

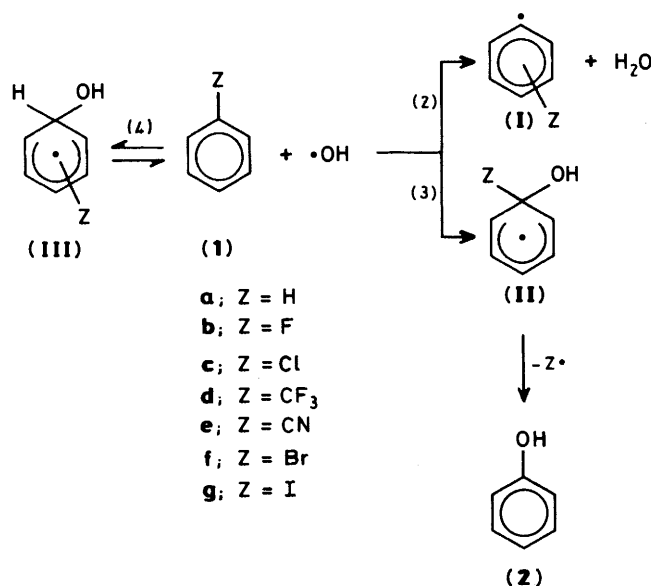
Vapour-phase Chemistry of Arenes. Part 13.¹ Reactivity and Selectivity in the Gas-phase Reactions of Hydroxyl Radicals with Monosubstituted Benzenes at 563 K

Peter Mulder and Robert Louw*

Center for Chemistry and the Environment, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

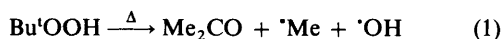
The reactions of hydroxyl radicals with benzene derivatives C_6H_5Z ($Z = H, Me, F, Cl, Br, I, CF_3, \text{ or } CN$) have been studied in a flow reactor at 563 K in nitrogen, using the thermolysis of Bu^tOOH as a source of $\cdot OH$. Under these conditions there are two product-forming pathways. The major one involves hydrogen abstraction to give aryl radicals $ZC_6H_4\cdot$ (II) as the first step; depending on Z , its displacement to form phenol may also occur. Relative rates for hydrogen abstraction were determined in competition experiments using side-chain hydrogen abstraction from added toluene as a reference. This resulted in the order (for $Z =$): 1.8(Me), 1.0(H), 0.47(F), 0.29(Cl), 0.34(CF_3), 0.20(CN), consonant with the electrophilic nature of $\cdot OH$. The site selectivity of hydrogen abstractions was determined by scavenging part of the aryl radicals (II) with iodine. A Hammett plot, using σ constants for *meta* and *para* positions, led to $\rho = -1.0$. The features of hydrogen abstraction by $\cdot OH$ are discussed and compared with those for the analogous reaction of Cl. The formation of phenol was found to decrease in importance in the order F, Cl, Br, and I. This result is rationalized on a thermochemical kinetic basis.

The gas-phase reactions of hydroxyl radicals with aromatic compounds are of interest in order to understand the processes of degradation both in combustion and in atmospheric chemistry. We have recently dealt with the reaction of hydroxyl radicals with benzene,² toluene,³ and chlorobenzene^{2,3,4} in the vapour phase at 570 K. The thermolysis (1) of *t*-butyl hydroperoxide was used as a source for $\cdot OH$. Scheme 1 summarizes



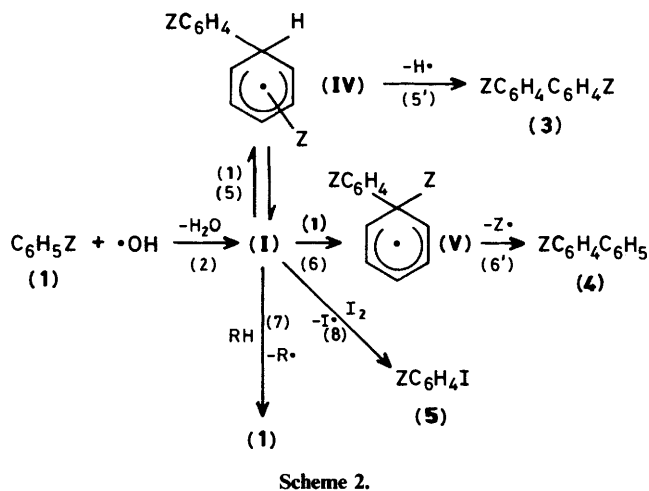
Scheme 1.

its possible reactions with monosubstituted benzenes C_6H_5Z (1). With chlorobenzene ($Z = Cl$), in nitrogen at 563 K,



reaction (2) predominates over *ipso*-substitution (3).^{1,2,4,5} Reaction (3) is not observed at all if $Z = Me, CN, \text{ or } CF_3$.¹

However, with *o*- and *p*- $ClC_6H_4CF_3$ both displacement of Cl and of CF_3 by OH is observed. Addition (4), which is the major step at ambient temperature, is reversible at 563 K and therefore unproductive in nitrogen.⁶⁻⁸ For example benzene (1a) led to biphenyl (3a) formed by arylation of benzene [equation (5), Scheme 2], without any phenol (2).



The ultimate isomer distributions of biaryl (3) and the *ipso*-product (4) will be determined by the site selectivity of $\cdot OH$ in hydrogen abstraction (2) and the rate and site selectivity of *o*-, *m*-, and *p*-(I) in the subsequent arylation of C_6H_5Z [steps (5) and (6)]. Therefore the observed isomer distributions of (3) and (4) are not readily interpretable in terms of the primary abstraction step (2).

