Vapour-phase Chemistry of Arenes. Part 11.[1] Autoxidation of Chlorobenzene between 500—1 100 K. Mechanisms of Formation of Chlorophenols and Phenol

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Slow combustion of chlorobenzene (**1**) has been studied at low degrees of conversion ($<5\%$); mostly at atmospheric pressure, but at *ca.* 1 080 K under FVT-like conditions. Emphasis was on formation of the hydroxy derivatives *o*/*m*/*p*-ClC_6H_4OH (**2**) and the *ipso* substitution product phenol (**3**).

A variety of ingredients, such as Bu^{t}OOH, cyclohexane, nitroethane, and hydrogen peroxide, forming $^{\cdot}OH$ *in situ* by thermolysis or autoxidation, has been used to induce the reaction of (**1**).

The change in product composition (**2**, **3**) with temperature revealed a major change in mechanism of hydroxylation between 600—700 K. Above *ca.* 600 K, H-abstraction (**1**) + $^{\cdot}OH \rightarrow$ *o*/*m*/*p*-$ClC_6H_4^{\cdot}$ [accompanied by (**1**) + $^{\cdot}OH \rightarrow Cl^{\cdot}$ + (**3**)] is followed by rapid addition of O_2 (step 4) to give $C_6H_4OO^{\cdot}$ radicals (v).

At moderate temperatures (v) reacts bimolecularly, with itself or with $HO_2{\cdot}$, leading to $ClC_6H_4O{\cdot}$ (iv) and therefrom to (**2**). Thermokinetic analysis emphasises that at elevated temperatures (v) decomposes into (iv) and O(^{3}P). The latter species adds to (**1**) and forms (**2**) rather efficiently, with an isomer distribution different from that associated with the pathway $Ar^{\cdot} \rightarrow ArO_2^{\cdot} \rightarrow ArOH$.

Data on model runs, including kinetic isotope effect measurements on *p*-DC_6H_4Cl and C_6H_6/C_6D_6, support our mechanistic interpretation.

The gas-phase oxidation of benzene to phenol is of interest in the study of the chemistry of polluted air, in combustion studies, and as a potential industrial process.

Compared with that of alkanes, the autoxidation of benzene vapour *per se* is slow. In our flow system, for example, no measurable reaction occurred in air at 500 °C, $\tau = 2$ min. Benzene does form phenol, however, in the presence of compounds susceptible to slow combustion. For example, Donald and Grover,[2] allowing benzene and cyclohexane (10:1) to react at 594 °C, $\tau = 4.5$ s, obtained a 1.1% yield of phenol, with a selectivity (S) of 26%. Krieble and Denton[3] found optimal results (*ca.* 5% conversion, S $\simeq$ 50%) with benzene:cyclohexane $\simeq$ 100:1 at 450 °C, in air at 67 atm. pressure. Other co-oxidants studied include toluene,[3] ether,[3] methanol,[4] HBr,[5,6] and HNO_3.[7] In all cases biphenyl was reported to be an important by-product. These conversions almost certainly proceed *via* free-radical reactions, hydroxyl radical being a very likely candidate for conducting the first step in benzene conversion. Studies on benzene itself, however, will do little to illuminate the mechanism of phenol formation. We therefore sought to examine substituted benzenes, so as to obtain data on isomer distributions and relative rates under varying conditions.

We now report the results of a study of chlorobenzene (**1**) with emphasis on the formation of chlorophenols (**2**) and the *ipso* substitution product, phenol (**3**). As (**1**) proved to be about as stable in air as benzene, co-oxidants were used, including t-butyl hydroperoxide,[8] cyclohexa-1,3-diene,[1] cyclohexane, nitroethane, and hydrogen peroxide. In this way, product formation was determined for the temperature region 500—800 K. By employing flash-vacuum-techniques we were able to conduct (slow) combustion to a limited degree at nearly 1 100 K. Our data therefore cover a temperature range of nearly 600 K.

Results and Discussion

An overview of relevant features and results of the various systems studied is given first; in the subsequent mechanistic discussion, the results of specific model experiments are considered.

Runs performed at atmospheric pressure were carried out in Pyrex or quartz tank-flow-type reactors of 300—900 cm^3, the residence time τ varying between 45—240 s. FVT-type runs were conducted in a quartz reactor of $V_r \simeq 43$ cm^3, at overall pressures of 50—100 mm Hg (0.06—0.13 M Pa). A list of representative runs is given in Table 1.

(i) *Rates and Products.—A. With t-butyl hydroperoxide.* Bu^{t}OOH is known to thermolyse smoothly between 450—600 K, τ *ca.* 100 s, producing $^{\cdot}OH$ radicals.[8] In air, compound (**1**) and Bu^{t}OOH, intake ratio 50:1, gave *o*-, *m*-, and *p*-(**2**) and (**3**), as major products (Table 1, series A). Biaryls, mainly ClC_6H_4-C_6H_4Cl, were found in amounts $<10\%$ based on (**2**). These features contrast with those of the thermolysis of (**1**) + Bu^{t}OOH under nitrogen, which led to biaryl:(**3**) molar ratios of 4—5.[8] Inspection of the composition of the phenolic products shows that the (**3**):*m*-(**2**) ratio is almost temperature independent, whereas the *o*-(**2**):*m*-(**2**) [and the *p*-(**2**):*m*-(**2**)] ratios appear to decrease with increasing temperature (Figures 1*a* and *b*). Note that, when oxygen is present, the induced decomposition of Bu^{t}OOH is diminished; therefore the increase in yield of (**2**) + (**3**) parallels the degree of decomposition of Bu^{t}OOH over the temperature range studied.[9]

B,C. Aliphatic hydrocarbons as co-oxidants. Elsewhere we have dealt with the formation of phenols by the slow combustion of (**1**) with small amounts of added cyclohexa-1,3-diene between 570—622 K.[1] Here we present new data covering the region 653—768 (Table 1, series B), comprising the low co-oxidant: (**1**) intake ratio, 0.22 at 58.7 mmol h^{-1} (*cf.* expt. 10 in Table 1 of ref. 1) only. The isomer distribution of (**2**) is clearly temperature dependent: the *o*-(**2**) : *m*-(**2**) ratio first decreases with increasing temperature,[1] passes a minimum of *ca.* 0.25 around 620 K, and then increases to *ca.* 1 at 750 K (Figure 1*a*). Between 640—740 K, cyclohexane induces hydroxylation of (**1**) equally well; the isomer distribution of (**2**) and the (**3**):(**2**) ratios

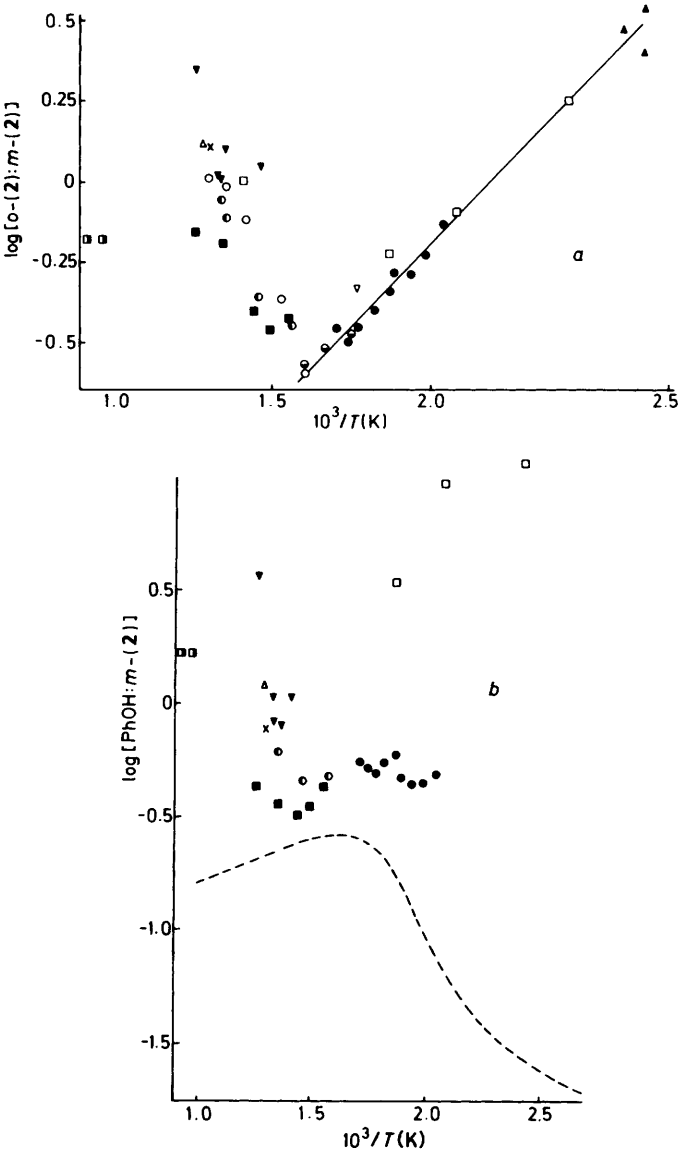
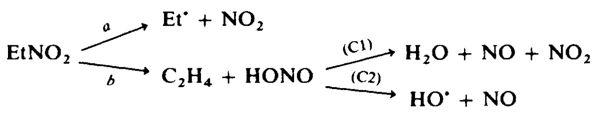


