Gas Phase Oxygenation of Benzene Derivatives at *ca* 300 K With O(^{3}P) Atoms Produced by Microwave Discharge of N$_2$O. Part 1. Rates and Mechanism of Phenol Formation

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The reactions of O(^{3}P) with benzene derivatives C$_6$H$_5$Z (Z = H, Cl, F, CH$_3$, CF$_3$, and OCH$_3$) have been studied in a flow reactor at ambient temperature in a helium atmosphere, using microwave discharge of nitrous oxide as the source of oxygen atoms. The main products are the substituted phenols; substituted cyclohexadienes were also observed. *ipso*-Substitution, with formation of phenol, is also an important path, except in the reaction with fluorobenzene and trifluorotoluene. The oxygen atom adds to the benzene ring to form a triplet adduct, which can isomerize to phenol or lose an H-atom, producing a phenoxyl radical. This phenoxy radical also leads to phenol *via* disproportionation with a cyclohexadienyl radical, the latter arising from H-atom addition to the substrate. Relative rates for O-addition were determined by competition experiments with benzene as a reference. A Hammett plot, using σ constants for the *meta*- and *para*-positions demonstrated the electrophilic character of O(^{3}P). A good correlation was found for the *para*-positions, with ρ = −1.1.

Reactions involving ground state atomic oxygen are important in combustion processes, atmospheric chemistry, and air pollution. A relatively large number of studies have been devoted to the kinetics and mechanism of oxygen atom reactions with alkenes and alkynes.[1] Relatively few studies have dealt with aromatics. The mechanism for the reaction of the O-atom with benzene is poorly understood, and product identification is complicated by the formation of non-volatile, possibly polymeric material. The major volatile reaction product, phenol, accounts for only 10%[2] to 13%[3,4] of the benzene consumed. Carbon monoxide has also been reported as a reaction product,[3,5] although others did not mention or address the formation of CO.[6] Spectroscopic examination of the polymeric material using IR and NMR suggested the presence of –OH, C–O–C, and CHO-functional groups.[2,3] The mass spectrometric analysis of the polymeric residue yielded m/z = 185 as the most intense peak;[2] this probably arose from (C$_6$H$_5$OC$_6$H$_5$O)-, suggested to be formed by sequential attack of intermediate phenoxyl radicals[6] on benzene. Oxidation of equimolar amounts of benzene and hexadeuteriobenzene gave a value of 1,[7] 1.1,[8] 1.03 ± 0.02,[2] and 1.14 ± 0.04[9] for the intermolecular kinetic isotope effect k_H/k_D. This means that cleavage of the aromatic C–H bond is of little or no significance in the rate-determining step.

The first step in the formation of phenol is generally believed to be (irreversible[7]) O-atom addition to the aromatic ring to form a triplet biradical adduct. This highly energetic reaction intermediate can decay in different ways: it can eliminate a H-atom or make a radiationless transition to the S$_0$ manifold of phenol.[6]

A number of studies have dealt with product formation and mechanism of the reaction of O(^{3}P) atoms with toluene[4,9–14] and ethyl-[7,8] and trimethyl-benzene.[7,8,15] However, few other substituted benzenes have been studied,[8] and hence no insight exists into the effects of substituents on rates and product formation. We have therefore studied the reaction of O(^{3}P) with a series of substrates comprising benzene, chlorobenzene, fluorobenzene, toluene, and anisole.

Table 1. Product distributions for the reaction of cyclohexene (or cyclohexene–benzene) with O(^{3}P) at 298 K.

S	In[a]			Out[b]			
	N$_2$O	He	S	CHE	CHN	CPC	PH
C$_6$H$_{10}$[c]	4.26	1 002	87	190	75.6	59.6	—
C$_6$H$_6$	4.26	810	56.4	—	—	—	24.0[d]
C$_6$H$_{10}$–C$_6$H$_6$	1.38	936	5.4/120	16.8	16.8	13.2	10.2[e]

[a] Flow in mmol h^{-1}, microwave discharge power 30 W, reflected 2 W.
[b] Flow in μmol h^{-1}, CHE = 1,2-epoxycyclohexane, CHN = cyclohexanone, CPC = cyclopentanecarboxaldehyde, PH = phenol.
[c] Based on GC analyses; the peak surface areas of CHE + CHN + CPC constitute 71% of the total amount of cyclohexene derived products; other identified products (μmol h^{-1}): hex-2-enal (6.6), hex-5-enal (9). [d] The surface area of phenol constitutes 58% of the total amount of benzene derived products; other identified product cyclohexa-1,4-diene (3 μmol h^{-1}). [e] k_{CH}/k_B (see the text) = (39.6 + 16.8 + 13.2)/(10.2) × (0.58/0.71) × (120/5.4) = 124.

