

GAS PHASE REACTIONS OF HYDROXYL RADICALS WITH ARENES

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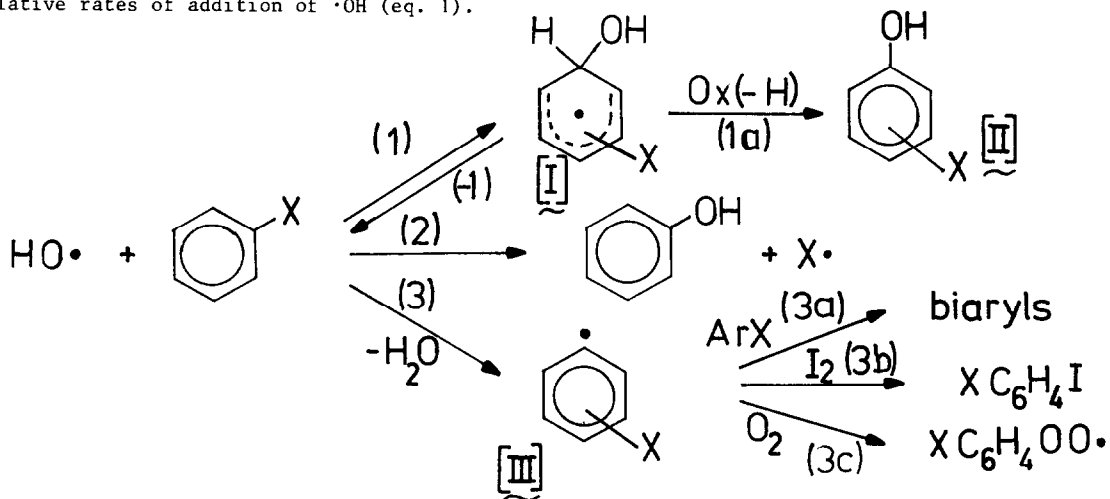
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Summary: At elevated temperatures ·OH is found to abstract H from benzene derivatives; in air, phenols are then generated via reversible addition of ArOO· to arene.

Following our studies on gas-phase homolytic chlorination¹, cyanation² and nitration³ of benzene derivatives, we are currently investigating (aut)oxidation of arenes. In autoxidation, reactions with hydroxyl radicals constitute important first steps in solution and in troposphere chemistry as well as in combustion⁴.

The interaction of ·OH with arenes has been extensively studied in solution at ambient temperature⁵. The major pathway is addition (eq. 1); depending on substitution, ipso-attack (2) may also obtain. Ring hydrogen abstraction (3) is not observed under these conditions. In appropriate cases (e.g. X=Me, or OMe) side-chain abstraction (4) competes with (1,2). With efficient oxidation intermediates (I) yield phenols (II)⁶-eq. 1a -; product compositions (isomer distributions and/or $v_{\phi X}/v_{\phi H}$) reflect relative rates of addition of the electrophilic ·OH radical.

As solvent effects on these relative rates are assumedly small⁷ relative rates of (1), (2) and (3) in the gas-phase at ambient temperature will be comparable with those in solution. In air the fate of I is rather complex, involving addition of O₂⁸; now product ratios for II may well differ from relative rates of addition of ·OH (eq. 1).



Recent kinetic studies have shown that, in nitrogen above 200°C, radicals \dot{I} can revert to arene and $\cdot\text{OH}$ (eq. -1), e.g. toluene then giving side-chain abstraction (4) only. The reversibility of $\cdot\text{OH}$ addition (1, -1) is also indicated in liquid-phase systems above 80°¹⁰. These publications prompt us to communicate some of our results on the reaction of $\cdot\text{OH}$ with benzene derivatives in nitrogen and in air at > 290°C.

Runs were performed in a flow system (atmospheric pressure, residence times 1-2 min.); at 290°C $\cdot\text{OH}$ was generated via thermolysis of tBuOOH¹².

In nitrogen, benzene yields biphenyl only (Table 1). Clearly \dot{I} cannot be oxidised under these conditions, resulting in (3) being the prominent first step, followed by (3a). With chlorobenzene comparable results are obtained, $\text{ClC}_6\text{H}_4\cdot$ producing $\text{ClC}_6\text{H}_4\text{-C}_6\text{H}_4\text{Cl}$ and some $\text{ClC}_6\text{H}_4\text{-C}_6\text{H}_5$ ¹⁵; ipso-substitution leads to phenol. Benzonitrile also gives biaryls but no phenol. Toluene gives side-chain abstraction (4), benzyl radicals dimerize or combine with $\cdot\text{CH}_3$ ¹⁶ stemming from tBuO radicals¹².