Figure 1. Product ratios *versus* temperatures. *a*: *o*/*m*-Chlorophenol; log (*o*/*m*) = $-2.2 + 19/\theta$, see text. *b*: Phenol/*m*-chlorophenol; log $[v_2/v_{1\mathrm{eff}} + v_3]$, see text. ●, expts. A1—9; ○, expts. B1—5; ◑, expts. C1—4; ■, expts. D1—5; ▼, expts. E1—5; □, expts. E6—9; ◨, expts. F1—2; △, expt. G1; ×, expt. G2; ▲, L-phase expt. (see text); ⊖, see Table 1,[1] expts. 7—9; ▽, *o*/*m*-IC_6H_4Cl obtained from PhCl + I_2.[8]

are comparable to those of series B (see Table 1, expts. C1—C3). Cyclohexene (expt. C4) acts accordingly.

Throughout this series, oxygen and the added co-oxidant are partly consumed. Biaryls arise in trace amounts only. In absence of added cyclohexane, *etc.*, no observable reaction takes place between (**1**) and air at the temperatures used.

D. Effect of nitroethane. Nitroalkanes decompose around 700 K;[10] both C–NO_2 bond scission (*a*) and elimination (*b*) have been advanced as the first step, the reported rate parameters implying roughly equal rates for *a* and *b* at 700 K[10] (Scheme 1).



Scheme 1.

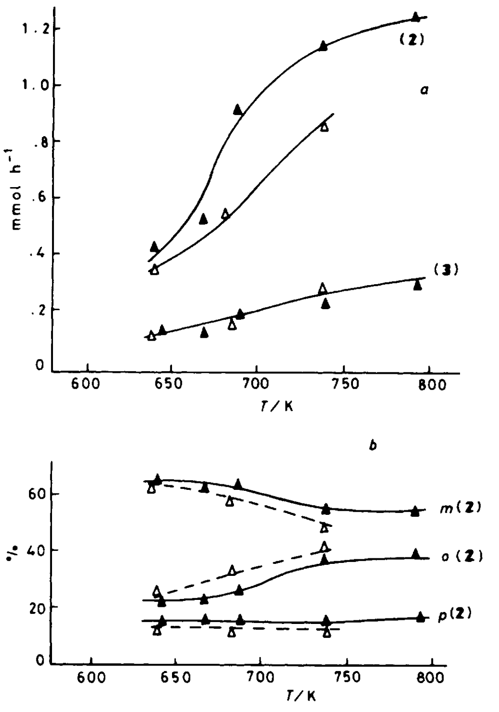


Figure 2. Autoxidation of chlorobenzene in the presence of cyclohexane (△) or cyclohexane + nitroethane (▲) as a function of temperature. *a*: Product formation, ClC_6H_4OH (**2**) and PhOH (**3**). *b*: Isomer distribution of (**2**).

Regardless, decomposing $EtNO_2$ introduces nitrogen oxides and very probably •OH and organic radicals (Et•), and therefore can be expected to influence the chemistry of slow combustion. Nitrogen oxides are known to take part in the conversion of phenols under atmospheric conditions.[11] Furthermore, the addition of nitroalkane to diesel fuel is claimed to engender cleaner combustion.[12]

Our observations (series D, Table 1) substantiate reported rates of conversion of $EtNO_2$.[10] As shown in Figure 2, it causes an increase in the yield of (**2**) when added to the system (**1**) + cyclohexane; the yield of phenol (**3**) appears to remain unaltered. Below 700 K, at best only trace amounts of other chlorobenzene-derived products are seen. At higher temperatures—hence at (near) complete conversion of $EtNO_2$—several other products are formed. Apart from some chlorinated biphenyls these include nitrobenzene, chloronitrobenzenes, dibenzofuran (**4**), and mono- and di-chloro-derivatives of (**4**) (Table 2). Without added $EtNO_2$ (hence, with cyclohexane as the only co-oxidant) the formation of (**4**) and derivatives is substantially reduced.

Analogous results were obtained using benzene in place of (**1**). Expt. 3, Table 2, shows a yield of (**3**) of *ca.* 5% based on benzene, and some biphenyl and (**4**) [5.6% of (**3**) each] and a little nitrobenzene. When cyclohexane is left out of the feed, the production of (**3**) is somewhat less, but that of (**4**) is increased (expt. 4). In absence of oxygen, benzene and $EtNO_2$ form biphenyl as the only detectable benzene-derived product (expt. 5). When phenol is added to such a feed, about one-half (expt. 6) is recovered. When benzene is thermolysed with cyclohexane and $EtNO_2$ (expt. 7) in nitrogen, no phenol is formed, the yield of biphenyl being somewhat smaller than that in expt. 5.

Clearly, the intermediate phenyl radicals are not converted into phenol by NO_x and/or RNO_2. The usual product is biphenyl, arising from the arylation of benzene.[13] This reaction

Table 1.