A better approach to determine the isomer distributions of (I) and hence the site selectivity of reaction (2), is addition of iodine to the reacting system; the iodo-transfer reaction (8) is very fast and essentially non-discriminating.²

With *p*-chlorotoluene (6b) at 563 K, hydrogen-abstraction (9)

Table 1. Product distributions for the reactions of $\cdot\text{OH}$ with $\text{C}_6\text{H}_5\text{Z}$ (1)

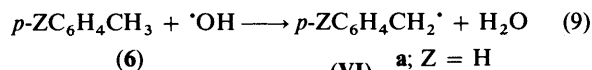
Exp. no.	In ^a		Out ^{a,c}		
			$\text{ZC}_6\text{H}_4\text{C}_6\text{H}_4\text{Z}$ (3)	$\text{ZC}_6\text{H}_4\text{C}_6\text{H}_5$ (4)	$\text{C}_6\text{H}_5\text{OH}$ (2)
1.0	(1a)	67.5	0.208	0	0
2.0	(1b)	63.8	0.144	0	0.077
3.0	(1c)	58.4	0.137	0.010	0.044
3.a	(1c)	56.5	0.120	0.030 (+0.0018) ^b	0.047
	(1a)	2.59			
3.b	(1c)	54.8	0.116	0.046 (+0.0041) ^b	0.042
	(1a)	4.55			
4.0	(1d)	48.8	0.110	0	0
5.0	(1e)	58.9	0.054	0.0081	0

^a Data in mmol h^{-1} ; inflows: N_2 , 433; $\text{Bu}^{\cdot}\text{OOH}$, 1.14; T 563 K, τ 98 ± 2 s. ^b Biphenyl. ^c 0 = below detection limit, *ca.* 0.001 mmol h^{-1} .

Table 2. Product distribution for reactions of $\cdot\text{OH}$ with $\text{C}_6\text{H}_5\text{Z}$ (1) plus $\text{C}_6\text{H}_5\text{CH}_3$ (6a)

Exp. no.	Z	In ^a		Out ^a			
		(1)	(6a)	$\text{ZC}_6\text{H}_4\text{C}_6\text{H}_4\text{Z}$ (3) + $\text{ZC}_6\text{H}_4\text{C}_6\text{H}_5$ (4)	$\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ (7)	$(\text{C}_6\text{H}_5\text{CH}_2)_2$ (8)	$\text{ZC}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$
1.1	H	65.0	2.11	0.194	0.037	0.0053	0.012
1.2	H	62.4	4.22	0.194	0.068	0.018	0.023
1.3	H	65.4	1.63 ^b	(1) ^c	(0.097) ^{c,d}	(0.018) ^{c,e}	n.d.
1.4	H	65.0	1.97 ^b	(1) ^c	(0.194) ^{c,d}	(0.026) ^{c,e}	n.d.
1.5	H	62.5	3.8 ^b	(1) ^c	(0.244) ^{c,d}	(0.096) ^{c,e}	n.d.
2.1	F	61.7	1.89	(1) ^{c,f}	(0.402) ^c	(0.059) ^c	n.d.
2.2	F	61.4	2.15	0.128 ^f	0.049	0.012	n.d.
2.3	F	59.6	3.71	0.085 ^f	0.065	0.017	0.023
3.1	Cl	56.5	1.94 ^b	(1 + 0.072) ^c	(0.542) ^{c,d}	(0.244) ^{c,e}	n.d.
3.2	Cl	54.8	3.39 ^b	(1 + 0.072) ^c	(0.670) ^{c,d}	(0.548) ^{c,e}	n.d.
4.1	CF_3	48.4	0.46	(1) ^c	(0.156) ^c	(0.009) ^c	n.d.
4.2	CF_3	46.9	2.15	0.079	0.056	0.013	0.021
4.3	CF_3	46.5	2.71	(1) ^c	(0.810) ^c	(0.299) ^c	n.d.
5.1	CN	56.5	2.15	0.045 + 0.014	0.043	0.008	0.016
5.2	CN	54.8	3.86	0.029 + 0.015	0.068	0.022	0.022
T1			56.4	0	0.40	0.58	0
T2			50.9 ^b	0	0.32 ^d	0.54 ^e	0

^a Data in mmol h^{-1} ; inflow: N_2 , 433; $\text{Bu}^{\cdot}\text{OOH}$, 1.14; T 563 K; τ 98 ± 2 s; n.d. = not determined. ^b *p*- $\text{ClC}_6\text{H}_4\text{CH}_3$ (6b). ^c Product ratio. ^d *p*- $\text{ClC}_6\text{H}_4\text{C}_2\text{H}_5$. ^e (*p*- $\text{ClC}_6\text{H}_4\text{CH}_2$)₂. ^f Together with phenol [exp. 2.1: (0.484); ^c 2.2: 0.052; 2.3: 0.039].



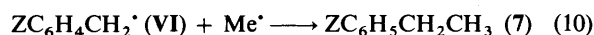
from the methyl group is at least 30 times faster than *ipso*-substitution to give *p*-cresol.¹ From the work of Ravishankara and co-workers,⁷ it appears that side-chain abstraction from toluene (6a) is much faster than removal of ring hydrogens. In air oxidation of (6a) at *ca.* 570 K some *o*-, *m*-, and *p*-cresol is formed in addition to benzaldehyde as the main product.⁹ Reaction (2) therefore is not negligibly slow compared with (9) and small proportions of (6) should be able to compete with (1) for $\cdot\text{OH}$ radicals.

With the aim of acquiring better insight into the substrate and site selectivity of reaction (2) and the relative importance of *ipso*-substitution (3) as a function of Z, we have investigated the thermolysis of *t*-butyl hydroperoxide at 563 K in nitrogen with 50-fold excesses of aryl derivatives (1). The substrate selectivity of $\cdot\text{OH}$ has been studied by adding small amounts of toluene (6a) or of *p*-chlorotoluene (6b) to the feed for (1a–d); using added iodine the site selectivities in reaction (2) with (1b, c, and e–g) have been determined.

Results

Arenes, or mixtures thereof (*ca.* 60 mmol h^{-1}), together with $\text{Bu}^{\cdot}\text{OOH}$ (1.1 mmol h^{-1}) and nitrogen (433 mmol h^{-1}) were fed into a Pyrex tank-flow-type reactor (620 ml) kept at 290 °C as described before.^{4,10} Under these conditions the hydroperoxide is nearly completely consumed. The effluent was condensed in a trap cooled with liquid nitrogen and analysed for arene-derived products by gas chromatography.

