Relative Gas-phase Desubstitution Rates of Chlorobenzene Derivatives by Hydrogen Atoms near 1 000 K

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Thermolysis of arene/H_2 mixtures at atmospheric pressure near 1 000 K leads to desubstitution *via* attack of hydrogen atoms: ($Ar\text{–}X + H^{\bullet} \longrightarrow ArH$). Rates of dechlorination (and, where appropriate, dehydroxylation and defluorination) have been examined for a variety of chlorobenzene derivatives, including *o,m,p*-dichlorobenzenes, 1,2,4-trichlorobenzene, *o-,m*-chlorofluorobenzenes, *o-,m-,p*-chlorophenols, and 2,4-dichlorophenol. Employing competitive studies and computer analysis of product distributions, the rates of desubstitution have been determined relative to (**1**), ($C_6H_5Cl + H^{\bullet} \longrightarrow C_6H_6$). Observed per-site rate constants for dechlorination of the substrates were 0.66–1.44 times that of C_6H_5Cl. Electron-withdrawing substituents retard the reaction rate, and electron-donating groups lead to rate enhancement. Substituent effects on dehydroxylation were found to be similar; rates of defluorination were less affected by ring substituents. The results are discussed in terms of the reaction mechanisms,

Gas-phase thermal hydrogenolysis of organic chlorine-containing compounds near 1 000 K leads to dechlorination *via* hydrogen-atom attack on C–Cl bonds[1–4] and is of interest as a potential method of treating chlorinated industrial waste compounds such as polychlorinated biphenyls (PCBs).[5–7] Substituents other than Cl are also removed[1,8] and hydrogenolysis appears to be an effective general method of waste disposal. Aromatic compounds such as chlorobenzene are converted more slowly than chloroalkenes,[3] hence the reaction rate of arenes will dictate the conditions necessary for effective treatment of complex waste mixtures. Relative and absolute reaction rates of substituted benzenes with hydrogen atoms are therefore of interest from a practical point of view; theoretically speaking, information regarding structural effects on rates may contribute to a better mechanistic understanding of the reaction. Such data will also be useful in the study of complex pyrolysis and combustion systems, where desubstitution of aromatics by H atoms is likewise important.

Recently we have reported[8] that desubstitution rates of a series of monosubstituted benzenes ($C_6H_5X + H^{\bullet} \longrightarrow C_6H_6$) differ by a factor of up to 6.5 at 1 000 K and follow the order, for X, of $CH_3 \approx D > Cl \approx OH > CF_3 > F$, which correlates with the electrophilic nature of H atoms.

In the present work we have extended our studies to polysubstituted benzenes. Hydrogen atoms were thermally generated by reacting arene/H_2 mixtures at atmospheric pressure at temperatures near 1 000 K. In experiments of this type the concentration of hydrogen atoms is near that dictated by equilibrium dissociation of H_2,[3,8–10] but its precise value is unimportant since relative rates are determined by the establishment of a direct competition reaction. Using our previous results[8] on monosubstituted benzenes as a data base, we have first studied some disubstituted benzenes, employing competitive studies and computer analyses to obtain relative rates based on product distributions. With these data in hand, we have then extended our studies to two trisubstituted benzenes.

All rate constants are ultimately related to that for hydrogen-atom attack on chlorobenzene [equation (1)], for which we have previously determined[8] $\log k_1/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 10.48 - (4\,148/2.3T)$, or $\log [k(1\,000\ \text{K})/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}] = 8.68$.

$$H^{\bullet} + C_6H_5Cl \longrightarrow C_6H_6 \qquad (1)$$

A variety of chlorobenzenes have been examined, including *o-,m-,p*-dichlorobenzenes, 1,2,4-trichlorobenzene, *o-,m*-chlorofluorobenzenes, *o-,m-,p*-chlorophenols, and 2,4-dichlorophenol; these substrates thus provide information not only on dechlorination reactions, but also on dehydroxylation and defluorination.