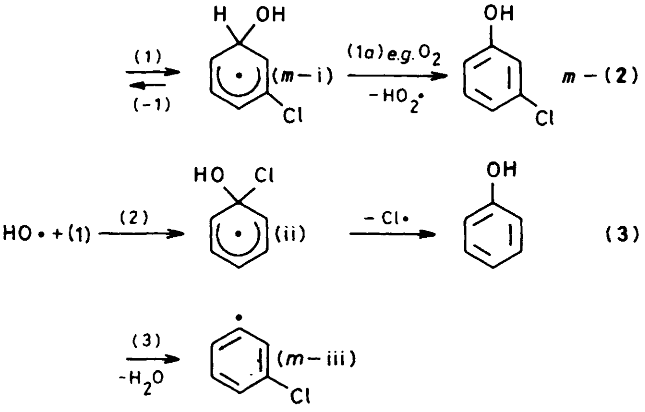
Run No.	T/K	τ/s	In[a]				Out[a]					
			(**1**)	Added	N_2	O_2	ClC_6H_4OH (**2**)	(o:m:p)	PhOH (**3**)	PhC_6H_4Cl	$ClC_6H_4-C_6H_4Cl$	Other data
(A) With Bu^{t}OOH[b]												
A1	488	105	58.9	1.17	335	135	0.024	(32/44/24)	0.005	—	—	
A2	504	102	58.9	1.17	335	135	0.082	(27/47/26)	0.017	—	—	
A3	520	99	58.9	1.17	335	135	0.146	(25/50/25)	0.032	—	t	
A4	527	98	58.9	1.17	335	135	0.183	(25/50/25)	0.043	—	0.0056	
A5	534	96	58.9	1.17	335	135	0.22	(24/53/23)	0.071	t	0.032	
A6	549	94	58.9	1.17	335	135	0.32	(22/56/22)	0.098	t	0.033	
A7	564	92	58.9	1.17	335	130	0.36	(20/58/22)	0.105	t	0.010	
A8	573	91	58.9	1.17	335	130	0.24	(19/61/20)	0.076	t	0.018	
A9	587	88	58.9	1.17	335	130	0.31	(20/58/22)	0.098	t	0.024	
(B) With cyclohexa-1,3-diene[c]												
B1[d]	622	124	58.7	0.22	124	33	0.031	(17/67/16)	0.021	—	—	
B2	653	118	58.7	0.22	124	33	0.034	(26/60/14)	0.926	—	—	
B3	704	110	58.7	0.22	124	33	0.083	(35/46/19)	0.060	—	—	
B4	740	104	58.7	0.22	124	33	0.192	(41/43/16)	0.092	—	—	
B5	768	101	58.7	0.22	124	33	0.224	(43/42/15)	0.105	t	t	
(C) With cyclohexane[e]												
C1	640	110	55.1	2.75	103	27	0.346	(23/63/14)	0.105	t	t	
C2	685	102	55.1	2.75	103	27	0.521	(31/57/11)	0.136	t	t	
C3	740	95	55.1	2.75	103	27	0.846	(38/49/13)	0.256	t	t	
C4	742	51[c]	35.3	2.10[f]	360	43	0.498	(41.5/46/12.5)	0.232	t	t	
(D) With cyclohexane + $EtNO_2$[e]												
D1	643	109	54.7	2.70 + 0.58	103	27	0.41	(21/64/15)	0.11	—	—	28[g]
D2	669	105	54.7	2.70 + 0.58	103	27	0.50	(22/63/15)	0.11	—	—	38[g]
D3	690	101	54.7	2.70 + 0.58	103	27	0.90	(25/61/14)	0.18	t	t	50[g]
D4	740	95	54.7	2.70 + 0.58	103	27	1.12	(34/53/13)	0.22	0.013	0.070	>98[g]
D5	793	88	54.7	2.70 + 0.58	103	27	1.22	(35/51/14)	0.27	t	0.094	>99[g]
(E) With H_2O_2[c]												
E1	703	50	118	0.33	359	0	0.082	(46.5/42/11.5)	0.037	0.024	0.215	
E2	747	45	295	0.15	203	0	0.078	(44/45/11)	0.028	0.067	0.49	
E3	748	53	37.3	0.40	380	0	0.051	(43/41/16)	0.023	0.008	0.055	
E4	733	45	56.5	0.40[h]	445	0	(1)[v]	(48/38/14)	(0.31)[v]	(0.16)[v]	(1.2)[v]	(1.6)[x,v]
E5	793	42	56.5	0.40[h]	445	0	(1)[v]	(59/26/15)	(0.98)[v]	(0.26)[v]	(1.6)[v]	(1.3)[x,v]
E6	410	239[i]	56.5	0.40[h]	285	59	(1)[v]	(51/29/20)	(3.55)[v]	t	t	t
E7	478	205[i]	56.5	0.40[h]	285	59	(1)[v]	(37/47/16)	(4.33)[v]	t	t	(0.34)[x,v]
E8	534	184[i]	58.9	0.40	285	59	(1)[v]	(32/53/15)	(1.82)[v]	t	t	
E9	736	133[i]	56.5	0.40[h]	285	59	(1)[v]	(42/40/17)	(0.71)[v]	nd	nd	nd
(F) FVT with butanol[j]												
F1	1 034	~0.03[k]	9.9	2.0	~3 200	~800	(1)[v]	(28/42/30)	(0.50)[v]	—	—	
F2	1 083	~0.02[l]	9.9	2.0	~12 000	~3 000	(1)[v]		(0.48)[v]	—	—	
(G) Miscellaneous[b]												
G1	773	89	58.9	1.20[m]	265	72	0.48	(48/39/13)	0.22	t	t	
G2	758	91	58.9	1.05[n]	265	72	0.097	(39/31/30)	0.024	t	t	
G3	1 053	~0.03[j,k]	7.0/6.4[o]	0.50[p]	~3 200	~600	0		(1)[w]	0	0	$k_H/k_D = 1.0$[t]
G4	1 033	~0.03[j,k]	9.9[q]	2.0[r]	~3 200	~800	(1)[v]	(27/47/26)	(0.58)[v]	—	—	$k_H/k_D = 1.3$[u]
G5	559	140	34.3/30.2[o]	*s*	218	63	0		(1)[w]	0	0	$k_H/k_D = 2.2$[t]

[a] Flow rates in mmol h^{-1}; t = trace (hence, composition uncertain); — = below detection limit (*ca.* 0.002 mmol h^{-1}); nd = not determined. [b] Reactor volume $V_r = 620$ cm^3. [c] $V_r = 380$ cm^3. [d] *cf.* Run 10, Table 1, ref. 1. [e] $V_r = 300$ cm^3. [f] Cyclohexene rather than cyclohexane. [g] Conversion of $EtNO_2$ (%). [h] Plus toluene, 2.4 mmol h^{-1}. [i] Reaction under u.v. illumination, using a high-pressure mercury lamp; $V_r = 900$ cm^3. [j] Quartz reactor, $V_r = 43$ cm^3. [k] Pressure in reactor *ca.* 50 mmHg. [l] Pressure in reactor *ca.* 100 mmHg. [m] Azobenzene; conversion 66%. [n] p-$ClC_6H_4CO_2CH_2CH{=}CH_2$; conversion 43%. [o] C_6H_6/C_6D_6. [p] Cyclohexane. [q] 4-DC_6H_4Cl: 93.4% D_1, 6.6% D_0. [r] Butanol. [s] Cyclohexane: 2.7, Bu^{t}OOH: 0.75 mmol h^{-1}. [t] Intermolecular kinetic isotope effect, based on $PhOH/C_6D_5OH$ product ratios. [u] Intramolecular kinetic isotope effect for formation of p-(**2**), based on p/m-(**2**) ratios of runs F1 and G4. [v] Product ratios only. [w] $PhOH/C_6D_5OH$ product ratio: 1.07 (expt. G3); 2.53 (expt. G5). [x] Bibenzyl.

Table 2. Conversion of benzene and chlorobenzene with added cyclohexane and/or nitroethane

Expt. No.	T/K	τ^a/s	Inflow/mmol h^{-1} N_2	O_2	PhX X	$EtNO_2$	C_6H_{12}	Products[b]/mmol h^{-1} PhOH (3)	ClC_6H_4OH (2)	Biaryls	$PhNO_2$
1	740	95	103	27	Cl, 54.7	0.58	2.70	0.22	1.12	0.013[c] + 0.070[d,g]	0.004 + 0.039[f]
2	740	95	103	27	Cl, 58.1	1.18	0	0.063	0.503	0.007[c] + 0.036[d,g]	0.009 + 0.024[f]
3	740	90	103	27	H, 63.5	0.67	3.17	3.18	0	0.178[e,g]	0.022
4	740	90	103	27	H, 67.1	0.69	0	2.65	0	0.15[e,g]	0.047
5	743	98	95	0	H, 67.2	0.66	0	0	0	0.26[e]	t
6	743	98	95	0	H, 67.2[h]	0.66	0	0.17[h]	0	0.26[e]	t
7	738	91	128	0	H, 63.8	0.67	3.17	0	0	0.085[e]	t
8	737	104	95	0	Cl, 58.1	1.18	0	0.010	0	0.004 + 0.017[c]	t
9	737	104	95	0	Cl, 55.7	0.58	2.72	0.012	0	0.0031 + 0.017[c]	t

[a] V_r = 300 cm^3. [b] Conversion of $EtNO_2 > 98\%$. [c] PhC_6H_4Cl, *o*:*m*:*p* = 12/65/23. [d] $ClC_6H_4C_6H_4Cl$, *o,o′*:*o,m′*:*o,p′*:*m,m′*:*m,p′*:*p,p′* = 5.2/23.3/12.6/24.7/26.7/6.8. [e] $(Ph)_2$. [f] $ClC_6H_4NO_2$, *o*:*m*:*p* = 12/63/25. [g] Also formed dibenzofurans; DBF + DBFCl + $DBFCl_2$: 0.0082 + 0.067 + 0.041 (expt. 1), 0.046 + 0.062 + 0.12 (expt. 2); DBF: 0.18 (expt. 3), 0.72 (expt. 4). [h] Added PhOH: 0.38 mmol h^{-1}; recovery: 45%.



$$\begin{aligned} \log k_1 &= 8.8 - 4/\theta^{18a} \\ \log k_{-1} &= 14.4 - 84/\theta^{1,18c} \\ \log k_2 &= 8.5 - 14/\theta \text{ (see text)} \\ \log k_3 &= 9.7 - 21/\theta^{18a} \\ \log k_{1a} &= 9.6 - 18/\theta^{1} \end{aligned}$$

Scheme 2. ($\theta = 2.303\ RT$ in kJ mol^{-1})

is suppressed by increasing amounts of *e.g.* cyclohexane, which acts as H donor to phenyl radicals.