Table 1 gives data for runs with individual compounds (1a–e). The main product is the biaryl $\text{ZC}_6\text{H}_4\text{C}_6\text{H}_4\text{Z}$ (3); depending on Z, $\text{ZC}_6\text{H}_4\text{C}_6\text{H}_5$ (4) and $\text{C}_6\text{H}_5\text{OH}$ (2) are also formed. Addition of some benzene (1a) to chlorobenzene (1c) results in an increased (4c):(3c) product ratio whereas biphenyl (3a) is also produced (Table 1). The effect of adding increasing amounts of toluene (6a) or *p*-chlorotoluene (6b) to the substrates (1a–e) is outlined in Table 2. Even the use of only 1–2% of (6a) on (1) leads to, in addition to biaryls (3) and (4), substantial proportions of ethylbenzene (7) and bibenzyl (8), showing the operation of reactions (10) and (11). When toluene is added to the feed, the cross-arylation product $\text{ZC}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$ is also formed.





For comparison, data on runs with Bu'OOH and (6a or b) only are also included in Table 2.

Whereas production of biphenyl from benzene seems hardly affected by addition of toluene, the yields of (3c–e) from the corresponding arenes (1) are markedly lower. For example, with benzonitrile (1e) the yield of (3e) is 0.054 mmol h⁻¹ (Table 1); addition of toluene lowers the yield to 0.045 and 0.029 mmol h⁻¹ respectively (Table 2). Meanwhile the cross-arylation product ZC₆H₄C₆H₄CH₃ rises from 0.016 to 0.022 mmol h⁻¹. When ca. 2% iodine rather than toluene is added to the feed [as has been done with (1b, c, f, and g) Table 3] comparable amounts of iodoarene (5) and biaryl (3) are produced.

With iodobenzene (1g) as a substrate, di-iodobenzene (5g) is a major product and a small amount of biphenyl is observed. Pertinent data on isomer distributions of (3)–(5) are given in Table 4.

Discussion

Table 1 reveals that under identical experimental conditions the yields of (3) markedly decrease along the series Z = H > F, Cl > CF₃ > CN. This substituent order is one of increasing electron-attracting capacity, as measured by e.g. σ_m constants.¹¹ Without detailing reactions of individual *ortho*-, *meta*-, and *para*-positions here, formation of (3) requires two steps, hydrogen abstraction from (1) by ·OH to give aryl radical (I) [reaction (2) Scheme 1] and arylation of (1) [reaction (5) Scheme 2].

When adding to substituted benzenes [reaction (4) Scheme 1] ·OH acts as an electrophilic radical.¹² It is likely, therefore, that in hydrogen abstraction (2) ·OH will behave analogously, which implies a decreasing rate for step (2) when going from Z = H to CN. However, (1e), formed in this way from benzonitrile (1e), is also electrophilic,¹³ entailing a slower arylation (5) of (1e) by (Ie) than, for instance, of (1a) by (Ia) at

the other end of our series. Note that reaction (5) involves competition with hydrogen transfer [step (7) Scheme 2] from unchanged Bu'OOH, or from acetone formed therefrom. The same holds for reaction (2).^{2,3} These competing reactions are relatively more important in conversions of (1e or d) than with (1b). As the observed decrease in yield of (3) is due to a combined effect of steps (1) and (5), no conclusions can be drawn for the magnitude of the substituent effect in step (2). Runs 3 (Table 1) involving mixtures of benzene (1a) and chlorobenzene (1c) allow an estimation of the relative rate of step (2) with these substrates. The routes of formation of (3c) and (4c) are depicted in Scheme 3. If we neglect the small differences in k₅ and k₆ values due to the chlorine substituents, k_{5ac} = k_{5cc} and k_{5aa} = k_{5ca}. Also, k_{5aa} = 6k_{5ac}/5 and k_{5ca} = 6k_{5cc}/5. From the (4c):(3c) product ratio (Table 1), k_{6cc}/k_{5cc} is calculated to be 0.010/0.137 = 0.071. For runs with (1a)–(1c) mixtures, the following relation holds: (4c)/(3c) = [v_{5ac} + v_{5ca} + v_{6cc}]/v_{5cc}, leading to (4c)/(3c) = (Ia)/(Ic) + k_{5ca}(Ia)/k_{5cc}(Ic) + k_{6cc}(Ic)/k_{5cc}. Using the data in Table 1 and applying the simplifications mentioned above: (4c)/(3c) (= 0.030/0.120) = (Ia)/(Ic) + 6 × 0.046/5 + 0.071, leading to (Ia)/(Ic) = 0.122. Therefrom, k_{2c}/k_{2a}, the relative rate constant for hydrogen abstraction (2) from chlorobenzene *vs.* benzene is calculated to be 0.046/0.122 = 0.37. Using the biphenyl:(3c) ratio instead, essentially the same result is obtained. An analogous calculation based on the data in Table 1 gives (Ia)/(Ic) = 0.225 which reproduces the k_{2c}/k_{2a} value of 0.37.

Table 1 also shows that the (4):(3) product ratio strongly depends on Z; Cl and CN appear to be displaced to produce (4b and e), respectively, whereas such reactions are negligible for Z = F and CF₃. To interpret this, heats of reaction of *ipso*-substitution (6) are relevant (Table 5). Displacement of Cl, exothermic by 71 kJ mol⁻¹,¹⁴ is well documented,¹⁵ but the analogous reaction with (1b) is not possible. Displacement of CF₃, mildly endothermic, occurs at best to a minor degree only.¹ Remarkably, formation of (4e) from benzonitrile is observed despite the large endothermicity of 57 kJ mol⁻¹.

Table 3. Product distribution for reactions of ·OH with C₆H₅Z (1) with added iodine

Exp. no.	Z	In ^a		Out ^b	
		(1)	C ₆ H ₅ OH (2)	ZC ₆ H ₄ C ₆ H ₄ Z (3) + ZC ₆ H ₄ C ₆ H ₅ (4)	ZC ₆ H ₄ I (5)
2.4	F	63.8	0.38	0.38	0.24
3.3	Cl	58.4	0.21	0.37 + 0.007	0.42
6.1	Br	57.1	0.14	0.59 + 0.039	0.23
7.1	I	53.8	0.12	0.032 ^c	0.85
5.3	CN	58.9		0.66 + 0.13	0.21

^a Data in mmol h⁻¹, inflow: N₂, 433; Bu'OOH, 0.94; I₂, 1.0; T 563 K; τ 98 ± 1 s. ^b Product ratios; sum = 1.0. ^c Biphenyl.