Results

The performance of the flow-discharge system was first tested using cyclohexene as the substrate. The main products (see Table 1) observed, 1,2-epoxycyclohexane (1), cyclohexanone (2), and cyclopentanecarboxaldehyde (3), are in accord with the reported[16] mechanisms for conversion of the initially formed cyclohexene–O(^{3}P) triplet biradical adduct (I) (Scheme 1). Under our experimental conditions, the relative product yields appeared to be independent of the pressure (20–100 mbar*) in the reaction vessel. Interestingly, a comparable product distribution[17] was obtained when 1,2-epoxycyclohexane was pyrolysed in an inert atmosphere at *ca.* 770 K. This similarity

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* 1 mbar = 100 Pa.

Table 2. Typical product distributions for reaction of O(^{3}P) with C$_6$H$_5$X.[a]

Exp.	X	In[b]		Out[b]		C$_6$H$_5$OH	T/K
		C$_6$H$_5$X	He	XC$_6$H$_4$OH	o:m:p^c	XC$_6$H$_4$OH	
1.1	H	78.0	1 250	0.052	—	—	293
1.2		78.0	1 027	0.017	—	—	293
2.1	Cl	61.2	896	0.008	47:33:20	0.27	335
2.2		61.2	896	0.020	48:30:21	0.25	335
3.1	F	83.4	1 175	0.066	54:27:19	0.052	300
3.2		139.2	1 169	0.057	46:35:19	0.057	307
4.1	CH$_3$	59.4	1 172	0.0069	66:22:12	0.15	316
4.2		59.4	1 172	0.0073	65:22:13	0.15	316
5.1	CF$_3$	90.0	1 122	0.028	24:59:17	0.058	314
5.2		90.0	1 122	0.032	26:58:16	0.062	314
6.1	OCH$_3$	40.2	1 024	0.0025	90:4:6	0.31	348
6.2		39.0	1 024	0.010	78:8:14	0.29	347

[a] Flow in mmol h^{-1}, in nitrous oxide 4.8 mmol h^{-1}, as 1% in He, microwave discharge power 100 W, reflected *ca.* 10 W. Pressure during experiments varying, from 10–40 to 150–300 mbar. [b] Flow: mmol h^{-1}. [c] Based on silylated phenols.
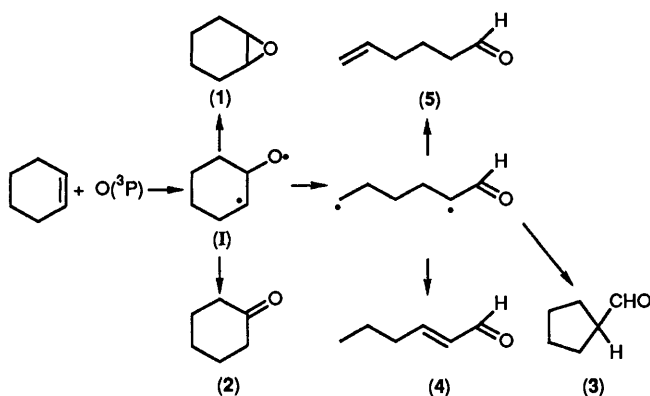
Scheme 1.

indicates that the rate of intersystem crossing of the adduct radical from the triplet to the singlet state must be comparable to that for loss of a hydrogen atom. Note that the overall yield of oxy compounds [and hence the proportion of O(^{3}P) atoms available for addition to cyclohexene], based on the initial amount of N$_2$O in the discharge cavity, is approximately 10%.

Next, competition experiments were conducted with benzene–cyclohexene mixtures. To ensure comparable rates of conversion of the two substrates, the benzene–cyclohexene intake ratios were kept well above 25. Phenol is the main product stemming from benzene/O(^{3}P) interaction (see below). When benzene was replaced by hexadeuteriobenzene no H/D exchange in cyclohexane or benzene derived products was observed. If essentially all adduct biradicals produced are converted into stable end products, the observed product ratios permit calculation of the relative rate of addition of O(^{3}P) to cyclohexene *versus* benzene (k_{CH}/k_B), using the initial intake ratio of these substrates [equation (1)]. The derived rate constant

$$k_{CH}/k_B = (\text{products})_{CH}/(\text{products})_B \times (C_6H_6)/(C_6H_{10}) \quad (1)$$

(120 ± 10) seems to be at variance with the reported absolute values[1] for the individual reactions at 298 K: $k_B = 1.2 \times 10^7$ mol^{-1} dm^{-3} s^{-1} and $k_{CH} = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. However,

these separate rate constants have been measured with different experimental techniques and their ratio (*ca.* 10^3) is therefore not well defined. Subsequently, experiments were performed with individual aromatic substrates.

Benzene.—Under proper conditions, *i.e.* low concentrations of N$_2$O, phenol was the major product and formation of nitro-derivatives was negligible.[18] In addition, small proportions of 1,4- and minor proportions of 1,3-cyclohexadiene were formed. Table 2 gives results of some representative experiments. The trapped product also contained some polymeric material, the nature of which has not been further examined.

Chlorobenzene.—The reaction of O(^{3}P) with chlorobenzene resulted in a product mixture with only three isomers of chlorophenol, the *ipso* substitution product phenol, and a chlorocyclohexadiene. The isomer distribution of chlorophenol was independent of the concentration of chlorobenzene used; likewise the phenol–chlorophenols ratio was essentially the same, *viz.* 1:4 (Table 2).