The reaction of chlorobenzene (**1**) with $EtNO_2$ (runs 8,9) leads to small amounts of phenol (**3**), but chlorophenols (**2**) are not found. Some biaryl is also produced. However, owing to the operation of H-atoms, which arise by decomposition of $Et^{\bullet}$[10] and by homolytic phenylation of chlorobenzene,[13] induced phenylation might occur. H-atoms and (**1**) will lead to HCl and phenyl radicals.[14,15]

E. Chlorobenzene and H_2O_2. The photolysis of H_2O_2 at 254 nm has been used as a source of $^{\bullet}OH$ radicals at ambient temperature.[16] As the HO–OH bond strength is *ca.* 210 kJ mol^{-1}, hydrogen peroxide should be able to produce $^{\bullet}OH$ radicals smoothly around 700 K.[17] In untreated Pyrex reactors, H_2O_2 was found to decompose around 730 K when fed in with a large excess of (**1**) and nitrogen. These runs did not lead to any phenol(s) and/or biphenyls. Presumably a surface-catalysed conversion into water and oxygen took place. After treatment with aqueous HF these supposed wall reactions seemed to be suppressed and (**2**), (**3**), and biphenyls were produced (Table 1, expts. E1—5). Given the large difference in experimental conditions of series D and E (in the latter, nitrogen rather than air was used) the isomer distributions of (**2**) in *e.g.* runs E2 and D4 are surprisingly similar, though not identical. Figure 1*a* shows that in expts. E1—3 the *o*-(**2**)/*m*-(**2**) ratios were the highest observed in this study. Addition of some toluene to the feed (runs E4,5) does not prevent formation of (**2**) and (**3**), although some bibenzyl is produced. This substantiates the theory that the primary attack on benzene is due to a reactive species with little selectivity.

We have also explored the behaviour of H_2O_2 upon u.v. irradiation. At 730 K light has little effect on the isomer composition of (**2**) (compare expts. E9 and E3). The (**3**)/*m*-(**2**) ratio (Figure 1*b*), however, is much larger in E9 than in E3. Photolysis at temperatures below 550 K, in N_2, did not result in measurable production of phenols or biaryls. In air, phenols do arise (expts. E6—8). Again, the (**3**):*m*-(**2**) ratio is greatly above the ratios seen with thermal reactions, for example series A. On the other hand, the *o*-(**2**)/*m*-(**2**) ratios seem to fit the trend shown by series A. It is therefore tempting to believe that conversion (**1**)→(**2**) is a thermal process, whereas (expts. E6—9) formation of (**3**) from (**2**) occurs, at least in part, *via* excited states (photosubstitution).

F. FVT-type reactions. When passing (**1**) with butanol* and air through a flash-vacuum reactor at 950 K (total pressure 50—100 torr/0.06—0.13 MPa, τ *ca.* 0.02 s), no reaction was observed. Smooth conversion into (**2**) and (**3**) occurred at 1 000—1 100 K, however (Table 1, expts. F1,2). The *o*-(**2**)/*m*-(**2**) ratios (Figure 1*a*) are not unlike those for cyclohexane assisted reactions at 800 K (series C), but the *p*-(**2**)/*m*-(**2**) ratio is higher for the FVT runs. Moreover, the (**3**)/*m*-(**2**) ratio is high (Figure 1*b*).

(ii) *Mechanisms for Hydroxylation* ArH(Cl)→ArOH.—Figures 1*a* and *b*, which we use as a basis for mechanistic discussion, present an overview for the hydroxylation of (**1**). Figure 1*a* shows that the *o*-(**2**)/*m*-(**2**) product ratio first decreases regularly with temperature, reaches a minimum at $10^3/T \simeq 1.6$ (around 650 K) and then increases. There is considerable scatter, which we will comment on later in this section. Figure 1*b* shows that below *ca.* 650 K the (**3**)/*m*-(**2**) ratio has little temperature dependency with, however, a clear tendency to increase with temperature above 650 K.

The plot of Figure 1*a* shows that there are different mechanisms for hydroxylation in the low and high temperature regions.

There is no doubt that hydroxyl radicals—produced *via*

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* The (**1**)–butanol mixture was introduced by evaporation; hence, this co-oxidant was chosen because of its vapour pressure which is almost identical with that of (**1**).

thermolysis of Bu^tOOH,[8] by decomposition of H_2O_2, or *in situ from e.g.* cyclohexa-1,3-diene[1]—can react as shown in Scheme 2, exemplified for attack on *meta* positions of chlorobenzene (**1**).

Addition (1) is the major reaction at ambient temperature[18,19] both in the gas phase and in solution.[20,21] Provided that the adduct radical (*m*-i) and its isomers are equally well converted into (**2**), the isomer distribution of (**2**) is a good measure for the site selectivity of addition of $^{\bullet}$OH to (**1**). Examples of reactions in solution are: γ-radiolysis in water, resulting in (**2**) with *o*:*m*:*p* *ca.* 37:22:41;[20] and our results on the thermolysis of *p*-$BrC_6H_4N{=}NCH(Ph)OOH$[22] in (**1**), with added O_2, *m*-dinitrobenzene, or benzoquinone, leading to chlorophenol (**2**) with *o*:*m*:*p* = 49:22:29 at *ca.* 370 K.[23] The differences between these results may be due to solvent effects on the site selectivity of step (1) and/or on relative rates of further conversions of adduct radicals. In any case, *ortho-* and *para*-substitution prevails, as is usual for homolytic aromatic substitution proceeding *via* irreversible addition.[20,24]

Addition of $^{\bullet}$OH according to step (2) will be followed by loss of the more weakly bound Cl$^{\bullet}$ atom to give (**3**); alternatively, loss of HCl to give phenoxyl radical (iv) may occur, especially in aqueous solution. In water the (**3**)/*m*-(**2**) ratio is *ca.* 0.26.[20] In chlorobenzene, at *ca.* 370 K, we have found the latter ratio to be only *ca.* 0.020.[23] [Note that Oae *et al.*[22] do not mention the formation of phenol at all in the photolysis of *p*-BrC_6H_4-N=NCH(Ph)OOH in chlorobenzene at 300 K.] Apparently, at 300 K k_2/k_1 is at best *ca.* 0.01—0.02; hence, in aqueous solution much of the *ipso*-product (phenol) is likely to arise in a way other than *via* step 2, presumably *via* radical cation intermediates formed from type (i) adduct radicals.[21]

The plot of Figure 1*a per se* does not point to a change in mechanism between 300—600 K. In that region, the temperature dependence is described by line (1) involving log (*o*-/*m*-) $\simeq -2.2 + 19/\theta$.* In view of the low energies of activation associated with reactions of $^{\bullet}$OH and benzene,[18] such parameters are unrealistic for a single reaction of $^{\bullet}$OH and its site selectivity, whether that single reaction is addition (1) or abstraction (3). We therefore suggest that the observed temperature dependence is due to a gradual change in mechanism. At lower temperatures the irreversible formation of type (i) radicals takes place. Addition of $^{\bullet}$OH becomes increasingly reversible with temperature, meaning that (relative) rates of conversion of (i) and its isomers into (**2**) are of decisive importance. In air, conversion of (i) and its isomers into (**2**) is likely to proceed by disproportionation with O_2, but such reactions are relatively slow[11,19] and therefore will have substantial activation energies. This in turn can result in different overall activation energies for the formation of isomers of (**2**).†

With increasing temperature, H-abstraction (step 3) gains in importance. Using the parameters given in Scheme 2—which represent direct measurements (k_1, k_{-1}, k_3) or the best available thermokinetic estimates (k_{1a}) with benzene,[1] taking into account the small retarding effect of Cl on reactions of electrophilic $^{\bullet}$OH[18d]—k_3/k_1 will increase with temperature; moreover, step (1) becomes reversible, which engenders that the effective rate $v_{1\mathrm{eff}} < v_1$. In that case, $v_3/v_{1\mathrm{eff}} = k_3{\cdot}\{k_{-1} + k_{1a}[O_2]\}/k_1k_{1a}[O_2]$.

