Vapour-phase Chemistry of Arenes. Part 10.† Formation of Phenols in Air Oxidation of Benzene, Chlorobenzene, *m*-Dichlorobenzene, and Benzonitrile in the Presence of Cyclohexa-1,3-diene at *ca.* 600 K

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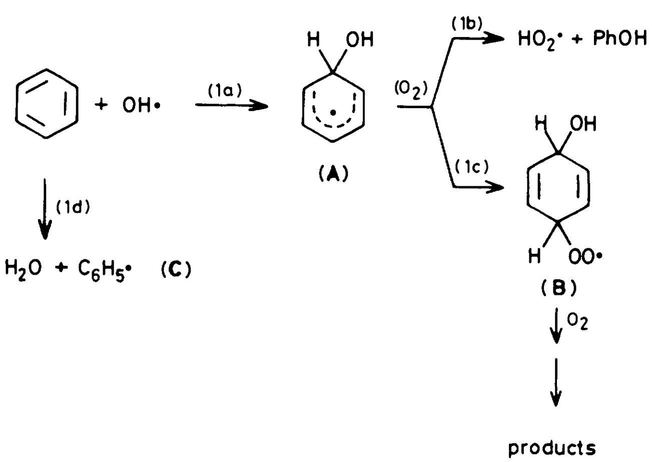
In a flow reactor at 573—623 K, flow time *ca.* 2 min, vapours of benzene and derivatives, *e.g.* chlorobenzene and benzonitrile, are not measurably oxidized by air. In the presence of small amounts of cyclohexa-1,3-diene (**1**), however, substantial conversion of (**1**) is accompanied by formation of phenols from arenes. The main oxidation product of (**1**) is benzene, but some phenol, and cyclohex-3-enone (**2**) is also formed. Conversion of (**1**) is largely due to hydrogen abstraction by O_2, $\log(A_2/\text{l mol}^{-1}\text{ s}^{-1}) = 8.9$, E_2 *ca.* 104 kJ mol^{-1}. The resulting cyclohexadienyl radical gives benzene by disproportionation with O_2. Formation of phenol is explained by addition of O_2 to cyclohexadienyl radical, followed by rearrangement and reaction with O_2. Addition of $HO_2^{\cdot}$ to (**1**) is shown to be the likely first step in forming non-aromatic oxygenated products such as (**2**). This slow combustion of (**1**) leads to $^{\cdot}$OH radicals which must be responsible for conversion of arene. Product data, especially isomeric composition of substituted phenols, as well as thermochemical–kinetic analysis indicate that, at *ca.* 600 K, a mechanistic transition occurs, from addition of $^{\cdot}$OH (prevailing at lower temperatures) to hydrogen abstraction to give aryl radicals, which lead to phenol *via* $ArO_2^{\cdot}$ and $ArO^{\cdot}$.

Although stable up to *ca.* 750 K in an inert atmosphere,[1] the vapour of the pollutant benzene is slowly oxidized in air at ambient temperature, its tropospheric half-life being around two weeks.[2] The predominant first step in the atmospheric chemistry is addition of $^{\cdot}$OH to give the adduct radical (A) [reaction (1a), Scheme 1]. Oxygen attack may now take two paths, hydrogen abstraction to give phenol directly [step (1b)] or addition to give species such as (**B**) [reaction (1c)] which ultimately lead to ring-opened products.[3] Studies on the rate of decay of $^{\cdot}$OH in benzene vapour as a function of temperature indicate that, above *ca.* 400 K, reaction (1a) is reversible. Thus, at higher temperatures, an alternative initial reaction, namely hydrogen abstraction by $^{\cdot}$OH [reaction (1d)], becomes increasingly important.[4]

As part of our investigations on gas-phase homolytic aromatic substitution[5] we now focus attention on rates, products, and mechanisms of the autoxidation of benzene and derivatives, with special emphasis on the reactivity of thermally generated $^{\cdot}$OH and $HO_2^{\cdot}$ radicals, at temperatures ranging from ambient to those for combustion.

Recently we have reported on the use of t-butyl hydroperoxide as a source of $^{\cdot}$OH between 480 and 565 K, both in the presence and absence of oxygen.[6] Hydrogen abstraction [reaction (1d)] was the only observable reaction between benzene and $^{\cdot}$OH under nitrogen.

Benzene in air is not measurably oxidized at 750 K, even after 2 min, the usual residence time in our tank-flow-type experiments. Addition of aliphatic hydrocarbons, however, initiated formation of phenol from benzene well below 750 K; a small percentage of cyclohexene, for example, causes product formation between 650 and 750 K,[7] and cyclohexa-1,3-diene (1) is effective even below 600 K. Whereas liquid-phase autoxidation of cyclohexa-1,4-diene is well documented,[8] neither this diene nor (1) appear to have been studied in the vapour phase. In the present paper we therefore report on rates, products, and mechanisms involved in the co-autoxidation of (1) with an excess of benzene or benzene derivatives (chlorobenzene, dichlorobenzene, or benzonitrile) in air, between 571 and 623 K.



Scheme 1.

Results

Runs were conducted in a Pyrex tank-flow-type reactor of *ca.* 380 cm^3 volume, as described earlier.[1a] The arene : air ratios in flow rates were *ca.* 0.3 (mol/mol) and the molar proportions of (1) to arene varied between 0.004 and 0.09. Representative examples are collected in Table 1. Not surprisingly, benzene is a major oxidation product of (1), but phenol and another oxidation product, presumably cyclohex-3-enone (**2**) (*vide infra*), are also formed, both in neat oxidations of (1) (runs 18, 19) and in the presence of arene. The arene itself (ArH) invariably yielded significant amounts of the corresponding substituted phenols, ArOH. *m*-Dichlorobenzene also gives the *ipso*-substitution product *m*-ClC_6H_4OH (run 17), whereas PhCN does not undergo this reaction. Presumably this is because the Ph–CN bond is *ca.* 70 kJ mol^{-1} stronger than that of OH, while the Ph–Cl bond is 65 kJ mol^{-1} weaker.[9] With PhCl, *ipso*-substitution provides a route to phenol other than that *via* (1). In the absence of other sources of phenol, we have often noted that the autoxidation of PhCl between 600 and 900 K shows a fairly constant product ratio PhOH : ClC_6H_4OH of *ca.*

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† Part 7, ref. 5*b*; Part 8, ref. 5*a*; Part 9, ref. 6*a*.