Table 5. Thermochemistry^a for *ipso*-substitution C₆H₅Z + Y· ⇌ C₆H₅Y + Z· + ΔH°

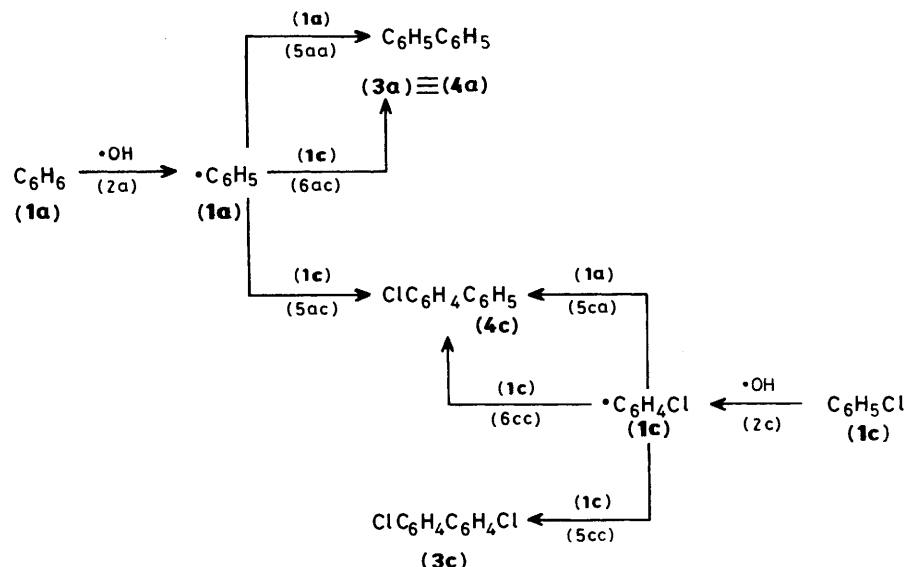
Z	Y = C ₆ H ₅	Y = OH ^b
F	55	61 (-146)
Cl	-71	-65 (-134)
Br	-133	-127 (-131)
I	-196	-190 (-126)
CF ₃	-10	-4 (-87)
CN	-57	64 (-74)

^a ΔH°/kJ mol⁻¹, data from ref. 12. ^b In parentheses is the overall heat of reaction for C₆H₅Z + ·OH ⇌ C₆H₅O· + HZ based on ΔH_f°(C₆H₅O·)_g = 47.7 kJ mol⁻¹.^{14c} ^c Based on ΔH_f°(CN)_g 416.5 kJ mol⁻¹.^{14d}

Table 4. Isomer distributions (%)^a for ZC₆H₄C₆H₄Z (3), ZC₆H₄C₆H₅ (4), and ZC₆H₄I (5)

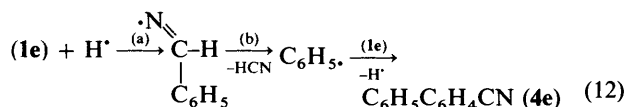
Exp.	Z	(3)						(4)			(5)		
		<i>o, o'</i>	<i>o, m'</i>	<i>o, p'</i>	<i>m, m'</i>	<i>m, p'</i>	<i>p, p'</i>	<i>o</i>	<i>m</i>	<i>p</i>	<i>o</i>	<i>m</i>	<i>p</i>
2.4	F	<i>b</i>											
3.3	Cl	14.4	34.4	18.7	13.1	15.5	3.9	12	59	29	17.1	57.5	25.4
6.1	Br	12.5	30.9	16.0	17.0	19.3	4.3	22.7	58.9	18.4	24.5	52.7	22.8
7.1	I										28.9	47.6	23.5
5.3	CN	19.8	32.2	24.6	7.3	11.4	4.7	55.9	17.2	26.9	33.8	40.9	25.3
											39.3	41.4	19.3

^a See Table 3 for product distributions. ^b Isomeric composition could not be determined.

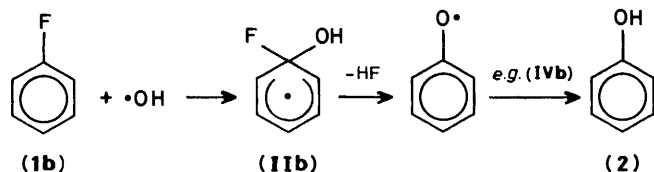


Scheme 3.

We therefore suggest that (4e) is formed exclusively via phenylation (5) of benzonitrile with unsubstituted $\cdot\text{C}_6\text{H}_5$. The latter species can arise by addition of $\cdot\text{H}$ [generated in step (5') Scheme 2] to the cyano group, leading to transcyanation¹⁶ as depicted in equation (12).*



Likewise, thermochemical kinetics are of help in explaining formation of phenol (2) from (1), due to *ipso*-substitution of $\cdot\text{OH}$ [reaction (3) Scheme 1]. Loss of Cl from intermediate (IIc) is straightforward⁶ (Table 4). Remarkably, fluorobenzene (1b), despite the endothermicity for loss of F from (IIb), produces sizeable amounts of (2) as well. This may be rationalized by loss of HF from (IIb)¹⁸ (Scheme 4), which makes formation of $\text{C}_6\text{H}_5\text{O}^{\cdot}$ from (1b) exothermic by no less than 146 kJ mol⁻¹ (Table 5). Phenoxy radicals are converted into (2) by *e.g.* disproportionation with (IVb).

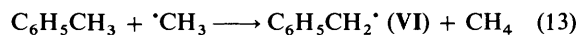


Scheme 4.