Using the data of Scheme 2 and taking $[O_2] = 0.2$ atm, $v_3/v_{1\mathrm{eff}} \simeq 0.1$ at 450 K, 1 at 540 K, and 10 at 600 K. Likewise, $v_2/(v_{1\mathrm{eff}} + v_3)$, the basis of the (**3**)/*m*-(**2**) product ratio, increases with temperature. Assuming that in non-aqueous solution both the reactivity and selectivity of $^{\bullet}$OH are identical with those in the gas phase, using our liquid-phase value of 0.020 at 370 K[23] and taking $A_2 = A_1$ (on a per-site basis), $E_2 - E_1 = 10$ kJ mol^{-1}. Hence, $E_2 = 14$ kJ mol^{-1}. With these values, $v_2/(v_{1\mathrm{eff}} + v_3)$ *versus* $1/T$ leads to line 2 in Figure 1*b*. Whereas this, of course, is a semi-quantitative approach only, it serves to show what type of temperature dependence the (**3**)/*m*-(**2**) product ratio should have. At a given temperature, above which the addition pathway is insignificant, (**3**)/*m*-(**2**) will not be very temperature dependent, as it is governed by k_2/k_3. Figure 1*b* shows that well above 600 K ($10^3/T < 1.5$), (**3**)/*m*-(**2**) has a clear tendency to increase rather than to give a slight continuous decrease. This phenomenon parallels the drastic change in the *o*-(**3**)/*m*-(**3**) product ratio seen in Figure 1*a*. Clearly, reactions other than those of Scheme 2 come into play at elevated temperature. In order to rationalise this, the fate of aryl radical (iii) and its isomers must be examined more closely.

If no oxygen is present (such as in expts. E1—3, Table 1), aryl radicals formed in step (3) (Scheme 2) will react with arene and thus form biaryls.[13,25] With O_2, rapid addition[26] leads to arylperoxyl radicals (v) [see Scheme 3, reaction (4)]. The fate of (v) will depend on experimental conditions. As peroxyl radicals are quite unreactive towards organic molecules,[27,28] steps (4*a*, 4*b*) are likely, resulting in formation of aryloxyl radicals (iv) (Scheme 3). With suitable H-donors, such as cyclohexa-1,3-diene, step (5) may also contribute to the conversion of (v) into (iv). Radicals (iv) can form the final product ArOH (**2**) by H transfer (step 9, Scheme 3). The formation of ArOH (**2**) from Ar$^{\bullet}$ (iii) in air necessarily involves a series of steps. The isomer distribution of the final product chlorophenol (**2**) will correspond to that of the intermediate chlorophenyl radicals (iii) only if reactions (4), (4*a* + 4*b*), and (10) proceed equally well for *o*-, *m*-, and *p*-(iii).

In one case we have shown that this condition is met: thermolysis of (**1**) with Bu^tOOH in N_2 at 568 K, in the presence of iodine, led to IC_6H_4Cl with an isomer distribution *o*:*m*:*p* = 14:52:24, close to that of (**2**) formed at such a temperature from (**1**), co-oxidant, and air[8] (Table 1, series A). *We may therefore accept this pattern as the one for H-abstraction by* $^{\bullet}$OH *from* (**1**) *at around* 550 K. There is little reason to believe that this pattern is markedly temperature-dependent. Therefore, the notable change in isomer distribution of (**2**) at temperatures above *ca.* 650 K (Figure 1*a*; series B—F of Table 1) is not thought to be due to an important shift in site selectivity for conversion of *o*-, *m*-, and *p*-(iii) with increasing temperature.

As a first alternative, the addition of $ArO_2^{\bullet}$ (v) to (**1**) needs consideration (Scheme 4).

Epoxide formation from alkenes and $HO_2^{\bullet}$ or alkylperoxyl radicals is amply documented.[28] The analogous reaction with benzene is energetically unfeasible,[1] but formation of benzene epoxide and phenoxyl radical from PhOO$^{\bullet}$ and benzene is exothermic due to resonance stabilisation of PhO$^{\bullet}$ (Figure 3*a*).

The O–O bond strength in ArOO$^{\bullet}$ (v) is much less than that in *e.g.* $HO_2^{\bullet}$, again owing to the stabilisation energy of ArO$^{\bullet}$ (iv). From Figure 3*b* it is seen that splitting of ArOO$^{\bullet}$ into ArO$^{\bullet}$ and O(^{3}P) needs no more than *ca.* 165 kJ mol^{-1}, making its thermal stability comparable to that of Et$^{\bullet}$ decomposing into C_2H_4 + H$^{\bullet}$ above *ca.* 600 K.[15,29]‡

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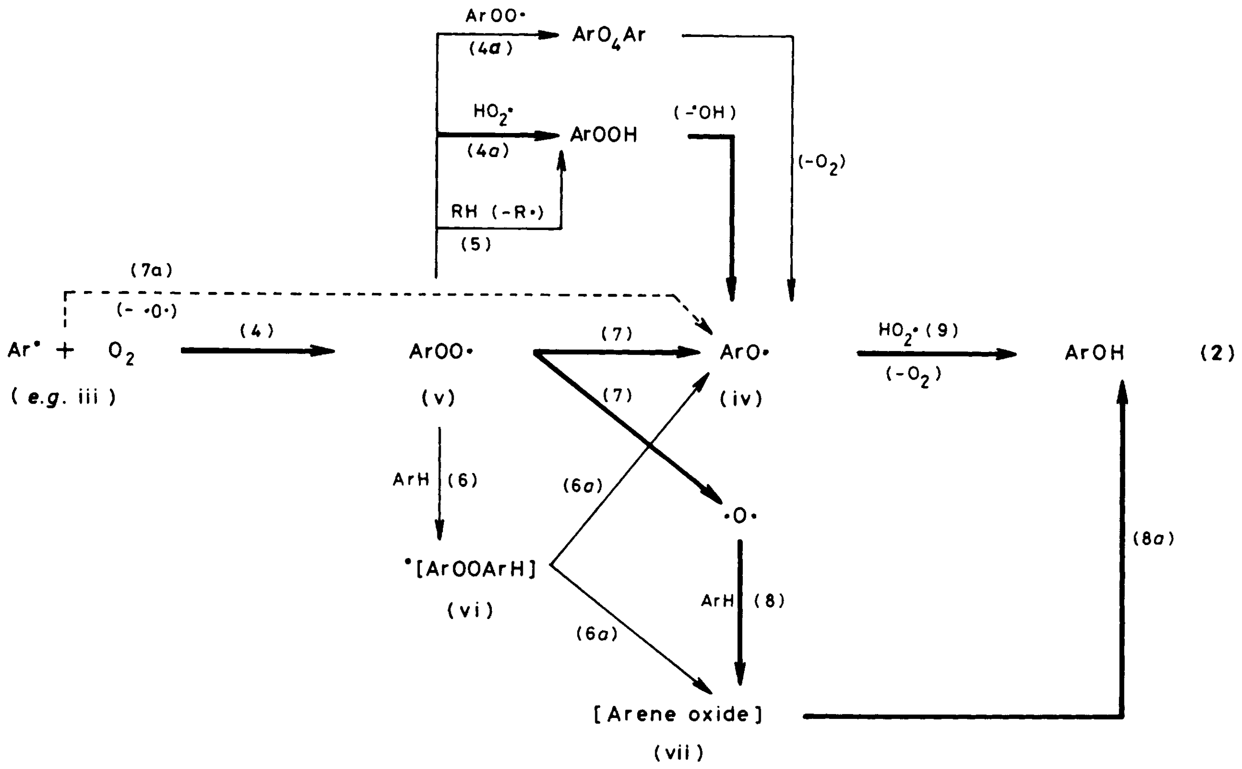
* An analogous treatment of the *p*-/*m*-(**2**) ratio leads to comparable parameters: log (*p*-/*m*-) $\simeq 1.8 - 14/\theta$.

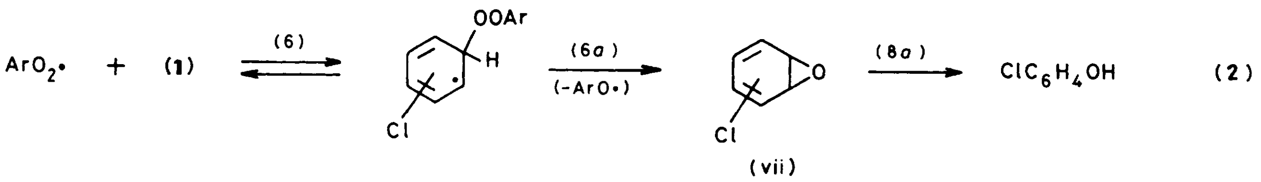
† At lower temperatures addition of O_2 to type (i) radicals, competing with steps (1*a*)—*cf.* atmospheric conversions of toluene[19]—may also contribute to the observed temperature dependence of the isomer distribution of (**2**).