Fluorobenzene.—The reaction of oxygen atoms with fluorobenzene showed qualitatively the same product pattern as chlorobenzene: the three fluorophenols, phenol and fluorocyclo-hexadiene(s). Representative data on product distribution are given in Table 2.

Toluene.—The reaction of O-atoms with toluene led to the expected products; the cresols (hydroxytoluenes) and phenol (see Table 2). Several other products were present, with benzaldehyde as the most important, which involves reaction of the methyl group of toluene. Other, minor peaks may have been due to reaction of the oxygen atom with impurities in the toluene. Anisole was searched for, but could not be found as a product.

α,α,α-Trifluorotoluene.—The main products are *ortho-*, *meta-*, and *para*-trifluoromethylphenol, the *meta* isomer being the major. Phenol was observed in low concentrations only (see Table 2). Trifluoromethylcyclohexadienes were also observed. Besides the substituted phenols, a number of other products were formed, and an attempt was made to identify some of these by means of GC–MS.

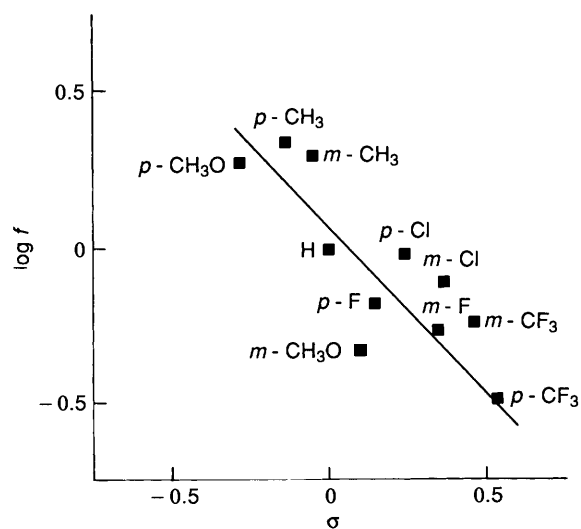**Table 3.** Product distributions for reactions of $O(^3P)$ with $C_6H_5X + C_6H_6$.[a]

		In[b]		Out[b]			
Exp.	X	C_6H_5X	C_6H_6	XC_6H_4OH	C_6H_5OH	$o:m:p$	k_{rel}[c]
2.6	Cl	30.6	78.0	0.0019	0.0088	49:31:20	0.89
2.7		27.6	73.8	0.0018	0.0073	50:32:18	0.79
2.8		31.8	102	0.0012	0.0062	49:32:19	0.85
3.8	F	48.6	25.8[d]	0.021	0.015[e]	47:32:21[f]	0.60[g]
3.9		37.8	12.9[d]	0.022	0.012[e]	46:35:19[f]	0.53[g]
3.10		51.6	25.8[d]	0.016	0.011[e]	51:31:18[f]	0.61[g]
4.5	CH_3	30.0	97.2	0.0018	0.0022	69:19:12	2.96
4.6		54.6	39.0	0.0033	0.0015	68:21:11	3.00
4.7		51.6	46.2	0.0027	0.0014	69:20:11	2.95
5.5	CF_3	60.6	39.6	0.0013	0.0003	25:61:14	0.35
5.6		49.8	44.4	0.0023	0.0005	27:56:17	0.31
5.7		68.4	22.2	0.0042	0.0001	26:58:16	0.34
6.6	OCH_3	32.4	75.6	0.0013	0.0018	81:6:13	2.97
6.7		24.6	75.6	0.0022	0.0026	82:6:12	2.22
6.8		32.4	75.6	0.0011	0.0019	83:6:11	2.68

[a] In 1% nitrous oxide in He, 4.8 mmol h^{-1}, microwave discharge power 100 W. [b] mmol h^{-1}. [c] Calculated based on a known % of phenol formation from *ipso* substitution, determined in experiments with C_6H_5X only; *i.e.* for chlorobenzene 0.25, toluene 0.15, trifluorotoluene 0.06, and anisole 0.30. [d] Chlorobenzene rather than benzene. [e] ClC_6H_4OH. [f] Fluorophenols; chlorophenols $o:m:p$ 46:32:22 (3.8), 46:33:21 (3.9), 50:31:19 (3.10). [g] Based on p-FC_6H_4OH-p-ClC_6H_4OH ratio, because phenol and o-fluorophenol could not be separated properly.

Table 4. Partial rate factors for phenol formation from C_6H_5X and $O(^3P)$.

X	f_p	f_m	f_{ipso}
F	0.66[a]	0.54[a]	0.17[a]
Cl	0.96[b]	0.78[b]	1.01[b]
CH_3	2.14[c]	1.96[c]	2.32[c]
CF_3	0.32[d]	0.58[d]	0.11[d]
OCH_3	1.89[e]	0.47[e]	3.65[e]

[a] Based on 19% p- and 31% m-FC_6H_4OH, and C_6H_5OH:FC_6H_4OH = 0.06. [b] Based on 19% p- and 31% m-ClC_6H_4OH, and C_6H_5OH:ClC_6-H_4OH = 0.25. [c] Based on 12% p- and 22% m-$CH_3C_6H_4OH$, and C_6H_5OH:$CH_3C_6H_4OH$ = 0.15. [d] Based on 16% p- and 58% m-$CF_3C_6H_4OH$, and C_6H_5OH:$CF_3C_6H_4OH$ = 0.06. [e] Based on 12% p- and 6% m-$CH_3OC_6H_4OH$, and C_6H_5OH:$CH_3OC_6H_4OH$ = 0.30.