Table 1. Vapour-phase autoxidation of benzene and derivatives with added cyclohexa-1,3-diene (1)

Run (arene[a])	T/K	τ/s	Air[b]	(1)[b]	Products: Benzene[c,d]	PhOH[b]	ArOH[b,e]	C_6H_8O[b,f]
1 (PhCl)	571	136	156	5.0	28.9 (0.34)	0.038	0.043 (38:49:13)	0.12
2 (PhCl)	596	120	175	5.0	53.4 (0.36)	0.099	0.102 (27:56:17)	0.20
3 (PhCl)	622	117	172	5.0	92.7 (0.37)	0.256	0.250 (19:61:20)	0.25
4 (PhCl)	575	124	175	2.36	18.9 (0.49)	0.028	0.039 (33:49:18)	*g*
5 (PhCl)	598	119	175	2.36	51.9 (0.36)	0.075	0.097 (25:56:19)	*g*
6 (PhCl)	622	115	175	2.36	69.3 (0.49)	0.187	0.163 (20:61:19)	*g*
7 (PhCl)	571	139	152	0.63	8.3 (1.22)	0.006	0.0011 (21:62:18)	*g*
8 (PhCl)	598	132	152	0.63	29.7 (0.68)	0.0251	0.0325 (20:66:14)	*g*
9 (PhCl)	622	127	152	0.63	58.7 (0.60)	0.059	0.089 (18:67:15)	*g*
10 (PhCl)	622	124	157	0.22	46.7 (0.74)	0.0214	0.0312 (17:67:16)	*g*
11 (PhCN)	573	125	175	1.40	14.2 (0.67)	0.059	0.043 (15:57:28)	0.11
12 (PhCN)	598	119	175	1.40	37.8 (0.50)	0.073	0.083 (11:61:28)	0.059
13 (PhCN)	622	115	175	1.40	*g*	0.086	0.147 (5:64:31)	0.032
14 (PhH)	579	132	175	2.06	*g*	0.033		0.069
15 (PhH)	603	127	175	2.06	*g*	0.163		0.155
16 (PhH)	630	121	175	2.06	*g*	0.219		0.17
17 (*m*-$C_6H_4Cl_2$)	598	125	171	2.46	45.2 (0.45)	0.079	0.069[h]	0.14
18 (none)	581	167	172	2.70	26	0.046		0.14
19 (none)	625	154	172	2.70	*g*	0.39		0.21

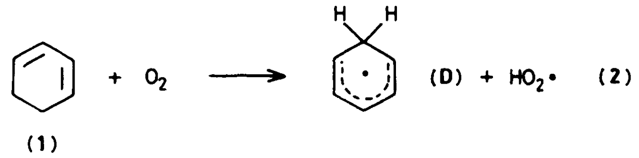
[a] Inflow (mmol h^{-1}): 1—10 [PhCl + (1)], 58.9; 11—13 [PhCN + (1)], 58.8; 14—16 [benzene + (1)], 66.9; 17 [*m*-$C_6H_4Cl_2$ + (1)], 53.0. [b] Inflow [air or (1)] or outflow (PhOH, ArOH, C_6H_8O) in mmol h^{-1}. [c] mol % on inflow of (1), based on the ratio of benzene and (1) recovered in the product condensed at −14 °C. In several control experiments, trapping in liquid N_2 proved that the material balance for (1) + benzene + PhOH + C_6H_8O was >95%. [d] In parentheses, fraction of benzene (α) formed due to reaction (2); see Discussion, section (i). [e] In parentheses, isomer distribution, *o*-, *m*-, *p*-XC_6H_4OH (X = Cl or CN). [f] Presumably cyclohex-3-enone (2); in addition, small proportions of epoxide (3) are also formed [see equation (8)]. [g] Not determined. [h] Three isomers of $Cl_2C_6H_3OH$; in addition to *m*-ClC_6H_3OH, 0.018 mmol h^{-1}.

1:4.[6,7b] If this ratio also holds for the present series (runs 1—10), the major part of the phenol originates from (1). For example in run 5, 0.075 − (0.097:4) ≃ 0.05 mmol h^{-1}, which in this case is *ca.* 4% of the benzene formed from (1). Analogous phenol:benzene ratios are calculated to range from 0.03 (run 1) to 0.14 (run 10). For comparison, this ratio is 0.16 with PhCN (run 12) and 0.07 with *m*-$C_6H_4Cl_2$ (run 17).

The degree of conversion of (1) increases with temperature, but, at a given temperature, it also increases with an increasing (1):arene intake ratio [= concentration of (1)]. Compare, for example, runs 7, 4, and 1; the benzene yield is 8.3, 18.9, and 28.9%, respectively. Tests for hydrogen peroxide (acidic solution of KI) were positive; quantitative determinations on H_2O_2 and/or organic (hydro)peroxides have not been performed.