‡ E_7 will be little more than the O–O bond dissociation energy of ArOO$^{\bullet}$ as the reverse of step 7, combination of ArO$^{\bullet}$ with $^{\bullet}$O$^{\bullet}$, is likely to have a negligible activation energy. Although E_4 is also very small,[26] Figure 3*b* shows that reversion of ArOO$^{\bullet}$ to Ar$^{\bullet}$ + O_2 will be unimportant.

Direct conversion of Ar$^{\bullet}$ + O_2 into ArO$^{\bullet}$ + O(^{3}P) (step 7*a* of Scheme 3) should have a transition state comprising partial dissociation of the strong bond of dioxygen, and is therefore thought to have a considerable activation energy. It is, in our opinion, an unlikely alternative to the two-step mechanism (4) + (7).



Scheme 3.



Scheme 4.

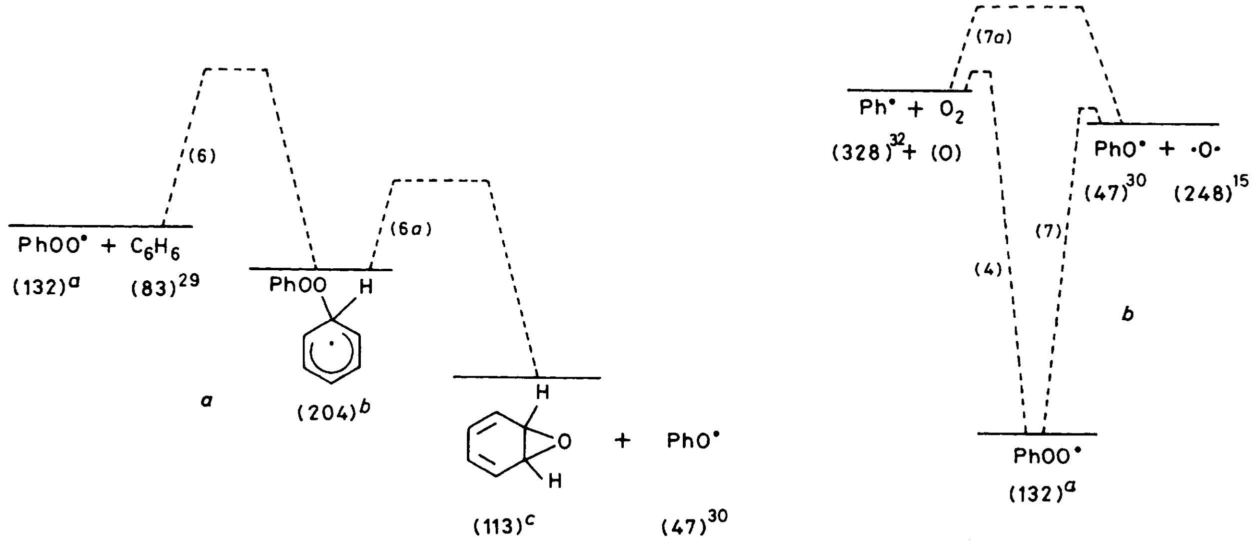


Figure 3. Energy diagrams for PhOO• + C_6H_6 (left) and Ph• + O_2 (right). *a*: Based on $\Delta H_f^\circ(\mathrm{PhOOH})_g \simeq -25$[1] and with an OO–H bond strength of 375 kJ mol^{-1}.[31] *b*: Starting from cyclohexane ($\Delta H_f^\circ = -5.5$[29]), adding the increment $\Delta\Delta H_f^\circ$ for ΔH_f° (alkene) $\longrightarrow$ ΔH_f° (alkeneoxide) *cf.*: propene→propene oxide, $\Delta\Delta H_f^\circ = -113$ kJ mol^{-1} [29] and for cyclohexane→cyclohexa-1,3-diene $\Delta\Delta H_f^\circ = 230$ kJ mol^{-1} [29].

Table 3. Rate-determining steps in phenol formation

No.	Mechanism	Rate expression	log k^a
A	4,4*a*, 9	$k_{4a}(v)^2$	9.5^{34}
B	4,6,6*a*, 9	$k_6(v)(\mathrm{ArH})$	$9 - 80/\theta^b$
C	4,7,8,9	$k_7(v)$	$13 - 170/\theta^c$

[a] k in $\mathrm{M}^{-1}\mathrm{s}^{-1}$ or s^{-1}. [b] E_a for addition of $HO_2^{\bullet}$ or $RO_2^{\bullet}$ to propene is *ca.* 60 kJ mol^{-1};[28] the value for addition to a benzene nucleus will be higher. [c] log A_7 = 13 is a common value for loss of an atom from a radical; [10,15] for E_7, *cf.* Figure 3*b*.

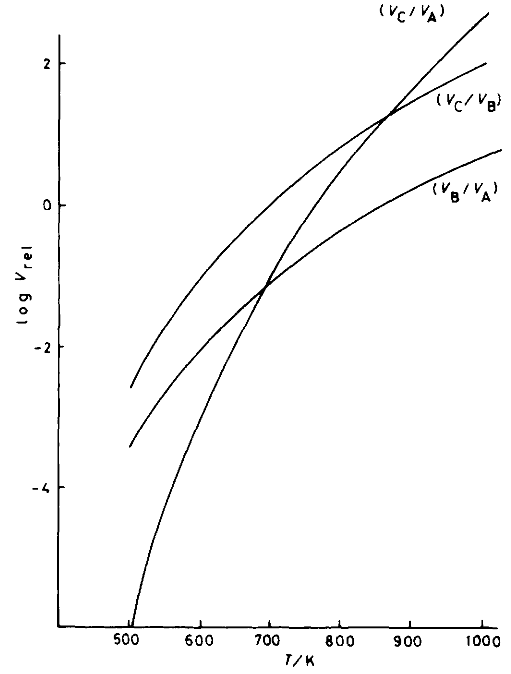
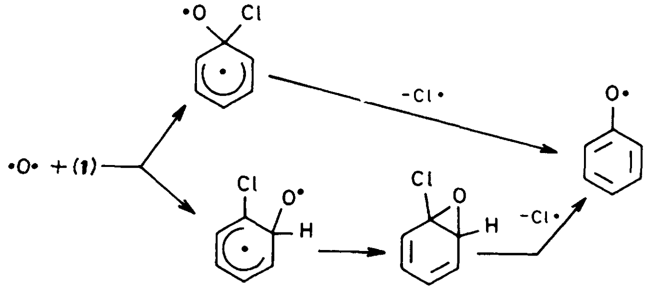


Figure 4. Importance of mechanisms of phenol formation as a function of temperature (*cf.* Table 3).



Scheme 5.

Oxygen atoms will add to (**1**) (Step 8, Scheme 3), a reaction well documented for aromatic hydrocarbons in both the gas phase and solution;[33] formation of ArOH (**2**) may proceed *via* arene oxide (vii).

In summary, there are essentially three mechanisms for conversion of $Ar^{\bullet}$ into ArOH: (A) addition of O_2, and subsequent combination/disproportionation reactions of $ArOO^{\bullet}$ (pathway 4, 4a/4b, 9)—likely to hold for relatively mild temperatures; (B) reaction of $ArOO^{\bullet}$ with ArH to give $ArO^{\bullet}$ and ArOH (bimolecular O transfer, pathway 4, 5, 6*a*, 8 + 9); and (C) unimolecular decomposition of $ArOO^{\bullet}$ to give $ArO^{\bullet}$ + $O(^3P)$, pathway 4, 7, 8 + 9—which may operate at elevated temperatures.

Semi-quantitative assessment of these three mechanisms is possible by the following thermokinetic analysis. Neglecting, for simplicity, reaction (4*b*) in mechanism (A) the rate-determining steps are as shown in Table 3.

Assigning proper values to the parameters of k_{4a}, k_6, and k_7, as given in Table 3, relative rates v_B/v_A and v_C/v_A can be estimated provided that the concentration of $ArO_2^{\bullet}$ (v) is known. Under our conditions, [v] is typically around 10^{-8}M: at lower temperatures, *e.g.* at 600 K, in system A (Table 1) the rate of formation of (**2**)—based on 0.6% conversion of (**1**) in 10^2 s—is *ca.* 10^{-7}M s^{-1}. Assuming that mechanism A holds, [v] is calculated to be *ca.* $10^{-8.2}$M. At higher temperatures, say 800 K, in cyclohexane-initiated slow combustion (series C of Table 1), the rate of formation of (**2**) is typically 10^{-6}M s^{-1}. If mechanism C is operative now (*vide infra*), $v = v_C = k_7$ [v]—see Table 3—entails [v] $\simeq 10^{-7.8}$M. When using [v] = 10^{-8}M and [ArH] = [(**1**)] = $10^{-2.6}$M throughout, Figure 4 is obtained.