Experimental

Chemicals.—*o*-Dichlorobenzene (Baker Analysed, ≥99%), *m*-dichlorobenzene (Fluka, 99.1% by GC analysis), *p*-dichlorobenzene (Aldrich 99+%), 1,2,4-trichlorobenzene (Aldrich 99%), *o*-chlorophenol (Fluka, 99.2% by GC analysis), *m*-chlorophenol (Fluka, 99.1% by GC analysis), *p*-chlorophenol (Fluka, 99.2% by GC analysis), 2,4-dichlorophenol (Janssen, 99%), and *o*-chlorofluorobenzene (Fluka, 99.0% by GC analysis) were used without further purification. *m*-Chlorofluorobenzene was distilled prior to use (after distillation 99.3% by GC analysis). In all cases the only major impurities were other isomers of the respective compounds.

Apparatus.—Experiments were conducted as previously described[10] at atmospheric pressure in spiralized quartz tubular flow reactors of effective volumes 29.1 cm³ (0.4 × 232 cm), 37.0 cm³ (0.45 × 233 cm) or 46.0 ml (0.45 × 289 cm). Liquid reagents were introduced *via* a motorized syringe and hydrogen *via* a calibrated flowmeter. Products were collected in liquid nitrogen traps and analysed *via* GC analysis.

Analyses.—GC/FID analyses were performed employing a 50 m CP-Sil 5 capillary column (Chrompack); conditions: H_2 carrier gas, 2 cm³ min⁻¹; temperature program 60 °C, 6 min, 10 °C min⁻¹ to 270 °C, 15 min, except for experiments with chlorofluorobenzene, for which a 50 m CP-Sil 19 capillary column (Chrompack) was used under similar conditions. Absolute amounts were determined from the peak surface areas, relative to that of an internal standard in conjunction with independently determined molar responses. All samples were analysed at least three times and the results averaged; standard deviations in the GC analyses were generally ±3%.

Data Analysis.—Certain assumptions have been made in our analyses of data; these assumptions and their effect on calculated relative rates for the various substrates are discussed in the following sections.

Di- and Tri-chlorobenzenes. Dichlorobenzenes are converted according to model equation (2) followed by (1). We have assumed that reactions (1) and (2) are the only important ones

$$\mathrm{H^{\bullet}} + o\text{-},m\text{-},p\text{-}\mathrm{C_6H_4Cl_2} \longrightarrow \mathrm{C_6H_5Cl} \qquad (2)$$

in our system. This assumption was checked by thoroughly examining the reacted mixture for other products. The largest secondary products, (substituted) biphenyls, accounted for <0.1% of the arene inflow. Traces of C_1 and C_2 gases were also present but were <0.05% of the inflow. In accordance with previous observations,[3] carbon formation was likewise minor. The conversion rate of *e.g.* o-$C_6H_4Cl_2$ is therefore given by $R(o\text{-}C_6H_4Cl_2) = k_{2,o}[H^{\bullet}][o\text{-}C_6H_4Cl_2]$ and the experimental pseudo-first-order rate constant by $k_{\mathrm{exp},o} = k_{2,o}[H^{\bullet}]$. We have reacted mixtures of o-,m-,p-$C_6H_4Cl_2$ in competitive studies and derived values of the pseudo-first-order rate constants for dechlorination of o,m,p-$C_6H_4Cl_2$ and of the primary product C_6H_5Cl, in order to match the observed distributions of o,m,p-$C_6H_4Cl_2$, C_6H_5Cl, and C_6H_6. Relative rates of hydrogen-atom attack are given directly by the ratio of the experimental rate constants.

Since there appear to be no other significant products, and because mass recovery is generally not perfect in product recovery studies of this type, due to experimental losses and slight variations in inflows, we have normalized our mass balances (typically 85–110%) prior to the calculation of relative rates. The accuracy of this assumption has almost no effect on the ratios $k_{2,o}:k_{2,m}:k_{2,p}$, but does slightly influence values derived for k_2/k_1. If the missing mass were due to reactions of the type (3), the normalization procedure would lead to a *ca.*

$$\mathrm{C_6H_4Cl_2} \longrightarrow \text{unobserved products} \qquad (3)$$

5% overestimation of k_1/k_1, in a hypothetical instance where 80% of the inflow was recovered and 20% reacted as per equation (3). Errors would be larger and more difficult to estimate if all products were undergoing reactions of this type with varying rates. We do not, however, feel that this is likely.

