_2 = \{[\text{2-HOC}_6\text{H4CH}_3/(\text{2-HOC}_6\text{H}_4\text{CH}_3 + \text{4-HOC}_6\text{H}_4\text{CH}_3)](\text{3-NO}_2\text{C}_6\text{H}_4\text{CH}_3) + \text{2-HOC}_6\text{H}_4\text{CH}_3\}(\text{total cresols} + \text{3-NO}_2\text{C}_6\text{H}_4\text{CH}_3)^{-1} \quad (14)$$

$$k_2(\text{p})/k_2 = \{[\text{4-HOC}_6\text{H}_4\text{CH}_3/(\text{2-HOC}_6\text{H}_4\text{CH}_3 + \text{4-HOC}_6\text{H}_4\text{CH}_3)](\text{3-NO}_2\text{C}_6\text{H}_4\text{CH}_3) + \text{4-HOC}_6\text{H}_4\text{CH}_3\}(\text{total cresols} + \text{3-NO}_2\text{C}_6\text{H}_4\text{CH}_3)^{-1} \quad (15)$$

To derive eq 13, we recall that 2- and 4-$NO_2C_6H_4CH_3$ are not found as products and that 3-$HOC_6H_4CH_3$ is the only observed product derived from OH attack at the 3 position. For eq 13 and 15, we note that 3-$NO_2C_6H_4CH_3$ results from attack by OH at either the 2 or 4 position and assumes that k_{11} is independent of the position of OH in the intermediate, I. In this case the total amount of product derived from OH attack ortho to the methyl group is equal to the observed amount of 2-$HOC_6H_4CH_3$ *plus* the fraction of the 3-$NO_2C_6H_4CH_3$ that was derived from I with OH in the 2 position, this fraction being equated to the product ratio

$$\text{2-HOC}_6\text{H}_4\text{CH}_3/(\text{2-HOC}_6\text{H}_4\text{CH}_3 + \text{4-HOC}_6\text{H}_4\text{CH}_3)$$

For toluene, the average values of $k_2(\text{o})/k_2$, $k_2(\text{m})/k_2$, and $k_2(\text{p})/k_2$ were 0.806 ± 0.022, 0.051 ± 0.009, and 0.143 ± 0.019, respectively. These values are compared in Table IV to values obtained for addition of OH to toluene in solution and for addition to toluene by other highly reactive species. From Table IV it is evident that, in reactions with toluene, gas-phase OH is both a highly reactive and highly selective species. The preference for attack at the ortho position over the para position by a factor of 5.6 is significantly greater than the statistical preference of a factor of 2. A similar parallel between reactivity and selectivity has been noted in some ionic electrophilic aromatic substitution reactions, although to a lesser extent, and Olah[52] has suggested that a π complex is involved in these reactions as a precursor to the formation of a σ adduct:



$$\text{ArH} + \text{X} \rightleftharpoons \underset{\pi\text{ complex}}{\text{X}\cdots\text{ArH}} \longrightarrow \underset{\sigma\text{ adduct}}{\text{Ar}{<}^{\text{H}}_{\text{X}}} \quad (16)$$

The intermediacy of π complexes in other reactions involving electron-deficient free radicals has been suggested,[53] and, indeed, the formation of an OH–aromatic π complex was considered by Perry et al. as a possible explanation for the reversibility of reaction 2 at elevated temperatures. Although it is not conclusive, our evidence concerning the unusually high selectivity of the addition of OH to toluene lends credence to the postulated participation of π complexes in OH–aromatic reactions. Regardless of the precise mechanism of the reaction, it is apparent that ortho attack by OH is highly preferred for the addition to toluene. This behavior confirms[22,54] the electrophilic nature of the hydroxyl radical. That ortho attack by OH occurs more readily in the gas phase than in solution is attributable to steric effects that are significant for solvated OH but not for the free radical in the gas phase.

Next, we wish to estimate the rate-constant ratio k_{11}/k_{10}, i.e., the relative reactivities of NO_2 and O_2 toward the adduct I. To do this, we combine and integrate the kinetic expressions for reactions 10 and 11, giving eq 17. With

$$k_{11}/k_{10} = \frac{(\text{3-NO}_2\text{C}_6\text{H}_4\text{CH}_3)}{(\text{total HOC}_6\text{H}_4\text{CH}_3)}\,\frac{[\text{O}_2]}{[\text{NO}_2]} \quad (17)$$