Note that the yield of combination products is quantitative: 100% H-abstraction by $\cdot\text{OH}$ (eq. 4), 44% of the $\cdot\text{CH}_3$ radicals reacting similarly. Likewise, anisole initially gives $\text{C}_6\text{H}_5\text{-OCH}_2\cdot$, which is known to isomerize to $\text{C}_6\text{H}_5\text{-CH}_2\text{O}\cdot$ ¹⁷; the latter species forms benzaldehyde.

In the presence of iodine (ca. 1% on arene) part of the aryl radicals is scavenged to give ArI (3b), cf isomer patterns in Table 2. As our earlier work on competitive arylation/chlorination¹ has shown e.g. o-, m- and p- $\text{ClC}_6\text{H}_4\cdot$ react equally fast with Cl_2 or CCl_4 it is fairly safe to assume that the isomer distributions for $\text{XC}_6\text{H}_4\text{I}$ reflect those for H-abstraction by $\cdot\text{OH}$ (eq. 1). These patterns are quite unlike those for hydroxylation via addition of $\cdot\text{OH}$ and subsequent oxidation of intermediates \dot{I} (1, 1a)⁶; our data (Table 2) show more resemblance to the isomer distribution for H-abstraction by $\text{Cl}\cdot$ atoms¹. These aspects will be discussed in more detail elsewhere¹⁸; suffice it to point out that H-abstraction by $\cdot\text{OH}$ is exothermal by ca. 10 kcal/mol and hence, will have a rather "early" transition state, whereas $\text{C}_6\text{H}_6 + \text{Cl}\cdot \rightarrow \text{C}_6\text{H}_5\cdot + \text{HCl}$ is endothermal by 6 kcal with a product-like transition state¹.

TABLE 1

X	nitrogen	Σ (%) ¹⁾	in air	Σ (%) ¹⁾
H	$\phi\phi$ (100)	25	ϕOH (100)	41
Cl	$\text{Cl}\phi\phi\text{Cl}$ (65); $\text{Cl}\phi\phi$ (12); ϕOH (23)	15	ϕOH (21); $\text{Cl}\phi\text{OH}$ (79)	58
CN	$\text{NC}\phi\phi\text{CN}$ (83); $\phi\phi\text{CN}$ (17)	6	$\text{NC}\phi\text{OH}$ (100)	16
CH_3	$\phi\text{CH}_2\text{CH}_3$ (56); $\phi\text{CH}_2\text{CH}_2\phi$ (44)	100	ϕCHO (65); $\phi\text{CH}_2\text{CH}_2\phi$ (6); $\phi\text{CH}_2\text{OH}$ (6); ϕOH (16); $\text{HO}\phi\text{CH}_3$ (7)	202
OCH_3	ϕCHO (68); ϕOH (32)	100	ϕCHO (10); ϕOH (86); $\text{HO}\phi\text{OCH}_3$ (4)	124

1) in mol% on tBuOOH

TABLE 2

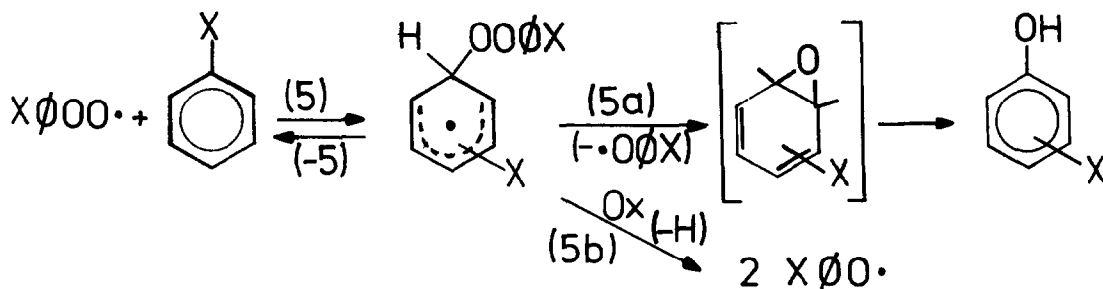
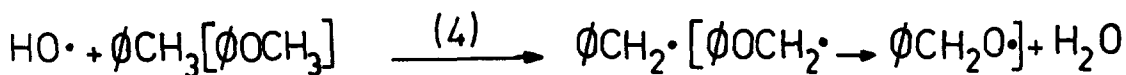
Isomer distributions for $\text{XC}_6\text{H}_4\text{I}$