In order to determine site-selectivities for 1,2,4-$C_6H_3Cl_3$, the ratios of k_2/k_1 were fixed at the values previously determined, and the rate constants for the individual 1,2,4-positions determined from product distributions. Absolute values were derived relative to k_2 rather than k_1. A determination relative to k_1 would not be as accurate since it depends on the ratio of C_6H_6/1,2,4-$C_6H_3Cl_3$, which is very small.

Overall, we estimate our site-selectivities resulting from direct competitions to be accurate within ±5% and our rates relative to C_6H_5Cl to ±10%.

Chlorofluorobenzenes. Mass balances were normalized as in the preceding analyses. In order to determine relative desubstitution rates (loss of Cl *vs.* loss of F) from the distribution of ClC_6H_4F, C_6H_5Cl, C_6H_5F, and C_6H_6, it is necessary to know the relative rates of reactions (1) and (4). This ratio was

$$\mathrm{C_6H_5F} + \mathrm{H^{\bullet}} \longrightarrow \mathrm{C_6H_6} \qquad (4)$$

taken from our previous study,[8] in which it was determined relative to dedeuteriation of C_6D_6. On this basis k_1/k_4 should be accurate within ±10% and uncertainty in this value should have little effect on the determined rate constants. Accuracies should be similar to those for the chlorobenzenes.

Chlorophenols. Determination of site-selectivities for phenolic compounds is complicated by an additional pathway leading to CO formation. Levels of CO formation were not measured

$$\mathrm{H_2} + \mathrm{C_6H_5OH} \longrightarrow \mathrm{CO} + \mathrm{C_5}\ \text{products} \qquad (5)$$

in most instances. We have estimated the rate of this reaction from our previous detailed study of phenol hydrogenolysis,[10] in which we found its rate relative to reaction (6) to be

$$\mathrm{H_2} + \mathrm{C_6H_5OH} \longrightarrow \mathrm{C_6H_6} \qquad (6)$$

$\log k(\mathrm{CO})/k_6 = 3.02 - (7\,440/2.3T)$. This same relative rate expression for CO formation was used for all phenolic compounds. Amounts of secondary products such as naphthalene, which arise from the CO formation pathway, were consistent with this assumption. Further, in an experiment where CO formation was determined at 1 063 K (*vide infra*, Table 4, experiment 3), this assumption leads to modelled amounts of CO which are within 6% of those observed. Finally it should be noted that, because we have used relatively low degrees of conversion, the accuracy of our expression is not critical: in the case of p-chlorophenol, for example, a two fold increase in the rate constant for CO formation would require a *ca.* 3.5% increase in the rate constant for Cl-desubstitution.

In order to account for mass 'lost' from the arene balance due to CO formation, a slightly different mass normalization procedure was used in the analysis of data from phenolic systems; in these cases outflows were normalized to inflows minus the amount of CO predicted by the reaction model.

With the exception of o-chlorophenol, chlorophenols are solids and it was necessary to liquify these compounds in order to introduce them *via* a syringe. Two experiments were therefore performed in order to obtain rate constants relative to k_1. In the first, the chlorophenol was dissolved in benzene and an approximate site-selectivity obtained from the distribution of chlorophenol, phenol, and chlorobenzene. In the second, a mixture of o-dichlorobenzene and chlorophenol was reacted and, based on phenol formation and the site-selectivity from experiment (1), rates were determined relative to the dechlorination of $C_6H_4Cl_2$. With these data in hand, the results of the first experiment were reanalysed and an improved estimate of the site-selectivity was obtained (one which accurately takes into account further conversions of phenol and chlorobenzene into benzene). This procedure was repeated until the results converged.

Because o-chlorophenol is itself a liquid, it was not necessary to liquify this compound with benzene, and rates relative to k_1 could be obtained directly from the product distributions. As before, the relative rate of phenol/chlorobenzene conversion was taken from our previous study.[8]

In general, because of the added complexity of phenolic systems, there is more uncertainty in our rate measurements. For these compounds, we estimate our site-selectivities to be accurate within ±10% and our rates relative to k_1 to within ±15%.

2,4-Dichlorophenol was also liquified with benzene. Relative conversion rates of the di- and mono-substituted benzenes were fixed and the site-selectivities of the trisubstituted compound determined from the product distribution. Absolute rates were determined relative to phenol and chlorobenzene formation.