These plots offer a rationale for the mechanistic change around 700 K so clearly demonstrated by Figure 1*a*. Below 700 K $v_A > v_C$, but at elevated temperatures the reverse is true. As $v_B < v_A$ (below 700 K) or $v_B < v_C$ (above 700 K), addition of $ArO_2^{\bullet}$ to arene (mechanism B of Table 3) seems, at best, of limited importance. Mechanism C, involving formation of $^{\bullet}O^{\bullet}$ (step 7) and subsequent addition of $^{\bullet}O^{\bullet}$ to arene (step 9), is the preferred pathway at high temperatures.

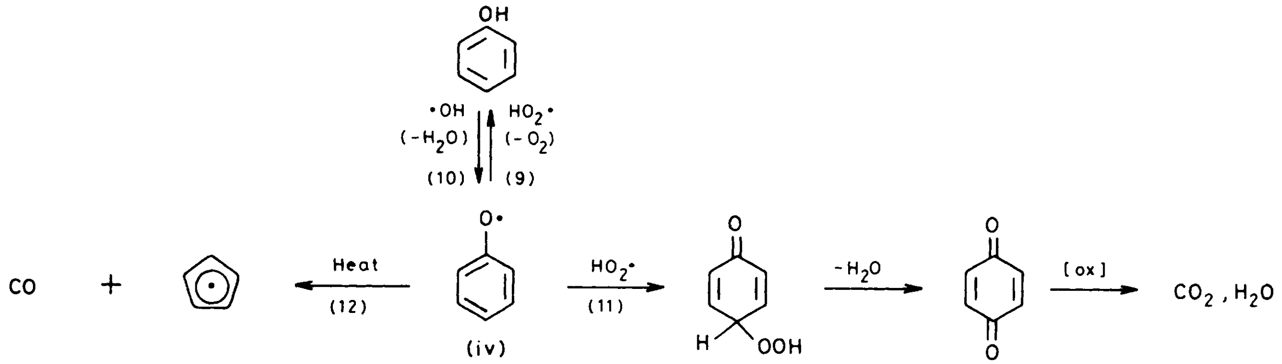
As $v_C/v_B = v_7/v_6$ is inversely proportional to the concentration of arene, reaction 6 (mechanism B) will not operate under FVT conditions (series F).

If, several pathways contribute to the formation of (**2**), a mixed isomer distribution of (**2**) will result. Even if pathway C were exclusively followed, the isomer distribution would be a composite of that of step 8, O atom addition to chlorobenzene, and that of step 9, conversion of *o*-, *m*-, and *p*-chlorophenyl radicals (iv). If, in that case, both intermediates $ArO^{\bullet}$ and $^{\bullet}O^{\bullet}$ were cleanly converted into ArOH, the resulting isomer distribution of ArOH would be a 1 : 1 composite of the two pathways 8 and 9; it should also be invariant at a given temperature. However, the scatter seen in Figures 1*a* and 1*b* shows that this is not the case; a change in the composition of the reaction mixture appears to affect the selectivity—and hence the contribution—of the various pathways leading to ArOH, including the ratio v_8/v_9. In any case, the *o*/*m*- (and *p*/*m*-)(**2**) product ratios are rather high at elevated temperatures, and this can be associated with the contribution of reaction 8: O atom addition at ambient temperature is known to lead to rather high degrees of *o*-/*p*- substitution, for example the isomer distribution of cresols from the reaction of $^{\bullet}O^{\bullet}$ atoms with toluene is found to be *o*:*m*:*p* = 64:16:20.[33b]

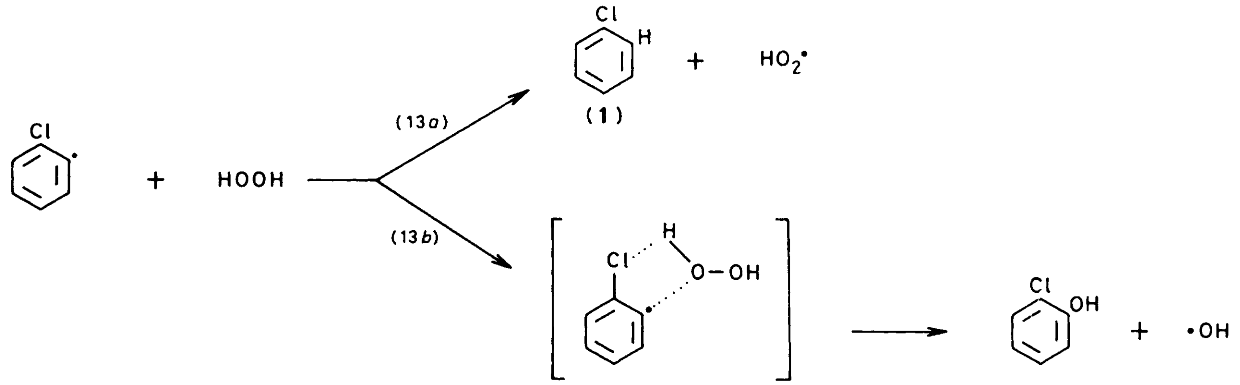
The accompanying high (**3**)/*m*-(**2**) ratio (Figure 1*b*) can be understood when considering the reaction of $^{\bullet}O^{\bullet}$ with (**1**) in more detail: both exothermal *ipso*-substitution and attack at *ortho* positions may result in net displacement of chlorine (Scheme 5).

The net isomer distribution of (**2**), and the (**2**)/(**3**) product ratio, can also be affected by further oxidation of (**2**) and (**3**). Phenol is more susceptible to air oxidation than benzene, due to its higher rate of reaction with $^{\bullet}OH$.[11] As we have worked at low degrees of conversion of (**1**), such further oxidations will have been insignificant. Under more severe conditions, *i.e.* high degrees of conversion of arene, ArOH will form $ArO^{\bullet}$ (step 10, see Scheme 6, exemplified for phenol). Oxidation of ArOH, *via* $ArO^{\bullet}$, may then proceed, for instance, by addition of $HO_2^{\bullet}$ at the *p*- or *o*-positions (step 11). (Note that step 11, when competing with step 9, will entail incomplete conversion $ArO^{\bullet} \rightarrow ArOH$.) Another possibility at high temperatures is spontaneous decomposition of $ArO^{\bullet}$ (step 12).[30]

Given that log $k_{12} \simeq 11.8 - 192/\theta$,[30b] and assuming that log k_{11} = 9.5 and that $[HO_2^{\bullet}] = 10^{-8}$M, log v_{12}/v_{11} is calculated to be < -2 at 800 K, *ca.* -0.3 at 1 000 K, and > 1 at 1 200 K. In other words, under our FVT conditions (series F), some of the



Scheme 6.



Scheme 7.

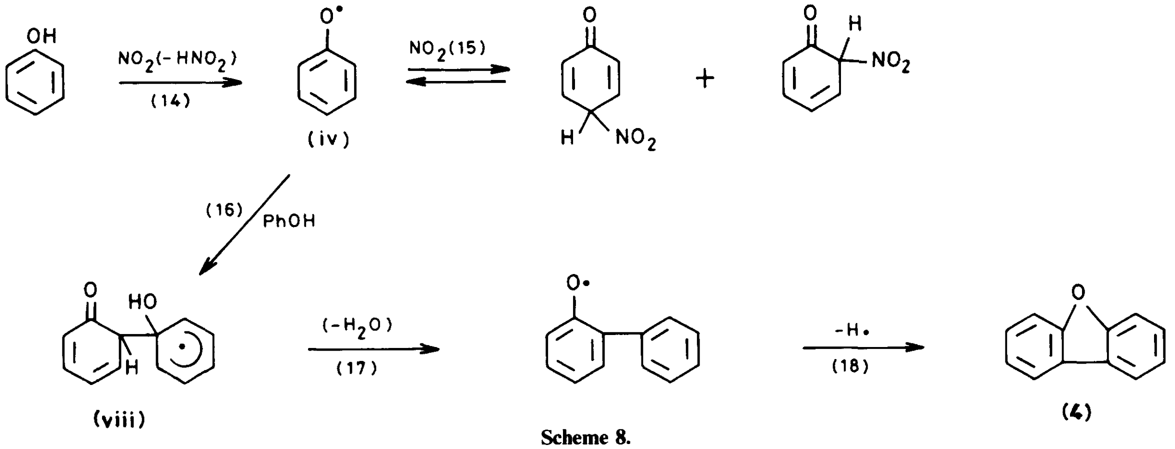
chlorophenoxyl radicals (iv) may decompose; if o-ClC$_6$H$_4$O$^•$ is thermally less stable than its m-isomer, the observed o/m-(**2**) ratio will be lower than expected (see Figure 1*a*).