Table 5. Phenolic products[e] from reactions of $O(^3P)$ + toluene.

Ref.	T/K	Phenol	o-Cresol	m-Cresol	p-Cresol
This work	316	13.0	57.4	19.1	10.4
15[a]	373	8.7	80.5	4.7[f]	
8[b]	273	1.0	62	37[g]	
22[c]	298	—	78	22[h]	
9[d]	303	8.0	58.8	15.3	17.9

[a] Hg photosensitized decomposition of N_2O in a closed circulating system at 67–530 mbar. [b] γ-Radiolysis of liquid CO_2 in a closed system. [c] Hg photosensitized decomposition of N_2O at 512 mbar. [d] Hg photosensitized decomposition of N_2O in a flow system at atmospheric pressure. [e] Normalized to 100%. [f] *meta* ≤ 10% of *para*. [g] *meta* and *para* not separated. [h] *meta* ≤ 4–5% of total isomers.

Figure 1. Partial rate factors f_m, f_p as function of σ_m and σ_p.

In summary, derivatives were found which must have been formed by 'single' addition of an O-atom to trifluorotoluene

(the phenols, hydroxylated trifluoromethylcyclohexadienes and two other products with the composition $C_6H_5CF_3O$); conpounds with an 'extra' F-atom, also indicating loss of fluorine from some intermediate [1-fluoro-2-trifluoromethyl-benzene and fluoro(hydroxy)trifluoromethylbenzenes]; compounds that demonstrated uptake of two O-atoms, and products which have even built in three O-atoms. The total amount of products other than $CF_3C_6H_4OH$ is similar to that of the regular phenols, but is distributed over at least 20 products, the most abundant comprised *ca.* 15% of the phenols. More details about the identification and mechanistic considerations concerning formation of these products can be found elsewhere.[18]

Anisole.—The product mixture from the reaction of O-atoms with anisole shows some analogy with that of trifluorotoluene. Table 2 gives some representative data. The most abundant products have been investigated, after silylation, by GC–MS. The following peaks could be identified upon comparison with pure compounds as to retention time and mass spectrum; *ortho*-, *meta*-, and *para*-methoxyphenol, phenol, and furthermore the three dihydroxybenzenes, catechol, resorcinol, and hydro-quinone. Three compounds seem to be dihydroxymethoxy-benzenes. More details concerning the identification and formation of the last six compounds can be found elsewhere.[18]

Table 6. Phenols from reactions of $O(^3P)$ with monosubstituted benzenes C_6H_4Z.

Substrate Z	Products (this work)				Products (ref. 9)			
	C_6H_5OH	ZC_6H_4OH			C_6H_5OH	ZC_6H_4OH		
		o	m	p		o	m	p
CH_3	13.0	57.4	19.1	10.4	8.0	58.8	15.3	17.9
F	4.8	47.6	29.5	18.1	2.0	43.5	27.0	27.5
CF_3	5.7	24.5	54.7	15.1	1.7	27.6	40.2	30.5
OCH_3	23.1	63.1	4.6	9.2	n.d.[a]	80.0	2.5	17.5

[a] Could not be determined because of concurrent photolysis to yield phenol.
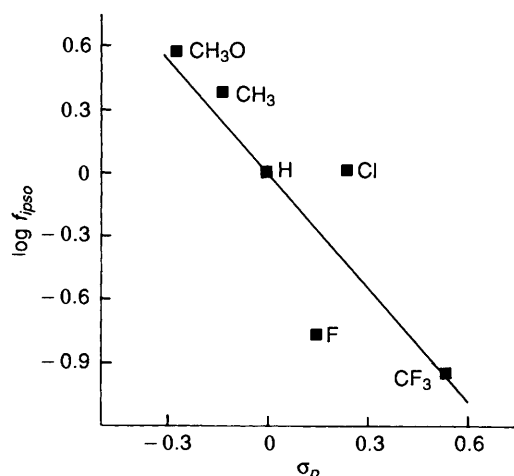
Figure 2. Partial rate factor f_{ipso} as function of σ_p.