This compound provides a substantial test for our previously determined relative rates. In order for the model to correctly predict the amounts of phenol and chlorobenzene, the relative rates and site-selectivities of m-dichlorobenzene, o-chlorophenol, and p-chlorophenol must all be correct. Although the model consistently slightly overestimated the $C_6H_5Cl:C_6H_5OH$

Table 1. Rate data for conversion of *o*-,*m*-,*p*-dichlorobenzenes.[a]

		Products/mmol h^{-1} [b]					Rate constants		
Experiment	T/K	*o*-DCLBZ	*m*-DCLBZ	*p*-DCLBZ	CLBZ	BZ	$k_{2o}/k_{2m}/k_{2p}$	$k_{2o}/2k_1$	$k_1[H^{\cdot}]/s^{-1}$
1[c,d]	1 033	2.01	2.36	2.23	3.48	0.565	1.39/1/1.16	0.972	0.0594
2[c,e]	1 033	1.97	2.30	2.20	3.11	0.430	1.41/1/1.19	1.043	0.0503
3[c,f]	1 113	0.240	0.473	0.353	4.34	4.67	1.34/1/1.16	1.150	0.244

[a] Tubular flow reactor (289 × 0.45 cm), effective volume 46.0 cm^3. [b] *o*-,*m*-,*p*-DCLBZ = *o*-,*m*-,*p*-dichlorobenzene, CLBZ = chlorobenzene, BZ = benzene. [c] Organic inflows: *o*-,*m*-,*p*-$C_6H_4Cl_2$ = 3.42, 3.44, and 3.53 mmol h^{-1}. [d] H_2 = 396 mmol h^{-1}, t = 4.85 s. [e] H_2 = 392 $mmol^{-1}$, t = 4.89 s. [f] H_2 = 377 mmol h^{-1}, t = 4.71 s.

Table 2. Rate data for conversion of 1,2,4-trichlorobenzene.[a]

	Products/mmol h^{-1} [b]						Rate constants[c]		
Experiment	TCLBZ	*o*-DCLBZ	*m*-DCLBZ	*p*-DCLBZ	CLBZ	BZ	$k_\alpha/k_\beta/k_\delta$	k_α/k_{2o}	$k_{2o}[H^{\cdot}]/s^{-1}$
1[d,e]	6.22	1.140	1.567	1.370	0.906	0.18	1.28/1.16/1	0.900	0.0304
2[d,f]	5.64	0.770	1.095	0.941	0.565	0.072	1.33/1.18/1	0.798	0.0302
3[d,g]	5.58	0.851	1.197	1.026	0.648	0.079	1.31/1.16/1	0.838	0.0297

[a] Tubular flow reactor (233 × 0.45 cm), effective volume 37.0 cm^3. [b] TCLBZ = 1,2,4-trichlorobenzene, *o*-,*m*-,*p*-DCLBZ = *o*-,*m*-,*p*-dichlorobenzene, CLBZ = chlorobenzene, BZ = benzene. [c] $k_{\alpha,\beta,\delta}$ = rate constants for Cl removal from the 1-, 2-, and 4-positions of 1,2,4-trichlorobenzene, respectively. Unspecified rate constants for CLBZ and *m*-,*p*-DCLBZ were set relative to k_{2o} as per values given in Figure 1. [d] Inflow TCLBZ = 9.62 mmol h^{-1}. [e] T = 1 028 K, H_2 = 237 mmol h^{-1}, t = 7.96 s. [f] T = 1 025 K, H_2 = 256 mmol h^{-1}, t = 7.37 s. [g] T = 1 024 K, H_2 = 245 mmol h^{-1}, t = 7.77 s.