* The heat of reaction for steps (12a) and (b) is 22 kJ mol⁻¹.^{14a,b} The analogous reaction with $\cdot\text{OH}$, leading to HOCN, can also be envisaged. The heat of formation of HOCN has not been measured, but using the calculated difference in heat of formation of HOCN and the isomeric species HNCO of ca. 40 kJ mol⁻¹¹⁷ and $\Delta H_f^\circ(\text{HNCO}) -117$ kJ mol⁻¹,^{14b} $\Delta H_f^\circ(\text{HOCN})$ is estimated to be -77 kJ mol⁻¹, making the overall reaction (12a) + (12b) with $\cdot\text{OH}$ 10 kJ mol⁻¹ exothermic.

Effect of Added Toluene.—Turning to the systems involving added toluene (6a, b), hydrogen abstraction therefrom [equation (9)] precedes formation of (7) and (8) [equations (10) and (11)]. However, reaction (9) is not the only way of making benzyl radicals (VI). Reaction (13) can be shown to be of importance even in experiments involving high (1):toluene ratios.

The concentrations of methyl radical (Table 2) can be derived from the proportions of (7) and (8) formed. The cross-



combination ratio for methyl and benzyl radical is 1.3.^{3,19} Using $(7)/(8)^{\ddagger} = 0.51$, the third combination product, C_2H_6 , is calculated to amount to 0.15 mmol h⁻¹. In our reactor (620 ml) the rate of formation of C_2H_6 , then, is 6.7×10^{-14} l mol⁻¹ s⁻¹. With a rate constant for combination of $\cdot\text{CH}_3$ of 2.2×10^{10} l mol⁻¹ s⁻¹,²⁰ $[\cdot\text{CH}_3] = 1.75 \times 10^{-9}$ M. Using k_{13} 8×10^{-4} l mol⁻¹ s⁻¹,^{3,19} and $[(6a)]$ 1.82×10^{-4} M, $v_{13} = k_{13}[\cdot\text{CH}_3][(6a)]$ is then found to be 2.54×10^{-8} l mol⁻¹ s⁻¹. The total rate of production of $\text{C}_6\text{H}_5\text{CH}_2^{\cdot}$ (VI), measured by (7) + 2(8), is 0.104 mmol h⁻¹ or 4.66×10^{-8} l mol⁻¹ s⁻¹. Therefore v_{13} is ca. 55% of this value. The absolute product ratios can be inferred from Table 2. $(7)/(8)^{\ddagger}$ remains almost constant at 0.50 ± 0.02 meaning that $[\cdot\text{CH}_3]$ is ca. 1.75×10^{-9} M in the series of experiments of (1) and (6a or b).

This observation is of help in further interpreting product formation as a function of Z. If formation of (VI) is due to the operation of $\cdot\text{CH}_3$ and $\cdot\text{OH}$ [steps (13) and (9)] and the aryl radicals (I) are produced by hydrogen abstraction by $\cdot\text{OH}$ [step (2)] and if (I) quantitatively leads to biaryls [steps (5) and (6)],

$$\frac{(7) + 2(8)}{(3) + (4)} = \frac{k_9}{k_2} \left(1 + \frac{k_{13}}{k_9} \cdot \frac{[\cdot\text{CH}_3]}{[\cdot\text{OH}]}\right) \cdot \frac{(6)}{(1)} \quad (14)$$

relation (14) is valid. The data in Table 2 are plotted accordingly in Figure 1. Note that [except for (1e)] good straight lines are obtained. Points for (1a) involving added (6b) rather than (6a) fall on the same line. Apparently the *p*-Cl substituent has very little effect on the rate of hydrogen abstraction from toluene both by $\cdot\text{CH}_3$ ²¹ and by $\cdot\text{OH}$. The line for (1a) has a slope of ca. 8. Taking $[\cdot\text{OH}]$ 10^{-13} M (ref. 2), $[\cdot\text{CH}_3]$

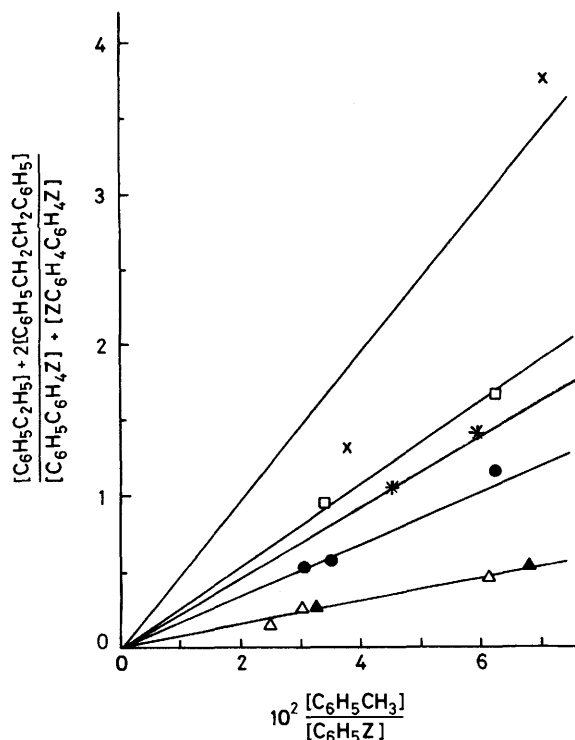


Figure 1. Product ratio $[\text{C}_6\text{H}_5\text{C}_2\text{H}_5] + 2[\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5] / [\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{Z} + \text{ZC}_6\text{H}_4\text{C}_6\text{H}_4\text{Z}]$ versus the $(\text{C}_6\text{H}_5\text{CH}_3 / \text{C}_6\text{H}_5\text{Z})$ intake ratio as a function of Z. Z = H (Δ , \blacktriangle); F (\bullet); Cl (\square); CF_3 ($*$); CN (\pm). Open symbols *p*- $\text{ClC}_6\text{H}_4\text{CH}_3$

$1.75 \times 10^{-9} \text{ M}$ as discussed above and k_9 $1.25 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$,⁷ one obtains k_{2a} $3.3 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. Given the approximations outlined above, this value agrees well with that deduced from the work of Ravishankara, k_{2a} $2.6 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ at 563 K.⁷

The different slopes in Figure 1 again are in the expected order for electrophilic hydrogen abstraction. The ratios of these slopes yield values for the substituent effect on k_2 (see Table 6, first column). Note that the value for chlorobenzene, $k_{2rel} = 0.29$, is in satisfactory agreement with that derived from competitive reactions with benzene (Table 1).