Competition Experiments.—Competition experiments were conducted by studying each substrate except fluorobenzene in admixture with benzene. Fluorobenzene could not properly be separated from benzene by gas chromatography so instead, a competition experiment between fluorobenzene and chlorobenzene was conducted. The results are summarized in Table 3. From the isomer distributions and the relative rates partial rate factors f_i can be calculated (Table 4). Figure 1 shows a plot of the partial rate factors, f_p and f_m versus the Hammett σ_p and σ_m constants.[19] The correlation is quite good, especially for the para-positions; for that case the drawn line has $\rho = -1.1$ (correlation coefficient 0.94). (A plot against σ^+ gave a correlation coefficient of only 0.77.) We have also calculated partial rate factors for *ipso* substitution, $f_{ipso} = (\% \ ipso/100) \times [k_{rel}/k_{\Phi H}/6)]$, with $\%$ *ipso* used as found in experiments with the single substrates. When searching for a proper substituent constant to correlate these data, σ_p, σ_m, σ^*,[20] and R[21] were tried, however, with limited success. σ_p values appeared to give the best values, see Figure 2. The drawn line represents $\rho = -1.8$, $r^2 = 0.75$.

Discussion

Formation and Composition of Phenols.—In general, the gas phase reaction of $O(^3P)$ atoms with monosubstituted benzenes leads to (substituted) phenols as major products. In this section we discuss isomer distributions of ZC_6H_4OH, and the importance of *ipso* substitution $C_6H_5Z \longrightarrow C_6H_4OH$, in relation to the mechanism for $O(^3P)$–C_6H_5Z reactions.

As toluene is the best studied substrate we can compare our observations with data from the literature. A summary of products obtained near room temperature is given in Table 5. There appear to be considerable differences in product distribution which may be due to the difference in techniques and conditions used. Grovenstein and Mosher[9] have reported product distributions for reaction with a range of benzene derivatives at room temperature using the Hg photosensitized decomposition of nitrous oxide at atmospheric pressure in a flow system. Table 6 gives an overview of some of these data compared with our results. There is a clear parallel in the $o:m:p$ distributions; note the high *ortho* content for toluene and anisole, the medium value for fluorobenzene, and the lower percentage for trifluorotoluene. The latter is very likely due to steric hindrance. A high *ortho* content is typical for homolytic aromatic substitution, governed by relative rates of addition of the radical to the respective *ortho-*, *meta-*, and *para*-sites.[23] In this sense, formation of phenols *via* addition of the O-atom is apparently no exception. However, $m/2p$ ratios show important differences, which are consistently higher in our case. Qualitatively the results are the same, with $m/2p$ smallest for anisole, and highest for trifluorotoluene. In our case, $m/2p = 1.8$ for trifluorotoluene, whereas Grovenstein and Mosher's[9] results entail $m/2p = 0.7$. The origin of these differences is as yet unknown. Our value of $\rho = -1.1$ in Figure 1 is comparable to the value of Grovenstein and Mosher.[9] They plotted partial rate factors for *meta-*, and *para*-isomers against σ^+ and reported a good correlation with $\rho = -1.15$. Zadok and Mazur[14] reported $\rho^+ = -1.4$ in their liquid phase experiments with substituted benzenes. A comparatively small negative value for ρ is consistent with the addition of electrophilic O-atoms and with the intermediacy of triplet diradicals. Data on the relative importance of *ipso* substitution do not show great discrepancies; in both studies, fluorobenzene and trifluorotoluene gave rise to low yields of phenol.

Mechanistic Aspects.—Formation of substituted phenols in the reaction of an O-atom with a benzene derivative is not a single step reaction. Addition of $O(^3P)$ to a site of the monosubstituted benzene C_6H_5Z will primarily result in the triplet biradicals (II) and (III) in Scheme 2. Kinetic studies revealed that with benzene itself step i has an activation energy of ca. 18 kJ mol^{-1}.[1]