our experimental method, the values for (3-$NO_2C_6H_4CH_3$)/(total $HOC_6H_4CH_3$) and [O_2] are readily determined, but the value for [NO_2] is not. The difficulty with [NO_2] is that a fraction of the added NO_2 is consumed in titrating H· through reaction 3 and that there is no direct measure of [H·] in our system. To estimate the [NO_2] in our system, we have developed a detailed kinetic model for the OH–toluene reaction and have used [H·] as a variable to obtain a best fit of the model to the experimental data in a given run. Once an optimum value for the initial [H·] is chosen, the [NO_2] present in the experiment can be obtained by subtracting [H·] from the initial [NO_2]. Applying this method to the data of Table I, we calculate $k_{11}/k_{10} = (4 \pm 2) \times 10^3$, where the uncertainty is caused primarily by inaccuracies in estimating [NO_2]. Assigning a rate constant for reaction 11 similar to others for the reaction of carbon radicals with NO_2 of 3×10^9 M^{-1} s^{-1} (ref 36) sets $k_{10} \simeq 7.5 \times 10^5$ M^{-1} s^{-1}. This value is very similar to the value reported for the reaction $CH_3O\cdot + O_2$.[40] Table II shows that the ratio of 3-$NO_2C_6H_4CH_3$ to total cresols is essentially invariant for the range of oxygen pressures investigated. This observation is consistent with the relatively constant [NO_2]/[O_2] ratio predicted by our kinetic model for these reaction conditions.

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On the basis of the product distributions and relative rate constants discussed above, we can address the implications of the OH–aromatic reactions with respect to the environment. As was stated initially, the two major pathways for the reaction are hydrogen atom abstraction (reaction 1) and ring addition (reaction 2). The fate of the benzylic radical formed in reaction 1 will be governed by reactions 4, 5, and 7, and aromatic aldehyde will be the sole product. This judgment is based on the rate constants for the analogous reactions of methyl,[37] methylperoxy,[38,39] and methoxy[40,41] radicals and the typical value of $[O_2]/[NO_2] \approx 10^6$ under ambient conditions. The ambient $[O_2]/[NO_2]$ ratio also plays an important role in estabilishing the ultimate products from reaction 2 because the adduct I is partitioned between reaction 10, with O_2, to give phenolic products and reaction 11, with NO_2, to give nitroaromatics. Using eq 18 and our values of $k_1/(k_1 + k_2)$

$$3\text{-}NO_2C_6H_4CH_3/(\text{total products}) = \{1 - [k_1/(k_1 + k_2)]\}(k_{11}/k_{10})([NO_2]/[O_2]) \quad (18)$$

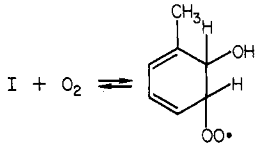
$= 0.15$ and $k_{11}/k_{10} = 4 \times 10^3$ for toluene, we have calculated the yield of $3\text{-}NO_2C_6H_4CH_3$ expected for various concentrations of NO_2 at ambient O_2 pressure. These calculations predict less than 1% $3\text{-}NO_2C_6H_4CH_3$/(total products) at typical ambient levels for NO_2 (i.e.; $\leq$1.0 ppm) but substantially greater amounts of 3-nitrotoluene (as much as 15% of total products) under conditions of artificially high (5–10 ppm) NO_2.

Thus, we would expect that, in the environment, reaction 2 will lead exclusively to reactions of I with oxygen. Extrapolation of our low-pressure results to atmospheric pressure indicates that substituted hydroxycyclohexadientyl radicals will react primarily to form phenolic materials. However, various investigators[55–61] report that, under simulated atmospheric conditions, the yields of phenolics are considerably lower than our results would predict.

The central question that obtains is whether undefined secondary reactions of phenolics can account for the low yields of these materials or whether a pressure-dependent change in mechanism for subsequent reactions of the initially formed hydroxycyclohexadienyl radicals is involved. The former possibility cannot be rigorously excluded since the reported investigations[5–61] at atmospheric pressure either have generally employed abnormally high reactant concentrations or have not established a reasonable product balance.

In the latter regard the observation of volatile carbonyl compounds as products of the photooxidation of aromatics has been interpreted in terms of the ring cleavage reactions of the OH–aromatic adduct I.[57,59,60,61] While the observation of these products cannot be discounted, proposed mechanisms for their formation directly from hydroxycyclohexadienyl radicals seem implausible in several respects.

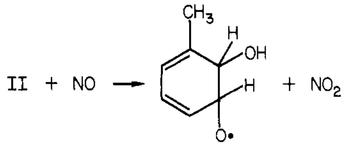
The most probable route for cleavage involves addition of oxygen to the hydroxycyclohexadienyl radical, as shown in reaction 19.[1,57,58] This type of peroxy radical (II) is



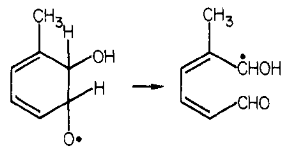
(19)

II

extremely unstable and is expected to dissociate readily back to I and O_2. We estimate the C–O bond strength of II at ~8 kcal/mol. Assigning an A factor for dissociation of 10^{16} s^{-1} gives a lifetime of 10^{-9} s at 300 K. The only reaction that appears likely to compete with reaction −19 is the reaction with NO, which could lead to ring cleavage:



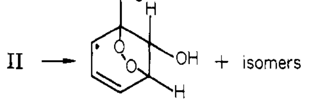
(20)



(21)

In the atmosphere NO concentrations generally do not exceed 1 ppm (3×10^{13} molecules cm^{-3}). In this case the lifetime for reaction 20 will be greater than $(3 \times 10^9 \times 4 \times 10^{-8})^{-1} = 0.01$ s. Because of the velocity of reaction −19, less than 1 in 10^7 of the II radicals formed can be expected to react by reaction 20. Since k_{19} can be set at $\sim 10^9$ M^{-1} s^{-1}, similar to values for other carbon radicals reacting with O_2[37] and ~1000 times larger than the value for reaction 10, the relative rates of reactions 10, 19, −19, and 20 are 1, 10^3, 10^2, and $<10^{-4}$, respectively. Thus cleavage by reaction 19 is difficult to rationalize.