Runs with Added Iodine; ipso-Substitution.—In the presence of iodine, some aryl radical reacts with I_2 to give iodoarene [step (8) Scheme 2]. Under these conditions the isomer distributions of biaryl (3) entail a larger proportion of *ortho*- and *para*-isomer than in the absence of I_2 (Table 4). The apparent shift to

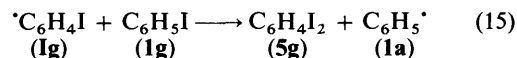
distributions governed by the site selectivity of step (5) has been noted before² and points to reaction of (IV) with I_2 , thereby making the reversal of the arylation [step (5)] less important. The proportion of *ipso*-substitution, measured by the (2)/[(3) + (4) + (5)] product ratio, is highest for (1b), namely 0.61, and decreases in the series Z = Cl, Br, I to 0.14 in the last case (Table 3). Net displacement of F by OH has been discussed above (see Scheme 4).

As straightforward *ipso*-substitution is exothermic for Z = Cl, Br, and I (Table 5), with (3) as the rate-determining step, there is no need for assuming loss of HZ from the corresponding intermediates (II) in these cases.

The ratio of phenol versus the products of hydrogen abstraction allows an estimation of k_3/k_2 for Z = Cl. From Table 1 it can be shown that $k_{3c}/k_{2c} = 0.31$. For $k_{2c} = 0.36k_{2a}$ and k_{2a} $3.3 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ the rate constant for *ipso*-substitution is calculated to be k_{3c} $3.7 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$. Taking the A factor, on a per site basis, to be equal to that for addition of $\cdot\text{OH}$ to benzene⁵ ($\log A_{4a}$ 9.3⁷) the activation energy for *ipso* addition is ca. 10 kJ mol^{-1} .

As the overall rates of hydrogen abstraction from (1c, f, and g) are expected to be very close to each other, the decreasing proportion of *ipso*-substitution means that the rate constant for *ipso*-substitution (3) decreases in the series fluoro-, chloro-, bromo-, and iodo-benzene. This order, while familiar for nucleophilic substitution,²² is unexpected for a reaction involving the electrophilic $\cdot\text{OH}$ radical.¹² Presumably steric hindrance is important, as in free radical addition to alkenes.²³ Alternatively, an entering $\cdot\text{OH}$ radical may form a transient complex, by hydrogen bonding, to the halogen atom. This tendency will be greater with F than with other halogens.

When using iodobenzene as a substrate only di-iodobenzenes (5g) are formed. The predominance of (5g) tallies with the known rapid iodine transfer from organic iodides to (aryl) radicals²⁴ [equation (15)]. The low yield of biaryl [biphenyl



rather than iodobiphenyl(s) is at present not well understood. Possibly part of $\cdot\text{OH}$ reacts with iodobenzene to give IOH which may act as hydrogen donor for aryl radicals.

Hydrogen Abstraction by $\cdot\text{OH}$.—As outlined above, conversion of aryl radicals (I) into ArI is considered as a good method for the determination of the site selectivity for hydrogen abstraction by $\cdot\text{OH}$ [step (2)]. Combination of the data of Table 4 on isomer distributions of (5) with the relative rates (Table 6) yields partial rate factors f for hydrogen abstraction by $\cdot\text{OH}$ (Table 6).

Table 6. Relative rates for hydrogen abstraction from $\text{C}_6\text{H}_5\text{Z}$ by $\cdot\text{OH}$ or Cl \cdot at 563 K

Z	$\cdot\text{OH}$ [reaction (2)]			f_m/f_p	Cl \cdot (ref. 24)	
	k_{2rel}^a	$\log f_m$	$\log f_p$		k_{17rel}	f_m/f_p
CH_3^b	1.8	0.53	0.31	1.7	(1)	(1)
H	(1)	(0)	(0)	(1)	(1)	(1)
F	0.47	-0.09	-0.14	1.1	0.16	1.42
Cl c	0.29 (0.37)	-0.34 (-0.24)	-0.41 (-0.32)	1.2	0.18	1.33
CF_3	0.34				0.095	0.85
CN	0.20	-0.66	-0.66	1.0	0.05	0.77

^a k_2 relative to that for benzene, k_{2a} ca. $3.3 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ (see text). ^b See text. ^c In parentheses: values derived from Table 1.

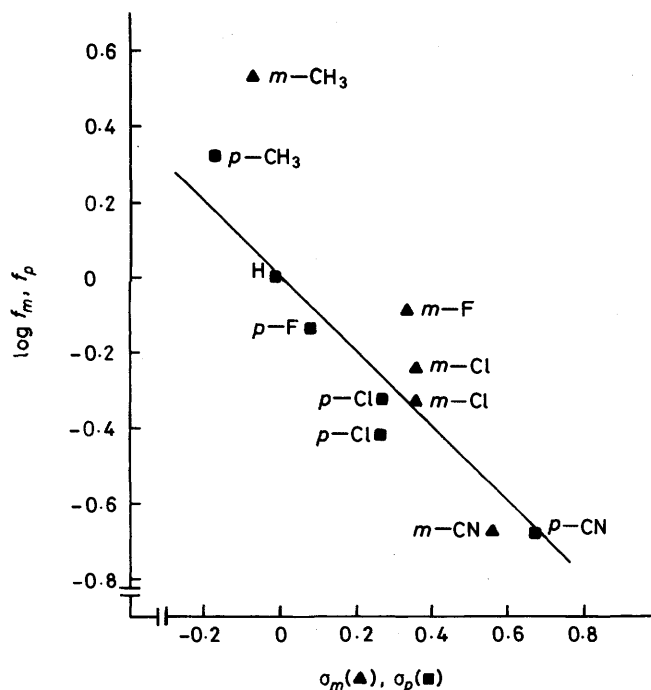
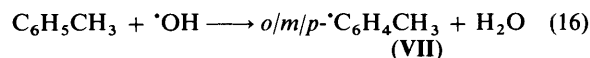