At this point we wish to comment on two other series of results which take rather extreme positions in Figures 1*a* and 1*b*. First, the thermolysis of (**1**) with H_2O_2 in nitrogen (series E). Aryl radicals (iii) will arise in an isomer distribution of *ca.* 25:50:25 owing to abstraction by $^•$OH (step 3, Scheme 2). These radicals lead to $ClC_6H_4C_6H_4Cl$ as a main product. If o-, m-, and p-(iii) react with equal overall rates, the isomer distribution of dichlorobiphenyl (see Table 2) results from the arylation of (**1**) with an $o/m/p$ pattern of $\simeq$ 18:50:32, which is usual for gas-phase phenylation around 750 K.[25] Some of the radicals o-, m-, p-(iii) lead to (**2**), with an isomer distribution (such as 44:45:11 for expt. E2) greatly different from those underlying formation of $ClC_6H_4C_6H_4Cl$. Formation of (**2**) may be due to traces of O_2, resulting from decomposition of H_2O_2, reacting *via* step 4 to give ArOO$^•$ (v). Reaction of (iii) with H_2O_2 is a likely alternative, however, whether by H-donation to restore starting (**1**), [step 13*a*, Scheme 7, exemplified for o-(iii)] or by O–O bond splitting, a reaction which is comparable with the reactions of H$^•$ atoms[35a] or alkyl radicals[35b] with alkylhydroperoxides (step 13*b*). This latter reaction may proceed with a higher rate for o-(iii) than for its m- and p-isomers, owing to complexation between HOOH and the chlorine substituent, as depicted in Scheme 7.

Second, slow combustion of (**1**) with added nitroethane, giving rather low o/m-(**2**) and (**3**)/m-(**2**) ratios in the higher temperature region. Nitrogen dioxide may be responsible for this as NO_2 converts ArOH into ArO$^•$ (step 14, see Scheme 8, exemplified for phenol). Furthermore, NO_2 can react with ArO$^•$[11] (step 15). Although the C–NO$_2$ bonds thus formed probably are not stronger than *ca.* 170 kJ mol^{-1}, the nitrodienone intermediate may be susceptible to further oxidation, as tautomerisation to phenol is slow in the vapour phase.[36] Nitrogen oxides also engender formation of DBF (Table 2, expts. 1—4). We will discuss the mechanism(s) of its formation from phenol in a forthcoming paper,[37] but wish to suggest that, consonant with findings on pyrolysis of ^{14}C-labelled phenol,[38] phenoxyl radicals add to phenol (16) to give intermediates such as radical (viii), Scheme 8, which can lose H_2O (step 17) and then cyclise (18) with the elimination of an H atom.

(iii) *Model Experiments.*—In the oxidations of (**1**) discussed above, with chlorophenyl radicals (iii) as intermediates, no direct insight can be obtained into the contributions of pathways 8 and 9 (Scheme 3) to the production of chlorophenols (**2**). In order to learn more about the fate of Ar$^•$ and ArO$^•$ under relevant conditions at elevated temperatures, we have conducted model runs with *in situ* sources of specific aryl radicals (expts. G1, G2, Table 1). In run G1 azobenzene decomposed to give Ph$^•$[25] whereas in G2 'extra' p-ClC$_6$H$_4^•$ was generated.[39] Without these addends, no (**2**) would have been formed. Even in the absence of aliphatic compounds (G1) both (**2**) and (**3**) are formed. When taking into account that phenol (**3**) is also made from (**1**), obviously the yield of chlorobenzene-derived products [0.48 mmol/h of (**2**) and, say 0.12 mmol/h of (**3**), or together *ca.* 0.4 equiv. based on the amount of C$_6$H$_5^•$ which, at best, had been produced from azobenzene] is much higher than that of phenol made from the said phenyl radicals (0.1 equiv. or less).

In expt. G2, clearly 'extra' p-(**2**) is formed, which amounts to *ca.* 0.015 mmol/h. The main portion of (**2**) (0.084 mmol/h) plus *ipso* product (**3**) (0.024 mmol/h) is seven times larger. Clearly only a very limited fraction of Ar$^•$ intermediates succeed in forming ArOH, whereas the accompanying conversion of 'bulk' arene ArH⟶ArOH is at least several-fold. This strongly



Scheme 8.

suggests that in the slow combustion of (**1**), at elevated temperatures, pathway 8, the reaction of (**1**) with O atom, is the major contributor to the formation of (**2**).

In an effort to substantiate further the O-transfer mechanism, we have studied the slow combustion of *p*-deuteriochlorobenzene and mixtures of benzene and C_6D_6. A full report will be published separately,[40] but some main features can be inferred from the data reported in Table 1 for runs G3, 4, and 5. The formation of (**3**) and C_6D_5OH from C_6H_6/C_6D_6 (run G3) does not involve a significant intermolecular kinetic isotope effect. However, the isomer distribution of the chlorophenol mixture obtained from *p*-DC_6H_4Cl (run G4) under comparable conditions reveals a substantial internal isotope effect. Both facts are in perfect accord with O-atom addition as a major reaction, the internal isotope effect being due to the necessary rearrangement (step 8*a*, Scheme 3) following O-atom addition (**8**). Interestingly, slow combustion at lower temperatures (expt. G5) of C_6H_6/C_6D_6 does lead to an external isotope effect; k_H/k_D = 2.2, which supports the importance, if not the exclusive role, of pathway 4, 4*a*/4*b*, 9, the kinetic isotope effect stemming from the difference in rates for H(D) abstraction by ˙OH from the two substrates.

Experimental

Chemicals.—Starting and reference compounds were, in general, available as high-grade commercial products, and used as such. Hydrogen peroxide of *ca.* 90% purity was obtained as reported earlier,[41] and t-butyl hydroperoxide was purified as described elsewhere.[8] Allyl *p*-chlorobenzoate[42] was available from earlier investigations. C_6D_6 had a D content of 99.5%. [4-^{2}H]-Chlorobenzene was prepared by reaction of the Grignard compound of *p*-ClC_6H_4Br in THF, with CH_3CO_2D, D content 93.4%.

Apparatus and Techniques.—Gas-phase thermolyses were performed using Pyrex or quartz stirred-tank flow type reactors with volumes ranging from 43—900 cm^3; the capacity of inlet and outlet tubes being less than 10% of the reactor chamber volumes. In general, organic substrates were introduced as liquid mixtures by using a motor-driven syringe; *cf.* ref. 13. H_2O_2 and Bu^{t}OOH were introduced as a vapour by passing a calibrated stream of nitrogen through a set of two washing bottles containing the liquid peroxide, at a constant temperature of 295 K. Products were collected in a trap cooled with liquid nitrogen. Usually a known amount of internal standard, such as *p*-dichlorobenzene, was added before g.c.-analyses.

Flash-vacuum experiments were conducted in a quartz tank flow reactor of 12 cm × 3.6 cm^2 ($V_r \simeq 43$ cm^3). The organic feed, a mixture of (**1**) and butanol, was placed in a washing bottle which was connected to the reactor inlet by means of a capillary tube. The bottle and tube were kept at 60 °C and vapours of the feed were introduced by means of measured stream of air which passed through the feed due to the operation of a vacuum pump. This pump was connected to the second of two receiving flasks which were cooled with liquid nitrogen. The pressure in the reactor system was measured by a manometer connected to the reactor outlet.

Another known stream of air was introduced at the entrance of the reactor *via* a needle valve, so as to control the feed/oxygen intake ratio and the residence time at a given temperature.

Photochemical experiments were performed as described before.[43]

Analyses.—Organic products were qualitatively and quantitatively determined by g.l.c. as described earlier;[1] phenolic products were in general silylated[1] before analysis.

PhOH/C_6D_5OH product ratios were measured by g.c.–m.s. (LKB-2091).

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