Table 3. Rate data for conversion of *o*-,*m*-chlorofluorobenzene.[a]

		Products/mmol h^{-1} [b]					Rate constants[c]		
Experiment	T/K	*o*-CLFBZ	*m*-CLFBZ	FBZ	CLBZ	BZ	k_{Cl}/k_F	k_{Cl}/k_1	$k_1[H^{\cdot}]/s^{-1}$
1[c,d]	972	12.30	0.12[e]	1.947	0.511	0.0958	3.56	0.874	0.0570
2[c,f]	999	12.27	0.12[e]	2.418	0.632	0.138	3.55	0.886	0.0690
3[c,g]	1 017	10.02	0.13[e]	2.884	0.766	0.219	3.42	0.943	0.0900
4[h,i]	986	0.11[e]	11.83	2.031	0.626	0.147	2.97	0.672	0.0717
5[h,j]	1 004	0.09[e]	11.96	2.538	0.796	0.213	2.89	0.723	0.0847
6[h,k]	1 017	0.09[e]	10.84	2.844	0.891	0.294	2.83	0.722	0.1059

[a] Tubular flow reactor (232 × 0.40 cm), effective volume = 29.1 cm^3. [b] *o*-,*m*-CLFBZ = *o*-,*m*-chlorofluorobenzene, FBZ = fluorobenzene, CLBZ = chlorobenzene, BZ = benzene. [c] k_{Cl} and k_F are the respective rate constants for removal of Cl and F from CLFBZ; the ratio k_1/k_4 was taken as that determined in reference 7. [d] Inflow *o*-CLFBZ = 17.9 mmol h^{-1}. [d] H_2 = 402 mmol h^{-1}, t = 3.13 s. [e] Impurity in starting mixture. [f] H_2 = 416 mmol h^{-1}, t = 2.89 s. [g] H_2 = 405 mmol h^{-1}, t = 3.02 s. [h] Inflow *m*-CLFBZ = 17.5 mmol h^{-1}. [i] H_2 = 375 mmol h^{-1}, t = 3.30 s. [j] H_2 = 386 mmol h^{-1}, t = 3.15 s. [k] H_2 = 394 mmol h^{-1}, t = 3.05 s.

Table 4. Rate data for conversion of *o*-chlorophenol.[a]

		Products/mmol h^{-1} [b]					Rate constants[c]		
Experiment	T/K	*o*-CLPH	PH	CLBZ	BZ	CO	k_{Cl}/k_{OH}	k_{Cl}/k_1	$k_1[H^{\cdot}]/s^{-1}$
1[d,e]	1 009	8.00	1.132	0.822	0.0906	*f*	1.41	1.47	0.0145
2[d,g]	1 016	7.46	1.277	0.955	0.1301	*f*	1.38	1.42	0.0184
3[d,h]	0 068	1.72	1.98	1.89	1.24	2.90[i]	1.28	1.57	0.0666

[a] Tubular flow reactor (233 × 0.45 cm), effective volume = 37.0 cm^3. [b] *o*-CLPH = *o*-chlorophenol, PH = phenol, CLBZ = chlorobenzene, BZ = benzene, CO = carbon monoxide. [c] k_{Cl} and k_{OH} are rate constants for the respective removals of Cl and OH from CLPH; the ratio k_1/k_4 was taken as that determined in reference 7. [d] Inflow *o*-CLPH = 11.6 mmol h^{-1}. [e] H_2 = 249 mmol h^{-1}, t = 6.18 s. [f] Not determined. [g] H_2 = 253 mmol h^{-1}, t = 6.05 s. [h] H_2 = 210 mmol h^{-1}, t = 6.90 s. [i] CO modelled as described in the text = 3.06 mmol h^{-1}.

ratio, in all experiments the modelled amounts of phenol and chlorobenzene were within 4% of their observed values, which gives added confidence to the relative rates determined here.

Results and Discussion

Rates of desubstitution by H atoms, relative to that for chlorobenzene, are summarized in the Scheme, while the primary data are contained in Tables 1–7. Although the relative rates were not strictly determined at a single temperature, the temperature dependencies are rather slight: *e.g.* the determined relative desubstitution rates of *o*-,*m*-,*p*-$C_6H_4Cl_2$ at 1 113 K ($k_{2,o}$:$k_{2,m}$:$k_{2,p}$ = 1.34:1:1.16) are nearly the same as those found at 1 033 K ($k_{2,o}$:$k_{2,m}$:$k_{2,p}$ = 1.40:1:1.18, *cf.* Table 1). The relative rates reported in the Scheme are all from experiments at 1 000 ± 33 K and should be valid at 1 000 K to within experimental error (deviations due to temperature