Discussion

(i) *Formation of Benzene from Cyclohexa*-1,3-*diene* (1).—In accord with the mechanism advanced for the liquid-phase oxidation of cyclohexa-1,4-diene,[8] the initiating step will be hydrogen abstraction by O_2 [equation (2)], followed by rapid dehydrogenation of $C_6H_7^{\bullet}$ (D) [equation (3)]. Hydroperoxyl radicals will give hydrogen peroxide and O_2 [equation (4)], eventually *via* the dimer HO_4H.[10] Assuming steady-state conditions for concentrations of intermediate radicals, equation (i) holds for the concentration of $HO_2^{\bullet}$. This expression remains valid if reaction (5) contributes to the conversion of (1), as this slow step is followed by (3) which regenerates $HO_2^{\bullet}$. Given the set of reactions (2)—(5), linear extrapolation of the rate of formation of benzene to zero inflow rate (concentration) of (1) should yield v_2 and hence allow an estimation of k_2. Figure 1 shows a plot based on expression (ii). Regression analysis, excluding the value for run 7, results in the following values for k_2/l mol^{-1} s^{-1}: 0.23 at 573 K, 0.72 at 598 K, and 1.32 at 623 K; these are plotted in Figure 2. The best Arrhenius line has log (A_2/l mol^{-1} s^{-1}) 8.91, E_2 104 kJ mol^{-1}. This activation energy is surprisingly close to that calculated from the endothermicity of reaction (2), 96 kJ mol^{-1},[11] *viz.* $E_2 = \Delta H_2^{\ddagger} + 2RT = 96 + 10$ kJ mol^{-1} (600 K). The value for A_2 is as expected for this type of hydrogen-atom transfer.[8a]



(1)

$$(D) + O_2 \longrightarrow C_6H_6 + HO_2^{\bullet} \qquad (3)$$

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad (4)$$

$$(1) + HO_2^{\bullet} \longrightarrow (D) + H_2O_2 \qquad (5)$$

$$[HO_2^{\bullet}] = \{2\,k_2/k_4\cdot[(1)][O_2]\}^{\frac{1}{2}} \qquad (i)$$

$$k_2 = [C_6H_6]/[(1)]_o\cdot[O_2]\cdot\tau \qquad (ii)$$

$$(v_5/v_2)^2 = 2\,k_5^2/k_2\cdot k_4\,\{[(1)]_o/[O_2]\} \qquad (iii)$$

If the additional conversion of (1), at 'realistic' concentrations of (1), is due to reaction (5), the rate ratio v_5/v_2 is governed by expression (iii). Values of v_5/v_2 have been derived as follows. First, using k_2 values calculated from the Arrhenius plot of Figure 2, 0.26 (573 K), 0.62 (598 K), and 1.50 l mol^{-1} s^{-1} (623 K), the fractions of the benzene formed from (1) due to reaction (2) have been determined (α values; see also footnote *d* in Table 1).*

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* Taking run 5 (Table 1) as an example: (C_2), the % conversion of (1) due to reaction (2), is calculated from the tank-flow expression $k_2[O_2]\cdot\tau = (C_2)/[100 - (C_2)]$ with k_2 0.62 l mol^{-1} s^{-1}, $[O_2]$ 3.25×10^{-3}M, and τ 119 s, (C_2) 19.3%. As the total conversion of (1), due to reactions (2) and (5), = 51.9% (see Table 1) α = 19.3/51.9 = 0.37.

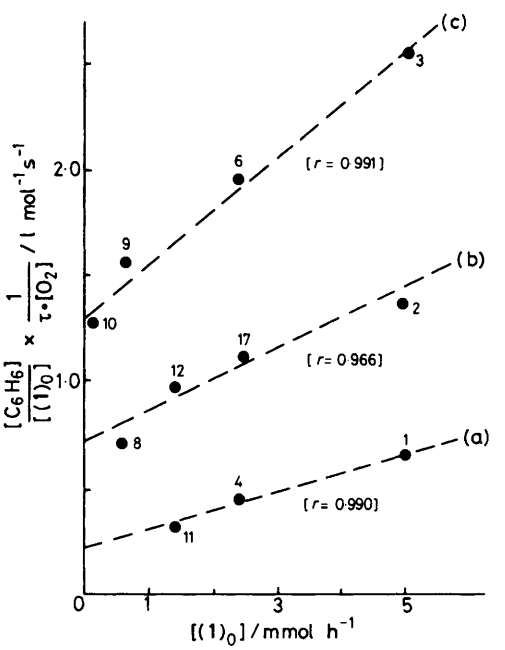


Figure 1. Determination of k_2, using equation (ii) (see text): (a) 573 K, k_2 0.23; (b) 598 K, k_2 0.73; (c) 623 K, k_2 1.32 l mol^{-1} s^{-1}

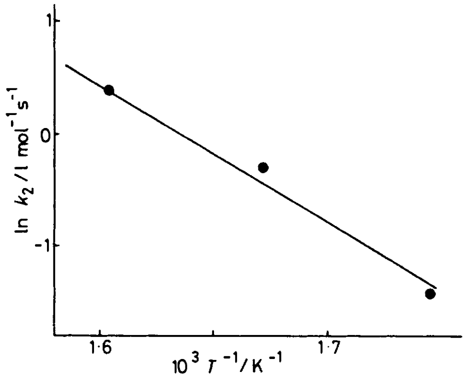


Figure 2. Arrhenius plot for k_2 [E_2 104 kJ mol^{-1}, log (A_2/l mol^{-1} s^{-1}) 8.91; r 0.987]

Then, v_5/v_2 is represented by $(1 - \alpha)/\alpha$. Figure 3 shows a plot of $(v_5/v_2)^2 = (1 - \alpha)^2/\alpha^2$ *versus* $[(\mathbf{1})]_0/[O_2]$ as demanded by equation (iii). Despite its scatter, the slope is seen to be *ca.* 24 with no apparent temperature dependence. Hence, $k_5/k_4^{\frac{1}{2}} \simeq 3k_2^{\frac{1}{2}}$ at (600 ± 25) K.