Darnell et al.[57] have suggested that the adduct II cyclizes to give bicyclic peroxy intermediates, III, via reaction 22



(22)

III

and that subsequent reactions of III lead to cleavage. However, the activation energy for the cyclization reaction is predictably high. Addition of peroxy radicals to conjugated dienes typically proceeds with $E_a \approx 9$ kcal/mol.[62] Moreover, additional enthalpy of activation due to ring strain and entropy loss on ring closure must be considered. Using the A factor of 10^{10} s^{-1}, 9 kcal/mol activation energy, and 16 kcal/mol ring strain assumed by Atkinson et al.,[16] we estimate the rate constant for reaction 22 to be $k_2 \approx 10^2$ s^{-1}, corresponding to a lifetime of $\sim 10^{-2}$ s. Given the appreciably shorter lifetime of the adduct II with respect to dissociation back to I and O_2, it is difficult to rationalize the formation of substantial amounts of ring cleavage products via this route. Further work clearly is needed to determine the fate of the hydroxycyclohexadienyl radical under atmospheric conditions and its effect on overall atmospheric chemistry.

A final point concerns recent smog-chamber experiments[5,56] with toluene, in which 2-, 3-, and 4-nitrotoluene

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and isomeric nitrocresols are found as products in addition to the expected benzaldehyde and cresols. The appearance of 3-nitrotoluene is readily accounted for by the elevated ($\approx$1 ppm and greater) concentrations of NO_2 and high conversions used in the experiments. That the 2 and 4 isomers of nitrotoluene are observed is perplexing, because we have shown that OH attack meta to the methyl group (the reaction that would lead to the 2- and 4-nitrotoluenes) is of minor importance. Because ionic nitrations typically give predominately 2- and 4-substitution, and because we find[27] NO_x to be a powerful nitrating agent in condensing our reaction mixtures, we suggest that the observance of 2- and 4-nitrotoluenes in smog-chamber studies is indicative of heterogeneous reactions that occur in the aerosol phase or during sampling of the products. Phenolic compounds are especially susceptible to heterogeneous nitration, and the origin of nitrophenols in smog-chamber experiments must be interpreted with extreme caution.

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Surface-Enhanced Raman Spectroscopy of Metal–Halide Vibrations on Ag and Cu Electrodes

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Halide ions play an important role in the surface-enhanced Raman (SER) process in electrochemical environments. They are usually specifically adsorbed at Ag and Cu electrodes in the same potential range used in the SER experiments. This intimate contact with the metal surface is not sufficient to obtain an enhancement even when a rough metal is immersed in the electrolyte. After an oxidation–reduction cycle (ORC) is performed, however, an enormous enhancement appears when highly concentrated electrolytes are used. The Raman intensities observed for M–X vibrations are comparable to those found for the ring modes of pyridine. The irreversible potential dependence of the enhancement (vanishing with sufficiently negative potential) indicates that particular silver (copper) halide structures are responsible for these effects. It is argued that these structures are different from simple specifically adsorbed halide ions.

Introduction

In a recent paper Fleischmann, Hendra, Hill and Pemble[1] reported the first observations of a surface-enhanced Raman (SER) spectrum for water at a roughened Ag electrode. In a second paper Fleischmann, Robinson, and Waser[2] reported an electrochemical study of the adsorption of pyridine and chloride ions on Ag electrodes. Stimulated by these results, we have measured the SER spectra of water, D_2O, and halide ions on Ag and Cu electrodes under a variety of conditions, in particular at much higher halide concentrations[3,4] than those used by Fleischmann and co-workers. The great utility of SER spectroscopy (SERS) for in situ investigation of the interfacial region of an electrode is amply justified by these and previous investigations.[5-18] Initially SER scattering was found only with some organic molecules (such as pyridine and other amines,[7] and carboxylic species[19]) adsorbed on Ag electrodes. However, in the last few years it has been reported for many neutral molecules and ions adsorbed on Ag electrodes.[1-19] There has also been an increase in the variety of substrates from which strongly enhanced Raman emission have been observed. In addition to Ag, SER effects have been observed from Cu and Au electrodes.[19-22] Raman spectra have also been reported for adsorbates on Pt electrodes.[23] Not all observations refer to polycrystalline electrodes. Enhanced Raman spectra have been reported from singel-crystal Ag electrodes with (111) and (100) surfaces after very weak electrochemical activation.[24] There are also observations made in UHV of the Raman

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