Figure 2. Partial rate factors f_m, f_p as a function of σ_m (▲) and σ_p (■)

The plot of $\log f$ versus σ_m and σ_p of (1b, c, and e) (Figure 2), while not leading to a perfect correlation, does reveal a clear trend, with $\rho = -1.0$. This value may be compared with those known for addition of $\cdot\text{OH}$ at ambient temperature. Shevchuk *et al.*^{12a} reported $\rho = -0.3$ whereas from the data of Atkinson *et al.*^{12a} a value of ρ ca. -1.4 can be deduced. Whatever the origin of this discrepancy, if our result for hydrogen abstraction at 563 K $\rho = -1.0$ is extrapolated to ambient temperature (by assuming

that rate differences are due to enthalpy differences only) $\rho(298\text{ K}) = -1.9$. That hydrogen abstraction by $\cdot\text{OH}$ from arenes has a higher substrate selectivity than addition is not surprising. The former reaction is markedly slower than the latter one, with activation energies E_2 ca. 20 and E_4 ca. 5 kJ mol^{-1} , respectively, which leaves more room for discrimination in reaction (2).

Accepting $\rho = -1.0$ at 563 K, the relative rate for ring hydrogen abstraction from toluene [equation (16)] can be estimated. In earlier experiments, when nitrogen was partly replaced by oxygen and toluene was used as a substrate, we observed formation of cresols with an isomer distribution *o:m:p* 18:63:19.⁹ When this isomer distribution is governed by the site selectivity for ring hydrogen abstraction only, k_{16}/k_{2a} ca. 1.3. Taking our values of k_{2a} 3.3×10^{-8} and k_9 1.25×10^9 $\text{l mol}^{-1} \text{s}^{-1}$, k_{16}/k_9 in ca. 0.34. In other words on a per hydrogen basis, the side-chain hydrogen is abstracted about five times as fast as ring hydrogen, in agreement with the value of k_{16}/k_9 ca. 0.2 at 500 K inferred by Ravishankara and co-workers.⁷



If the cross-arylation product $\text{CH}_3\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Z}$ is formed by arylation of (1) by (VII) (Table 2), the relative rate for ring hydrogen abstraction (2) is given by the product ratio $\text{CH}_3\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{Z}/[(3) + (4)]$. The calculated values are k_{16}/k_{2a} 1.8 ± 0.1 when (1) is benzene and k_{16}/k_{2e} 9.9 ± 0.7 when (1) is benzonitrile. Note that k_{2e}/k_{2a} 0.18, a value which nicely corresponds to the average result (ca. 0.20) derived from Figure 1.

Comparison between $\cdot\text{OH}$ and $\cdot\text{Cl}$.—It is of interest to compare the features of hydrogen abstraction by $\cdot\text{OH}$ (2) with those for the analogous reaction of Cl atoms (17) which have been determined earlier.²⁵ Owing to the difference in thermochemistry, reaction (2) has an early transition state but (17) involves a very late, product-like, transition state (Figure 3). In other words, relative rates in reaction (17) are governed by

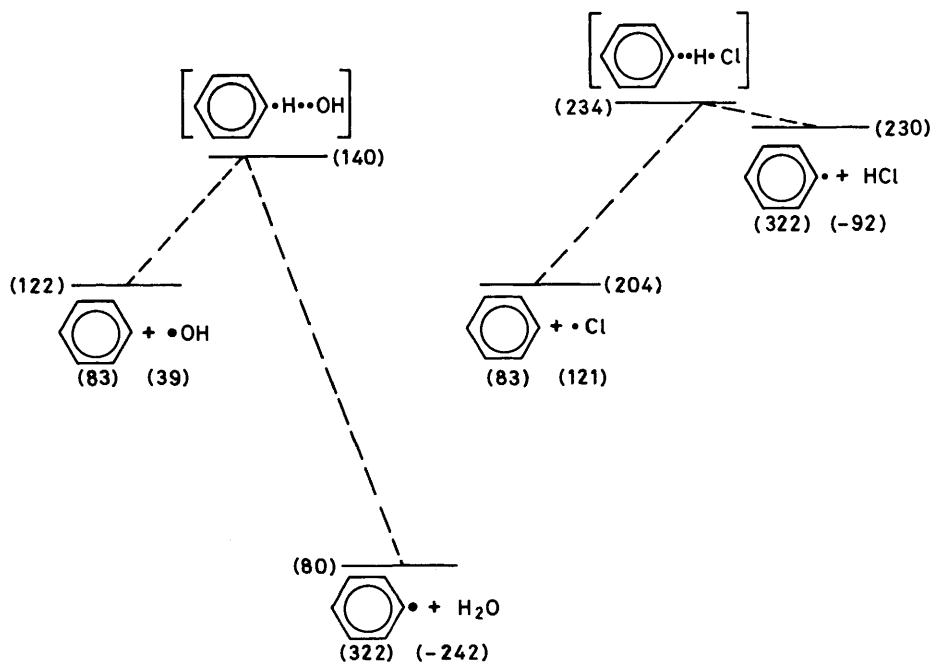


Figure 3. Energy diagram for hydrogen abstraction from benzene by $\cdot\text{OH}$ and by $\cdot\text{Cl}$. In parentheses heats of formation at 298 K in kJ mol^{-1} ¹⁴

differences in C-H bond strengths (final-state approach), whereas substituent effects on reaction (2) have to be rationalized by looking at initial states.