Using the Arrhenius parameters of Figure 2, $k_5/k_4^{\frac{1}{2}} \simeq 3.5$ at 600 K. The value of E_5 is not known, but should be slightly smaller than that for hydrogen abstraction by Bu^{t}OO$^\bullet$ from comparably activated hydrocarbons,[8b] 45—50 kJ mol^{-1}. Such a value is very close to $\frac{1}{2}E_2$, which explains the absence of a notable temperature effect on v_5/v_2 (Figure 3). Taking $E_5 = 40$ and $\log k_4$/ l mol^{-1} s^{-1} = 9.5,[12] $\log A_5$ is found to be 9.0. Such a value is on the 'high side' for hydrogen abstraction by peroxyl radicals,[8a] which leaves room for another contribution to the conversion of (**1**) into benzene, namely by reaction with $^\bullet$OH, to be discussed later. Note that with the parameters as indicated above, $k_5/k_4^{\frac{1}{2}} \simeq 3.5$ at 600 K extrapolates to *ca.* 0.03 at 310 K, a value in satisfactory agreement with results on liquid-phase autoxidation of cyclohexa-1,4-diene, *ca.* 0.05.[8b]

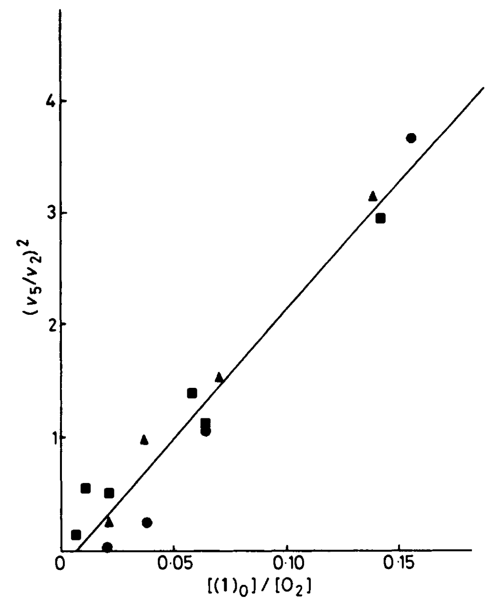
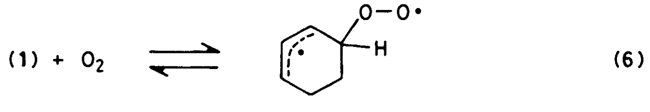
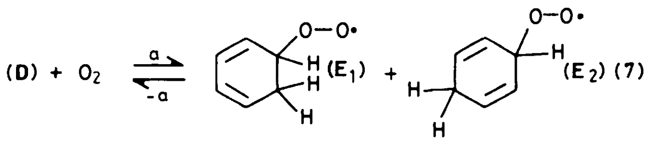


Figure 3. Plot of $(v_5/v_2)^2$, see equation (iii): ● 573 K; ▲ 598 K; ■ 622 K


(6)


(7)

(ii) *Phenol from* (**1**).—Pathways involving reversible addition of O_2 to (**1**) are out of the question as reaction (6) is endothermal by no less than 90 kJ mol^{-1}.[13] Addition of O_2 to cyclohexadienyl radical (**D**) [reaction (7)] which is exothermal by 20—25 kJ mol^{-1} [8b] is a likely possibility, however. In general, addition of O_2 to carbon-centred radicals has a negligible activation energy,[14] but addition to the resonance-stabilized radical (**D**) could involve a barrier of several kJ mol^{-1}. In any case, equilibrium (7a, −a) will be established. Accepting $\Delta S^\circ_7 \simeq -80$ kJ mol K^{-1} for the 1M state, the ratio ($\mathbf{E}_{1,2}$):(**D**) is calculated to be *ca.* 10^{-5} at 600 K.

An adequate description of the conversion of ($\mathbf{E}_{1,2}$) into phenol must be compatible with the actual reaction rates. Taking run 5 (Table 1) as an example, 0.05 mmol h^{-1} of PhOH made from (**1**) is equivalent to a rate constant of $10^{-7.5}$ l mol^{-1} s^{-1}. Such a rate is much too high to be due to some bimolecular reaction of (**E**), *e.g.*, with oxygen. As (**D**), typically, is *ca.* 10^{-11}M,* (**E**) ≃ 10^{-16}M. With $[O_2] \simeq 10^{-2.5}$M the corresponding bimolecular rate constant k, for $v = k[(\mathbf{E})][O_2]$, should be *ca.* 10^{11} l mol^{-1} s^{-1}, a value which is some five orders of magnitude larger than those usually encountered in disproportionation with O_2.[15,16] Therefore, only unimolecular conversion of ($\mathbf{E}_{1,2}$) can be taken into account. This is likely to involve intramolecular hydrogen transfer, as exemplified for radical ($\mathbf{E}_1$) in

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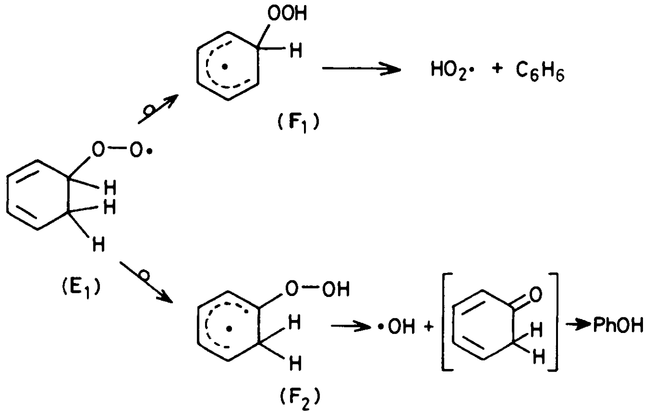
* As $k_2[(\mathbf{1})][O_2] \simeq k_3[(\mathbf{D})][O_2]$, $[(\mathbf{D})] \simeq k_2/k_3\cdot[(\mathbf{1})]$. In run 5, $[(\mathbf{1})] \simeq 1.0 \times 10^{-4}$M; $\log k_2 \simeq 0.5$ at 600 K (see Figure 2). $\log k_3$, being *ca.* 6.5 at 300 K,[15–17] is likely to be close to 8 at 600 K (see also Table 2, note *d*).