For the addition of $O(^3P)$ to toluene an activation energy of 14 kJ mol^{-1} has been reported.[1] Substituent effects are likely to be small. A comparison with data on OH radical reactions seems appropriate, as both the $O(^3P)$ atom and the OH radical have electrophilic character and add to C=C double bonds. Moreover, good correlations exist between $O(^3P)$ and OH· reaction rate constants for certain classes of organic compounds, like (a)cyclic alkenes and aromatic hydrocarbons.[24] The activation energies for addition of OH· to monosubstituted benzenes at temperatures <350 K are all near zero: E_a for benzene is 1.6,[25] for bromobenzene 1.5,[25] and for methoxybenzene -3.3[26] kJ mol^{-1}.
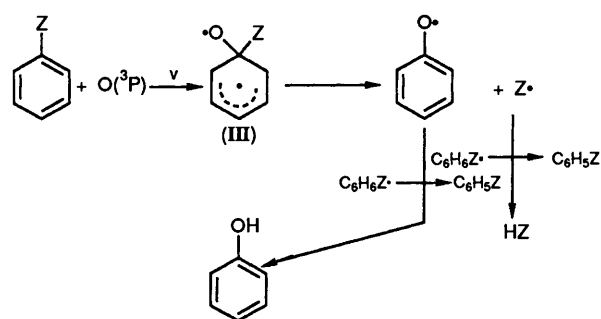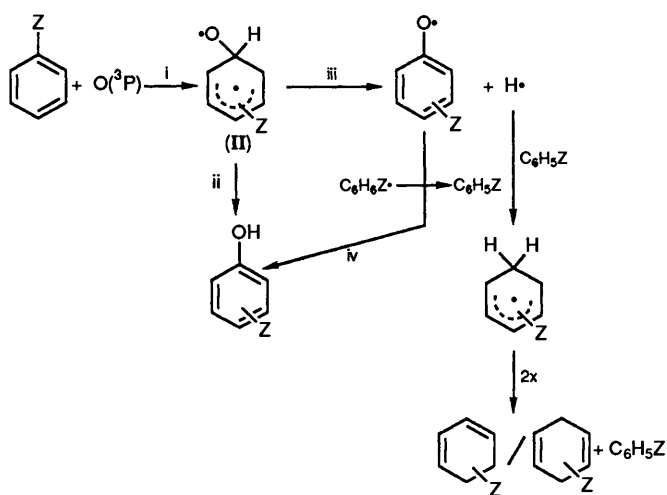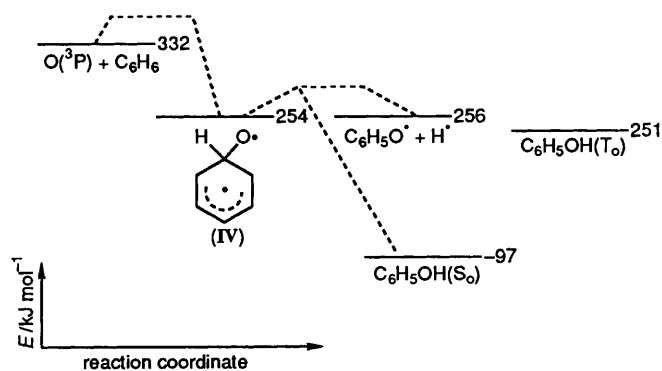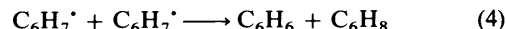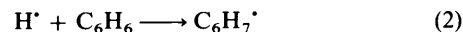
Scheme 2.

Figure 3. Energy diagram for O(^{3}P) + benzene in kJ mol^{-1}. Heats of formation from refs. 32 and 34, ΔH_f^o of (IV) was calculated from the heat of formation of the methyl substituted triplet biradical, 222 kJ mol^{-1}, reported by Baseman et al.[11] and the increment due to introduction of a methyl group, $C_6H_6 \longrightarrow C_6H_5CH_3$ or $C_6H_5OH \longrightarrow o$-$CH_3C_6H_4OH$ (-32.5 kJ mol^{-1}).[32]

The fate of type (II) intermediate (Scheme 2) will depend on reaction conditions such as pressure, radical concentration, and temperature. (II) Has two available channels to products: either triplet–singlet conversion and rearrangement to phenol, step ii, or decomposition to yield a phenoxyl radical, step iii. The relative importance of both paths could be substantiated on the basis of a study on the reaction of O(^{3}P) with C_6H_6–C_6D_6 mixtures which will be fully described elsewhere.[18] In short, while for C_6H_6 step iii predominates, only one-third of the C_6D_6O intermediates undergo the corresponding reaction.

Inspection of the enthalpy diagram (Figure 3) reveals that the overall reaction to ground state phenol is highly exothermic, no

less than 431 kJ mol^{-1}. Using the most recent value for the O–H bond strength of phenol,[27] 351.5 kJ mol^{-1}, direct formation of phenoxyl + H is still 79 kJ exothermic (Table 7). Loss of a H-atom from the intermediate (IV) is close to thermoneutral but the activation energy will be substantial.[28] Our observation of cyclohexadienes as products points to at least partial formation of H-atoms from (IV). The H-atom adds to a benzene ring and forms a cyclohexadienyl radical, exemplified for benzene itself in equations (2)–(4). Disproportion of this radical

$$H^{\bullet} + C_6H_6 \longrightarrow C_6H_7^{\bullet} \qquad (2)$$

$$C_6H_7^{\bullet} + C_6H_5O^{\bullet} \longrightarrow C_6H_6 + C_6H_5OH \qquad (3)$$

$$C_6H_7^{\bullet} + C_6H_7^{\bullet} \longrightarrow C_6H_6 + C_6H_8 \qquad (4)$$

with phenoxyl leads to phenol (and benzene), whereas two cyclohexadienyl radicals give rise to cyclohexadienes. Addition of a H-atom to benzene has E_a ca. 17 kJ mol^{-1}.[29] The activation energies for the mono-substituted benzenes are not very different (10–24 kJ mol^{-1}).[30] According to James and Suart,[31] the combination–disproportionation ratio is 0.45 for the cyclohexadienyl radical, which implies formation of combination products $C_{12}H_{14}$. These may be oxidized during work-up and/or analysis. (In the reactions with benzene, we did see in some cases, a very small peak in the gas chromatogram having the retention time of biphenyl with a mass spectrum that resembled that of cyclohexadiene, and in one experiment a biphenyl peak was indicated.)