Interestingly, electron-attracting substituents retard hydrogen abstraction in both cases (see Table 6), abstraction by Cl involving a larger selectivity. In reaction (2) such substituents decrease the electron density at *meta*- and *para*-positions, making those hydrogens more suitable for removal by electrophilic $\cdot\text{OH}$. The features of reaction (17) entail that $\text{ZC}_6\text{H}_4\cdot$ radicals thus formed are destabilized if Z is an electron-attracting substituent.²⁵ In both reactions, plots of $\log f_m$ and/or f_p versus Hammett σ or σ^+ constants show a poor correlation (Figure 6 of ref. 25), which means that substituent electronic effects in side-chain processes such as ionization of benzoic acids (σ), cumyl chloride solvolysis (σ^+), and in hydrogen-atom abstractions (2) and (17) show a rough parallel only. Comparison of the site selectivities of reactions (2) and (17) (as measured by the isomer distributions of $\text{ZC}_6\text{H}_4\text{I}$ and $\text{ZC}_6\text{H}_4\text{Cl}$, formed in the respective reactions with I_2 and Cl_2) reveal some distinct differences. For example $f_m/f_p (= m/2p)$ ratios (Table 6) show again that Cl \cdot is more selective than $\cdot\text{OH}$. Note that the 'nucleophilic' ratio, f_m/f_p 0.77 for Z = CN in abstraction by Cl \cdot , contrasts with the statistical value of 1.0 for $\cdot\text{OH}$. A better insight into the mechanistic details of hydrogen abstraction (2) is to be expected if the H-D kinetic isotope effects are determined. For the analogous abstraction by Cl \cdot (17) a temperature-independent primary kinetic H-D isotope effect was observed, pointing to complexation between Cl \cdot and arene prior to hydrogen abstraction.²⁵ Results on H-D isotope studies in conversions of $\text{ArH} \longrightarrow \text{ArOH}$ will be reported shortly.²⁶

Experimental

Chemicals.—Starting and reference compounds were, in general, available as high-grade commercial products, and were used as such. Benzonitrile and *p*-chlorotoluene were distilled first, g.l.c. analyses showing >99% purity.

Apparatus and Techniques.—The gas-phase reactions were performed in a Pyrex tank-flow-type reactor with a capacity of 620 ml. In general, organic substrates were introduced as liquid mixtures by using a motor-driven syringe.¹⁰ Bu $\cdot\text{OOH}$ was 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.

Analysis.—Usually *p*-dichlorobenzene was added as an internal standard prior to the analysis. Organic products were qualitatively and quantitatively determined by g.l.c. analysis using a HP 5700 gas chromatograph equipped with a glass

capillary column (SE-30, 40 m \times 0.32 mm). Conditions: H_2 , 0.4 atm.; flow ca. 1 ml min^{-1} ; $T_{\text{inj}} = T_{\text{det}} = 220^\circ\text{C}$, temperature programme 100 $^\circ\text{C}$ (8 min), 8 $^\circ\text{C min}^{-1}$, 200 $^\circ\text{C}$ (10 min). For products of runs involving benzonitrile the final temperature was 230 $^\circ\text{C}$. Iodoarenes were separated on a capillary Carbowax Ca-5 column (22 m \times 0.32 mm).

References

- Part 12, P. Mulder and R. Louw, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 220.
- P. Mulder and R. Louw, *Recl. Trav. Chim. Pays-Bas*, 1984, **103**, 282.
- P. Mulder and R. Louw, *Recl. Trav. Chim. Pays-Bas*, 1984, **103**, 148.
- P. Mulder and R. Louw, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1541.
- P. Mulder and R. Louw, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1135.
- S. Madronich and W. Felder, *J. Phys. Chem.*, 1985, **89**, 3556.
- F. P. Tully, A. R. Ravishankara, R. L. Thompson, J. M. Nicovich, R. C. Shah, N. M. Kreutter, and P. Wine, *J. Phys. Chem.*, 1981, **85**, 2262.
- R. A. Kenley, J. E. Davenport, and D. G. Hendry, *J. Phys. Chem.*, 1981, **85**, 2740.
- P. Mulder and R. Louw, *Tetrahedron Lett.*, 1982, **23**, 2605.
- R. Louw and H. J. Lucas, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 55.
- C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, 1968, **90**, 4329.
- (a) R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., *Arch. Environ. Contam. Toxicol.*, 1985, **14**, 417; (b) A. Wahner and C. Zetzsch, *J. Phys. Chem.*, 1983, **87**, 4945; (c) M. Rinke and C. Zetzsch, *Ber. Bunsenges. Phys. Chem.*, 1984, **88**, 55; (d) L. G. Shevchuk, V. S. Zhikharev, and N. A. Vysotskaya, *J. Org. Chem. USSR*, 1969, **5**, 1606.
- M. J. Perkins, in 'Free Radicals,' ed. J. A. Kochi, Wiley, New York, 1973, vol. II, p. 231.
- (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; (c) A. J. Colussi, F. Zabel, and S. W. Benson, *Int. J. Chem. Kinet.*, 1977, **9**, 161; (d) T. Fueno, K. Tabayashi, and O. Kajimoto, *J. Phys. Chem.*, 1973, **77**, 575.
- (a) R. Louw and J. W. Rothuizen, *Tetrahedron Lett.*, 1967, 3807; (b) J. G. Traynham, *Chem. Rev.*, 1979, **79**, 323.
- K. van Nierop, F. J. Kuyers, W. F. M. Vonk, and R. Louw, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1062.
- J. R. Bews and G. Glidewell, *J. Mol. Struct.*, 1980, **67**, 141.
- R. Köster and K. D. Asmus, *J. Phys. Chem.*, 1973, **77**, 749.
- M. F. R. Mulcahy, D. J. Williams, and J. R. Wilmshurst, *Aust. J. Chem.*, 1964, **17**, 1329.
- J. A. Kerr in 'Free Radicals,' ed. J. A. Kochi, Wiley, New York, 1973, vol. I, p. 6.
- A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, 1969, **34**, 2018.
- J. Hine, 'Physical Organic Chemistry,' 1962, 2nd edn., McGraw-Hill, New York, 1962, p. 393.
- (a) J. M. Tedder, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 401; (b) B. Giese, *ibid.*, 1983, **22**, 753.
- (a) D. D. Tanner, D. W. Reed, and B. P. Setloane, *J. Am. Chem. Soc.*, 1982, **104**, 3917; (b) K. U. Ingold in 'Free Radicals,' ed. J. A. Kochi, Wiley, New York, 1973, vol. I, p. 37.
- W. Dorrepaal and R. Louw, *Int. J. Chem. Kinet.*, 1978, **10**, 249.
- P. Mulder and R. Louw, *Int. J. Chem. Kinet.*, in the press.

Received 19th May 1986; Paper 6/957