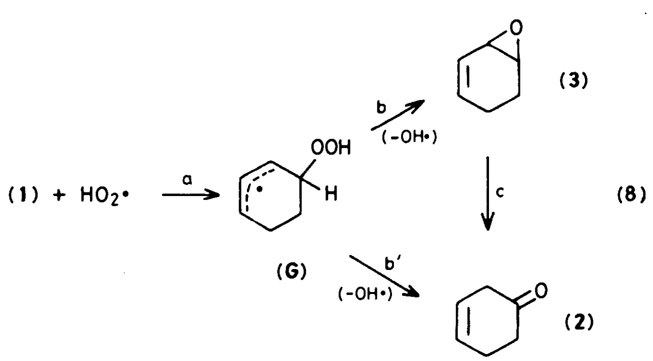
Scheme 2.

Scheme 2. Formation of species (F) from (E_1) is estimated[13] to be exothermal by *ca.* 75 kJ mol^{-1}; an activation energy of *ca.* 35 kJ mol^{-1} will allow formation of (F_2) and therefrom, of phenol, with the observed rate.

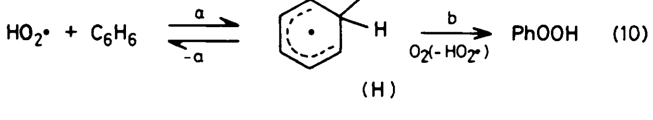
(iii) (**1**) + $HO_2^\bullet$; *Addition* versus *Abstraction*.—Aside from phenol, (**1**) yields comparable amounts of another by-product which, based on its g.l.c. retention time, appears to be cyclohex-3-enone (**2**) (Table 1). The isomeric cyclohex-2-enone is not formed, but small proportions [*ca.* 10% relative to (**2**), in runs 15 and 16] of cyclohexa-1-3-diene epoxide (**3**) are also observed. Formation of (**2**) and (**3**) can be rationalized on the basis of addition of $HO_2^\bullet$ to (**1**) [to give radical (G)] [equation (8a)].

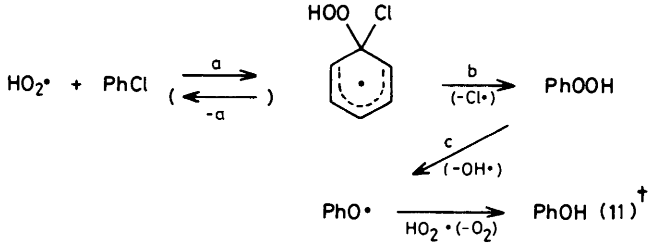
A point of interest is the relative importance of reactions (8a) (addition) and (5) (abstraction). With alkenes, in general, abstraction of allylic hydrogen appears to be much slower than addition.[18] With a conjugated diene such as (**1**) both processes will be faster due to resonance stabilization of the resulting radicals; the addition:abstraction ratio may also be different. We are not aware of studies on the reactivity of $HO_2^\bullet$ and dienes, but we have recently observed that peroxyhexanoyl radicals, in hexane or chloroform solution at 300—330 K, almost exclusively add to alkenes such as cyclohexene. With (**1**), however, hydrogen abstraction and addition were found to occur in a ratio of *ca.* 4:1.[19] An analogous increase in importance of abstraction is likely to hold for $HO_2^\bullet$ and (**1**), so as to make reactions (5) and (8) about equally important.

Epoxide formation from adducts of peroxyl radicals and alkenes is a general phenomenon even below 400 K.[20,21] In solution, such fragments $^\bullet$C–C–OOBu^t lose Bu^{t}O$^\bullet$ with a typical rate constant of 10^5 s^{-1} at 298 K.[20b,c] If log *A* is *ca.* 12,[20,22] the activation energy will be *ca.* 35 kJ mol^{-1}. Owing to the loss of resonance energy associated with formation of (**3**) from radical (G) [step (8b)], E_{8b} will be higher, but even a value of 80 kJ mol^{-1} will leave reaction (8b) as an efficient product-forming step under our conditions. Formation of (**2**) from (**3**) [step (8c)] is thought to involve[9] thermal isomerization analogous to that of ethylene oxide into acetaldehyde,[23] *i.e. via* C–O bond scission and a concomitant, 1,2-hydroxgen shift. Direct conversion of (G) into (**2**) [equation (8b′)] by O–O dissociation and accompanying hydrogen-shifts can also be envisaged. Step (8b) is inferred to be almost thermoneutral, but step (8b′) is exothermal by *ca.* 120 kJ mol^{-1}.[9a,13]



$HO_2\cdot + C_6H_6 \longrightarrow H_2O_2 + \cdot C_6H_5$ (9)