Formation of phenol from substituted benzenes can be rationalized by *ipso* addition of O(^{3}P), step v in Scheme 1. With regard to the fate of adduct radicals (II), thermochemical data (Table 7) are of interest. Displacement $C_6H_5Z + O \longrightarrow C_6H_5O^{\bullet} + Z^{\bullet}$ differ widely in heat of reaction. Formation of phenoxyl radical from fluorobenzene is exothermic by only 17 kJ mol^{-1}; this may explain the low phenol yield, because of the relatively strong C–F bond in intermediate (II). On the other hand, formation of chlorobenzene is much more exothermic, also compared with formation of chlorophenoxyl radical, yet the ratio phenol:chlorophenol is only 0.25. Compare, however, the higher ratio of phenol:methoxyphenyl from anisole, of 0.30, while formation of phenoxyl radical is now less exothermic. Clearly, differences in heat of reaction are not the only parameter. The low phenol yield in the reaction with trifluorotoluene will probably be due to both a polar and a steric effect of the CF_3 group, while the high phenol yield with anisole may be partly due to the mesomeric electron-releasing effect of OCH_3, reflected in $\sigma_p(OCH_3)$ (cf. Figure 2). Although some phenol may have been formed via H-abstraction from the CH_3O group and subsequent oxidative degradation of $C_6H_5OCH_2^{\bullet}$, the plot of Figure 2 suggests this channel to be unimportant compared with regular *ipso* substitution. Activation energies for O(^{3}P) *ipso* addition are not known, but will depend on the character of the substituent. Note, for comparison, that for addition of OH$^{\bullet}$ to benzene E_a ca. 1.6, whereas addition to the *ipso* site in chlorobenzene has an activation barrier of ca. 10 kJ mol^{-1}.[28]

Experimental

Apparatus.—The apparatus consisted of a flow tube (length 6 cm; i.d. 2 cm) pumped to a moderately low pressure of ca. 100 mbar. Flows of nitrous oxide in helium passed through a 1 cm i.d. quartz tube before entering the main flow tube. The quartz tube is equipped with a 'woodshorn' to trap the light that is formed during discharge to prevent photochemical reactions of the substrate.

Substrates were introduced by passing a stream of helium

Table 7. Thermochemistry at 298 K for *ipso* substitution and $O + C_6H_5Z \longrightarrow p\text{-}ZC_6H_4O^\bullet + H^\bullet$.

Z	ΔH/kJ mol^{-1}	
	$O + C_6H_5Z \longrightarrow C_6H_5O^\bullet + Z^\bullet$	$O + C_6H_5Z \longrightarrow p\text{-}ZC_6H_4O^{\bullet\,a} + H^\bullet$
H	-75	-75
Cl	-142	-75
F	-17	-79
CH$_3$	-112	-88
CF$_3$	-75	-63
OCH$_3$	-75	-100

^{a} Calculation of heats of formation of substituted phenoxyl radicals from OH bond dissociation energies in p-substituted phenols.[27] Example: $\Delta H_f^\circ(p\text{-}ClC_6H_4OH) = \Delta_f^\circ(C_6H_5OH) + [\Delta H_f^\circ(C_6H_5Cl) - \Delta H_f^\circ(C_6H_6)] = -127.2$, $\Delta H_f^\circ(p\text{-}ClC_6H_4O^\bullet) = \Delta H_f^\circ(p\text{-}ClC_6H_4OH) + E_{BD}(p\text{-}ClC_6H_4OH)^{27} - \Delta_f^\circ(H)^{32} = 8.4$. Data on equilibrium compositions of ZC_6H_4Y[33] reveal that Z/OH interactions in ZC_6H_4OH may range from *ca.* 4–8 kJ mol^{-1}. As a first approximation ΔH_f° was taken independent of substitution pattern.

through the liquid(s). The substrate reservoirs were thermostatted to ensure constant inflows. Mass flow meters and rotameters controlled the flows of helium and nitrous oxide. The lines from the substrate reservoirs to the flow tube were electrically heated several degrees above the temperature of the water/oil bath to prevent condensation. The pressure was measured by a digital manometer (Vacuubrand). The microwave discharge (Microtron 200 MKIII, EMS) operated at 2 450 MHz, set at 100 rf power, and was equipped with a forward and reflected power meter coupled to the flowing nitrous oxide with a cavity (EMS No. 214L).[35] The cavity was air-cooled so that the flow tube remains at room temperature. The discharge was ignited with a high frequency spark tester containing a high frequency coil (Edwards ST200K MKII). The products formed were collected in a cold trap cooled with liquid nitrogen.

Chemicals.—Starting and reference compounds were, in general, available as high-grade commercial products and used as such. α,α,α-Trifluorotoluene and fluorobenzene were distilled first, GC analysis then showed >99.9% purity. Tank gases (Hoekloos) helium (<5 ppm O$_2$) and nitrous oxide in helium were used as delivered.

Analyses.—Product quantification was performed on an HP 5890 gas chromatograph equipped with a flame ionization detector and was based on comparison with mixtures of authentic compounds using p-dichlorobenzene as an internal standard. Products were separated on a 50 m CP-Sil 5 column, conditions: H$_2$ carrier gas, 0.9 atm, flow 2 cm^3 min^{-1}, temperature program 60 °C (10 min isothermal), rate 10 °C min^{-1}, to 250 °C (isothermal 10 min). Product identification was performed on an HP 5890/5970 GC–MSD also equipped with a 50 m CP-Sil column, conditions: He carrier gas, 1 atm, flow 2 cm^3 min^{-1}, temperature program as above.