X	o(%)	m(%)	p(%)
Cl	24	53	23
CN	41	39	20
CH_3	48	(52)	
OCH_3	25	(75)	

TABLE 3

Isomer distributions for $\text{X}\phi\text{OH}$

X	o(%)	m(%)	p(%)
Cl	19	64	17
CN	6	65	29
CH_3	18	63	19
OCH_3	9	77	14



Reactions in air (Table 1) involve oxygen as an effective scavenger for aryl radicals¹⁹. Now benzene gives phenol as the only detectable product; chlorobenzene and benzonitrile produce $\text{XC}_6\text{H}_4\text{OH}$ analogously. Toluene gives products derived from $\text{C}_6\text{H}_4\text{CH}_2$. Remarkably, cresols are also formed, as is some $\text{CH}_3\text{OC}_6\text{H}_4\text{OH}$ from anisole. Isomer distributions are exemplified in Table 3. These patterns differ markedly not only from those in Table 2 but also from distributions associated with low temperature additions of $\cdot\text{OH}$ ^{5,6}. By reversibility (1, -1) thermodynamic factors as to isomeric composition of I come into play. Furthermore, relative rates of oxidation (1a) by O_2 may be different for the various isomers of I. Differences in free energy of formation of isomers of II will also play a part, favouring larger proportions of meta-isomers²⁰.

Altogether, the presence of large amounts of O_2 has made pathway (1, -1; 1a) productive at the expense of (3). Thermochemically the sequence²¹ (3; 3c; 5) is not a priori excluded²². If this mechanism is of importance at 290°C , it would be responsible for rather selective meta substitution on $\text{C}_6\text{H}_5\text{X}$.

We have therefore varied the reaction temperature, employing several other $\cdot\text{OH}$ sources (including $\text{HO}\cdot\text{NO}_2$, $\text{HO}\cdot\text{OH}$, alkene or alkane + O_2). A gradual, but marked change in isomer distributions

of $\text{XC}_6\text{H}_4\text{OH}$ is noticed. For example, at 450°C , chlorobenzene/air/cyclohexene (5% on arene) leads to $\text{ClC}_6\text{H}_4\text{OH}$, o:m:p= 40:43:17. At this temperature, pathway (1,-1;1a) can be discarded on thermochemical-kinetic grounds, leaving (3;3c;5) as the only realistic alternative. Within this scheme unimolecular step(s)(5a) will gain in importance with increasing temperature. It is of interest to note that, in solution at ambient temperature, arene epoxides from several monosubstituted benzenes preferentially isomerise to *o*- and *p*- substituted phenols²³. In conclusion: Autoxidation of arenes at ambient temperature involves homolytic hydroxylation; at elevated temperatures, reaction will start with H-abstraction by $\cdot\text{OH}$, introduction of OH groups being the final result of addition of $\text{ArOO}\cdot$ radicals to arene.

Notes and References.

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20. For substituted phenols accurate data on heats of formation (or equilibrium composition) are lacking. Note however that for alkylfluorobenzenes, m/2p ratios are ca. 2 (G.A. Olah, *J. Org. Chem.* **31**, 1262, 1268, 1271 (1966)).
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22. Based on RE(cyclohexadienyl) = 25 kcal/mol (D.G.L. James and R.D. Stuart, *Chem. Commun.*, 484, (1966)); $\Delta\text{H}_{(5-5)} \approx -4$; $\Delta\text{H}_{(5a)} \approx -8$; $\text{E}_a(5) \approx 10$, $\text{E}_a(5a) \ll -15$ kcal/mol. Note that $\text{HO}_2\cdot$ (or $\text{RO}_2\cdot$) is unable to react according to eq. 5 (cf R.A. Graham, A.M. Winer, R. Atkinson and J.N. Pitts, Jr., *J. Phys. Chem.* **83**, 1563, (1979) as an important driving force (resonance stabilization of $\text{ArO}\cdot$ (A.J. Colussi, F. Zabel and S.W. Benson, *Internat. J. Chem. Kin.* **9**, 161 (1977)) is absent. Step (5a) with $\text{HO}_2\cdot$ would be endothermic by some 15 kcal/mol. $\text{E}_a(5a)$ exceeding this value, peroxy radicals will preferentially disproportionate, e.g. $2\text{ArOO}\cdot \xrightarrow{(5a)} 2\text{ArO}\cdot + \text{O}_2$, or $\text{ArOO}\cdot + \text{HO}_2\cdot \rightarrow \text{ArOOH} + \text{O}_2$. For full thermochemical account, see ref. 18.
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