(iv) $HO_2^\bullet$ *and Benzenes*.—Hydrogen abstraction (9) is highly endothermic and can therefore be neglected. Addition [reaction (10a)], however, is slightly exothermal,* but k_{10a} will be small. As addition of $HO_2^\bullet$ to propene involves log $k = 9 - 58/2.303\,RT$,[20a] E_{10a} is likely to be at least 70 kJ mol^{-1}, which makes v_{10a}, at best, 10^{-8} mol l^{-1} s^{-1} at 600 K, or *ca.* 1% of v_2. Moreover, reaction (10a) will be reversible; even if disproportionation of (H) with O_2 [step (10b)] is assigned k_{10b} 10^8 l mol^{-1} s^{-1} (a value ten-fold that attributed to k_3, *vide supra*) $v_{10b}/v_{10a} \simeq 10^{-2}$ at 600 K. Clearly, $HO_2^\bullet$ and benzene cannot form products to a measurable extent.

ipso-Substitution of chlorinated benzenes [equation (11)] deserves separate attention, as a possible route to ArOH from ArCl. Formation of PhOOH + Cl$^\bullet$ from $HO_2^\bullet$ and PhCl is somewhat endothermic, *ca.* 23 kJ mol^{-1},‡ but due to the rather high value of E_{11a} (*ca.* 70 kJ mol^{-1}, compare E_{10a}) and the low activation energy for addition of Cl$^\bullet$ to arenes,[5a] $k_{11b} > k_{11-a}$. In other words, reaction (11a) will be rate determining. Should v_{11a} be as large as $v_{10a} \simeq 0.01\,v_2$ (see above), *ipso*-substitution of ArCl by $HO_2^\bullet$ cannot be fully discarded as a pathway to ArOH.

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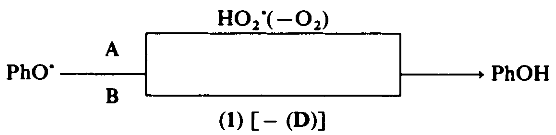
* ΔH_f°(H) is *ca.* 90 kJ mol^{-1}, a value obtained by adding the increment $CH_2 \longrightarrow CH(OOH)$ for secondary compounds, *ca.* −95 kJ mol^{-1},[13,24] to ΔH_f°(D) 183.[11] Using $\Delta H_f^\circ(HO_2^\bullet)$ 21 and $\Delta H_f^\circ(C_6H_6)$ 82 kJ mol^{-1},[9a,13] $\Delta H_{a,-a}$ is *ca.* −15 kJ mol^{-1}.

† The reaction of PhO$^\bullet$ with $HO_2^\bullet$ will be the most important mode of formation of phenol. Using equation (i), [$HO_2^\bullet$] is calculated to be *ca.* $10^{-8.5}$M. With k_A 3 × 10^9,[17] and taking $k_B = 10^{8-50/2.303RT}$ (which choice is based on the observation[8a,18] that PhO$^\bullet$ is about as reactive as Bu^{t}OO$^\bullet$ in hydrogen abstraction), and taking (**1**) $\simeq 10^{-4}$M, one arrives at $v_A/v_B \simeq 20$ at 600 K.



‡ Based on $\Delta H_f^\circ(PhOOH)_G$ −26 kJ mol^{-1}, a value which stems from adding the group increment for secondary ROH ⟶ secondary ROOH, *ca.* 70 kJ mol^{-1},[24] to ΔH_f°(PhOH), −96 kJ mol^{-1}.[9a]

In fact, reaction (11) appears to be of little importance. First, formation of ClC_6H_4OH from PhCl must be due to $^{\bullet}OH$ rather than to $HO_2^{\bullet}$ and reactive $^{\bullet}OH$ radicals will be able to displace Cl in competition with hydrogen abstraction (next section). Secondly, reaction (11) should increase in importance with lower (**1**):PhCl intake ratio, as reaction (5) loses its ability to prevent $HO_2^{\bullet}$ from attacking ArCl. No such trend can be inferred from our data, however.

(v) *Formation of Phenols* ArOH *from Arenes* ArH.—Hydroxyl radicals are generated in the autoxidation of (**1**) *e.g.*, by decomposition of intermediates ($\mathbf{F}_2$) (Scheme 2), or (**G**) [equation (8)]. For discussion of the reactions of $^{\bullet}OH$ with arene we refer to Scheme 1 dealing with benzene itself. Using rate parameters advanced by Ravishankara *et al.*,[4a] $k_{1a}/k_{1d} \simeq 3.5$ at 600 K (see Table 2), a ratio much lower than that holding for ambient temperature, *ca.* 90.[4a] Under our conditions, step (1c) is highly reversible, just as is addition of O_2 to **D** [equation (7)]. The effective rate v_{1c}, therefore, will be small compared with v_{1b}.

An important factor is the rate of reversal of (**A**) to give $^{\bullet}OH$ and benzene [reaction (1 −a)], a step whose activation energy strongly depends on the resonance stabilization energy RE(**A**). From the comprehensive kinetic and product study of James and Suart,[11] RE(**D**) is *ca.* 104 kJ mol^{-1}. We see no reason why RE(**A**) should significantly differ from RE(**D**), the only difference being that OH replaces H at the isolated sp^3-carbon atom. Using the best available thermochemical and kinetic data (Table 2), it is seen that at 600 K, step (1 −a) will be about as fast as step (1b). In the temperature region employed in our study, therefore, a transition occurs in the mechanism of phenol formation, shifting from one involving adduct radicals (**A**) (whose formation becomes increasingly reversible with increasing temperature) to a route *via* phenyl radicals generated in step (1d). This conclusion is corroborated by the shift in isomer distribution of ClC_6H_4OH and of NCC_6H_4OH towards lower *o*:*m* ratios with increasing temperature. High proportions of *ortho*-hydroxylation are typical for addition of $^{\bullet}OH$, both in solution[27] and in the atmosphere; in the latter case toluene, for example, is stated to involve addition, *o*:*m*:*p* = 81:5:14.[28]

Interestingly, studies on decay rates of $^{\bullet}OH$ seem to favour a much lower value of RE(**A**), *viz.* 70 ± 20 kJ mol,[4b] which value is not much larger than the allylic resonance energy *ca.* 52 kJ mol.[29] We have no explanation for this inconsistency, but it should be kept in mind that conclusions derived from the flash photolysis–resonance fluorescence work, albeit sound for reactions at ambient temperature,[30] are based only on observed net rates of disappearance of $^{\bullet}OH$ and rest upon the premises inherent to this type of work, expecially that there are no time- and temperature-dependent sources of $^{\bullet}OH$ in addition to photolytic decomposition of H_2O.