When analysing substituted phenols, the *meta-* and *para-* isomers were not (completely) separated in most cases. Derivatization of the hydroxy group was used to obviate this. The reaction mixtures which contained the phenols were dried (by adding molecular sieves) and the following reagents were subsequently added, pyridine, bis(trimethylsilyl)trifluoroacetamide, and chlorotrimethylsilane (in the ratio 2:1:2). The phenols were converted into their trimethylsilyl ethers within 5 minutes and o-, m-, and p-ZC$_6$H$_4$OSi(CH$_3$)$_3$ gave completely separated, sharp GC peaks; hence, silylation was applied to determine most phenols quantitatively.

References

1 R. J. Cvetanovic, *J. Phys. Chem. Ref. Data*, 1987, **16**, 261, and references cited herein.
2 R. A. Bonanno, P. Kim, J. H. Lee, and R. B. Timmons, *J. Chem. Phys.*, 1972, **57**, 1377.

3 G. Boocock and R. J. Cvetanović, *Can. J. Chem.*, 1961, **39**, 2436.
4 J. C. Chu, H. C. Ai, and D. F. Othmer, *Ind. Eng. Chem.*, 1953, **45**, 1266.
5 L. I. Avramenko, R. V. Kolesnikova, and G. I. Savinova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1965, **1**, 28.
6 S. J. Sibener, R. J. Buss, P. Casavecchia, T. Hirooka, and Y. T. Lee, *J. Chem. Phys.*, 1980, **72**, 4341.
7 J. M. Nicovich, C. A. Gump, and A. R. Ravishankara, *J. Phys. Chem.*, 1982, **86**, 1684.
8 A. Hori, H. Matsumoto, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 1978, 16.
9 E. Grovenstein and A. J. Mosher, *J. Am. Chem. Soc.*, 1970, **92**, 3810.
10 T. M. Sloane, *J. Chem. Phys.*, 1977, **67**, 2267.
11 R. J. Baseman, R. J. Buss, P. Casavecchia, and Y. T. Lee, *J. Am. Chem. Soc.*, 1984, **106**, 4108.
12 A. J. Colussi, D. L. Singleton, R. S. Irwin, and R. J. Cvetanović, *J. Phys. Chem.*, 1975, **79**, 1900.
13 S. Takamuku, M. Matsumoto, A. Hori, and H. Sakurai, *J. Am. Chem. Soc.*, 1980, **102**, 1441.
14 E. Zadok and Y. Mazur, *Tetrahedron Lett.*, 1980, **21**, 4955.
15 J. S. Gaffney, R. Atkinson, and J. N. Pitts, *J. Am. Chem. Soc.*, 1976, **98**, 1828.
16 J. J. Havel and K. H. Chan, *J. Am. Chem. Soc.*, 1975, **97**, 5800.
17 P. Mulder, unpublished work.
18 (a) V. M. Sol, Thesis, Leiden, 1989, in English; (b) V. M. Sol, R. Louw, and P. Mulder, *Recl. Trav. Chim. Pays-Bas*, in the press.
19 J. Shorter, 'Correlation Analysis of Organic Reactivity,' Research Studies Press, Chichester, 1982.
20 R. W. Taft, Jr., in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 556.
21 C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, 1968, **90**, 4328.
22 G. R. H. Jones and R. J. Cvetanović, *Can. J. Chem.*, 1961, **39**, 2444.
23 M. J. Perkins in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. II, p. 231.
24 R. Atkinson, *Chem. Rev.*, 1986, **86**, 1.
25 F. Witte, E. Urbanik, and C. Zetzsch, *J. Phys. Chem.*, 1986, **90**, 3251.
26 R. A. Perry, R. Atkinson, and J. N. Pitts Jr., *J. Phys. Chem.*, 1977, **81**, 1607.
27 P. Mulder, O. W. Saastad, and D. Griller, *J. Am. Chem. Soc.*, 1988, **110**, 4090.
28 P. Mulder, Thesis, Leiden, 1987, in English.
29 J. M. Nicovich and A. R. Ravishankara, *J. Phys. Chem.*, 1984, **88**, 2534.
30 W. E. Jones, S. D. Macknight, and L. Teng, *Chem. Rev.*, 1973, **73**, 407.
31 D. L. G. James and R. D. Suart, *Trans. Faraday Soc.*, 1968, **64**, 2752.
32 (a) D. R. Stull, E. F. Westrum Jr., and G. S. Sinke, 'The Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969; (b) 'JANAF Thermochemical Tables,' 2nd edn., NSRDS–NBS 37, Washington, 1971.
33 G. J. P. Augustijn, Thesis, Leiden, 1966.
34 M. J. S. Dewar and N. Trinajstic, *J. Chem. Soc. A*, 1971, **9**, 1220.
35 F. C. Fehsenfeld, K. M. Evenson, and H. P. Broida, *Rev. Sci. Instrum.*, 1965, **36**, 294.