In a subsequent paper[7b] we will deal in detail with the mechanism of formation of phenols from substituted benzenes over a large temperature range; suffice it to say here that, under the present conditions, aryl radicals are likely to yield the corresponding phenol mainly as outlined in equation (12). *via* ArO-OH homolysis $^{\bullet}OH$ is regenerated, which lends some chain character to the formation of ArOH from ArH. Note that more ClC_6H_4OH is produced from PhCl than phenol from (**1**), the latter reaction providing the 'initiating' $^{\bullet}OH$ radicals (Scheme 2).

$$Ar^{\bullet} + O_2 \longrightarrow ArOO^{\bullet} \xrightarrow{HO_2^{\bullet}(-O_2)} ArOOH \xrightarrow[(2)\ HO_2^{\bullet}(-O_2)]{(1)\ -OH^{\bullet}} ArOH \qquad (12)$$

$$ArCl + {}^{\bullet}OH \longrightarrow ArOH + Cl^{\bullet} \qquad (13)$$

$$PhOH + {}^{\bullet}OH \longrightarrow PhO^{\bullet} + H_2O \qquad (14)$$

Table 2. Kinetic parameters for reactions of benzene and $^{\bullet}OH + O_2$

Reaction	log A[a]	E_a/kJ mol^{-1}	Values at 600 K
(1a)	9.27	2.2[4a]	k_{1a}/k_{1d} 3.5
(1d)	10.16	18.8[4a]	
(1 −a)	14.4[b]	102[c]	log k_{1-a} 5.5
(1b)	9.6[d]	18[d]	log[k_{1b}·(O_2)] 5.6[e]

[a] In l mol^{-1} s^{-1} or s^{-1} units. [b] At 600 K the process $H^{\bullet} + C_6H_5-OH \underset{-x}{\overset{x}{\rightleftharpoons}} C_6H_7O^{\bullet} \underset{a}{\overset{-a}{\rightleftharpoons}} C_6H_6 + {}^{\bullet}OH$ has ΔS° = 12 J mol^{-1} K^{-1},[9a,c] corresponding to log (A_x·A_{-a}/A_{-x}·A_a) 0.65. When assigning to A_x,A_{-x} the same values as those for addition of $H^{\bullet}$ to benzene, log A_x (on a per-carbon basis) = 9.06,[25] log A_{-x} = 13.5.[11] With log A_a = 9.2,[4a] one obtains log A_{-a} = 13.5 + 0.65 + (9.27 − 9.06) ≃ 14.4. [c] Based on $\Delta H^{\circ}_{a,-a}$ −105 (see below); E_a of reaction (1 − a) then equals +105 + 2.2[4a] −RT (5.0 kJ mol^{-1} at 600 K). $\Delta H^{\circ}_{a,-a}$ is derived from H°_f values for $^{\bullet}OH$ (40),[13] C_6H_6 (82),[9a] and (**A**) (17 kJ mol^{-1}). The latter value is obtained when combining the group increment for $CH_2 \longrightarrow CH(OH)$ in secondary alcohols, *ca.* −165 kJ mol^{-1},[9a] with ΔH°_f(**D**) 183 kJ mol^{-1}.[11] [d] Reactions $R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$, typically, have $E_a \simeq 0$, log (k/l mol^{-1} s^{-1}) at 300 K ≃ 9.6,[14,26] Taking log k_{1b}(≃log k_3) ≃ 6.5 at 300 k,[15-17] and accepting log A_{16} = 9.6, E_a for step (1b) is calculated to be *ca.* 18 kJ mol^{-1}. [e] With [O_2] = $10^{-2.5}$M.

Exothermal *ipso*-substitution (13) will account for the formation of phenol from PhCl and of *m*-ClC_6H_4OH from *m*-$C_6H_4Cl_2$. Chlorine atoms will form HCl by reaction with $HO_2^{\bullet}$, or by H abstraction from (**1**). According to the very recent results of Zetzsch *et al.*[31] phenol vapour, at ambient temperature, reacts *ca.* 25—30 times faster with $^{\bullet}OH$ than does benzene. The course of the reaction of $^{\bullet}OH$ with phenol is not known; apart from addition, facilitated by the electron-donating OH substituent, hydrogen abstraction to give phenoxyl radical can also be envisaged [reaction (14)]. As is the case with benzene, addition of $^{\bullet}OH$ to phenol may also become reversible at *ca.* 600 K. Therefore, a simple extrapolation of $v_{rel} \simeq$ 25—30 at 300 K, which value would correspond to a difference in free energy of activation of *ca.* 8 kJ mol^{-1}, to v_{rel} *ca.* 5 at 600 K is unwarranted. On the other hand it is unlikely that v_{rel} is much higher at 600 K than at 300 K. Consider, to this end, the extreme situation in which, at 300 K, $^{\bullet}OH$ adds to benzene [step (1a)] but, at 600 K, abstracts hydrogen exclusively [step (1d); see Table 2], whereas abstraction (14) is the only reaction with phenol throughout; one can then assign log (A_{14}/l mol^{-1} s^{-1}) = 10.3 if E_{14} is taken as zero. These parameters cover $v_{rel} = k_{14}/k_{1a} \simeq$ 25—30 at 300 K and lead to $v_{rel} = k_{14}/k_{1d} \simeq 60$ at 600 K. In our experiments (Table 1), the arene:ArOH ratios are well above 200 and the degrees of conversion of arene are small. Hence, phenols will be further converted to very limited degrees only.

(vi) *Reaction of* (**1**) *with* $^{\bullet}OH$.—Using available rate parameters,[2] addition of $^{\bullet}OH$ to alkenes or to butadiene, at 600 K, is estimated to be *ca.* 50 times as fast as hydrogen abstraction from benzene. Such a ratio is also likely to hold for (**1**) and benzene. Given our (**1**):arene (intake) ratios, $^{\bullet}OH$ will therefore react not only with arene, but, to some extent, also with (**1**)*. This explains that the phenol-forming sequence [equations (1d), (12)] has only short-chain character, and it provides another

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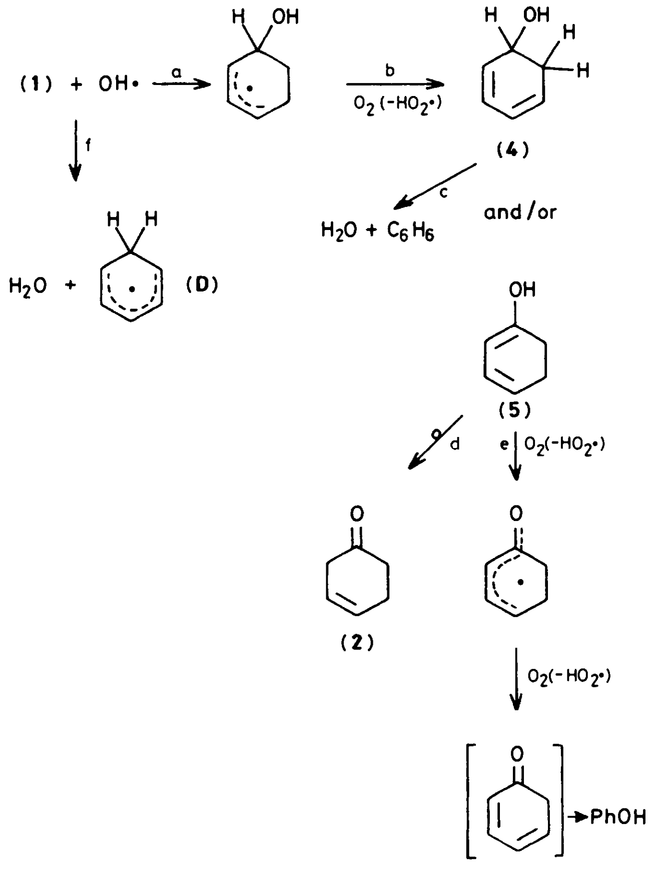
* *Note added in proof*: Gas-phase reactions of $^{\bullet}OH$ and (**1**), and reactions at 298 K, have recently been studied,[17] and the results substantiate both addition and abstraction as first steps.



Scheme 3.

route for conversion of (**1**), which, of course, is of special importance in the absence of added arene (Scheme 3). Addition (Scheme 3, step a) will result in formation of dienes (**4**) and/or (**5**) (step b). Intermediate (**4**) is likely to lose H_2O (step c), whereas (**5**) can tautomerize to give (**2**) (step d) and/or be subject to free-radical oxidation (step e) leading to phenol. With (**1**) hydrogen abstraction (step f) may occur to some extent in competition with addition (step a).

Experimental

Chemicals.—Starting and reference compounds were, in general, available as high-grade commercial products, and used as such. The three isomers of hydroxybenzonitrile were prepared by hydroxylation of benzonitrile with Fenton's reagent,[32] isomer distribution *o*:*m*:*p* = 36.6:39.7:23.6. 3,4-Epoxycyclohexene (**3**) was prepared from (**1**) and *m*-chloroperbenzoic acid in chloroform. After work-up and distillation *in vacuo*, b.p. 58—60 °C at 60 mmHg (lit.,[33] 62—64 °C at 65 mmHg) the product was 99% pure by g.l.c. and had a ^{1}H n.m.r. spectrum as described.[33]

The apparatus and techniques have been described elsewhere.[1a] In general, a mixture of arene and (**1**) was introduced into the reactor using a motor-driven syringe. In runs 18 and 19, (**1**) was introduced as vapour by passing a calibrated stream of dry nitrogen through a set of two washing bottles containing liquid (**1**). The effluents were condensed at −15 °C (ice–salt bath), except in runs 18 and 19, where liquid nitrogen was used.

Analyses.—Organic products and degrees of conversion were determined by g.l.c. on a capillary SE-30 column; conditions: H_2, 0.4 atm., flow *ca.* 1 ml min^{-1}; $T_{\rm inj} = T_{\rm det} = 220$ °C; temperature programme 100 °C (8 min), 8 °C min^{-1}, 200 °C; (10 min). Phenols were analysed as Me_3Si derivatives (see below). For g.l.c. separation of benzene and (**1**), samples were analysed at a constant oven temperature of 65 °C. The assignment of cyclohex-3-enone was based upon the small but significant difference in retention time between this isomer and cyclohex-2-enone.

Silylation of Phenols.—To dried (molecular sieve 3 Å) portions of reaction mixtures (2 ml) containing phenols, the following reagents were subsequently added: pyridine (0.2 ml), bis(trimethylsilyl)trifluoroacetamide (0.1 ml), and chlorotrimethylsilane (0.1 ml). Conversion was completed within 5 min as was shown by similar treatment of mixtures of, *e.g. o*-, *m*-, and *p*-ClC_6H_4OH. On g.l.c., *o*-, *m*-, *p*-$XC_6H_4OSiMe_3$ (X = Cl,CN) were well separated in contrast to the parent phenols.

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