Table 5. Rate data for site selectivities in conversion of *m*-,*p*-chlorophenols.[a]

		Products/mmol h^{-1} [b]					Rate constants[c]		
Experiment	T/K	*m*-CLPH	*m*-CLPH	PH	CLBZ	BZ	k_{Cl}/k_{OH}	k_{Cl}/k_1 [d]	$k_1[H^\cdot]/s^{-1}$
1[e,f]	990	4.53	0.015[g]	0.427	0.345	6.07[h]	1.27	0.89	0.0157
2[e,i]	998	4.47	0.013[g]	0.488	0.395	6.87[h]	1.27	0.89	0.0193
3[j,k]	995	0.025[g]	4.34	0.865	0.555	5.72[h]	1.61	1.32	0.0221
4[j,l]	998	0.022[g]	4.04	0.800	0.528	5.83[h]	1.57	1.32	0.0226

[a] Tubular flow reactor (233 × 0.45 cm), effective volume = 37.0 cm^3. [b] *o*-CLPH = *o*-chlorophenol, PH = phenol, CLBZ = chlorobenzene, BZ = benzene. [c] k_{Cl} and k_{OH} are rate constants for the respective removal of Cl and OH from *o*-,*m*-CLPH; the ratio k_1/k_4 was taken as that determined in reference 7, final values are those derived from iterative analyses of the data of Tables 5 and 6 (see the text). [d] From Table 5. [e] Inflows (mmol h^{-1}): *m*-CLPH = 6.31, BZ = 6.33. [f] H_2 = 245 mmol h^{-1}, t = 6.45 s. [g] Impurity in starting mixture. [h] Solvent. [i] H_2 = 256 mmol h^{-1}, t = 6.06 s. [j] Inflows (mmol h^{-1}): *p*-CLPH = 6.38, BZ = 6.31. [k] H_2 = 252 mmol h^{-1}, t = 6.22 s. [l] H_2 = 258 mmol h^{-1}, t = 6.01 s.

Table 6. Relative rate data for conversion of *m*-,*p*-chlorophenols *vs*. *o*-dichlorobenzene.[a]

		Products/mmol h^{-1} [b]						Rate constants[c]	
Experiment	T/K	DCBZ	*m*-CLPH	*p*-CLPH	PH	CLBZ	BZ	k_{Cl}/k_{2o}	$k_{2o}[H^\cdot]/s^{-1}$
1[d,e]	1 004	3.66	3.46	0.009[f]	0.185	0.567	0.051	0.934	0.0200
2[d,g]	1 015	3.29	3.08	0.010[f]	0.186	0.619	0.062	0.853	0.0253
3[h,i]	1 008	3.55	0.011[f]	2.93	0.224	0.565	0.059	1.284	0.0208
4[h,j]	1 013	3.38	0.011[f]	2.74	0.235	0.575	0.061	1.364	0.0224

[a] Tubular flow reactor (233 × 0.45 cm), effective volume = 37.0 cm^3. [b] DCLBZ = *o*-dichlorobenzene, *m*-,*p*-CLPH = *m*-,*p*-chlorophenol, PH = phenol, CLBZ = chlorobenzene, BZ = benzene. [c] k_{Cl} is the rate constant for removal of Cl from CLPH, k_{Cl} and k_{2o} were derived from the results with k_{OH}/k_{Cl} taken as the site-selectivity determined from the data in Table 5; the ratio k_1/k_4 was taken from reference 7; final values were arrived at from iterative analyses of the data in Tables 5 and 6 (see the text). [d] Inflows (mmol h^{-1}): *m*-CLPH = 4.26, DCLBZ = 4.29. [e] H_2 = 272 mmol h^{-1}, t = 5.76 s. [f] Impurity in starting mixture. [g] H_2 = 275 mmol h^{-1}, t = 5.64 s. [h] Inflows (mmol h^{-1}): *p*-CLPH = 3.93, DCLBZ = 4.41. [i] H_2 = 272 mmol h^{-1}, t = 5.76 s. [j] H_2 = 280 mmol h^{-1}, t = 5.56 s.

differences are estimated at ≤1%). Values can be placed on an absolute basis from our previously determined rate constant for hydrogen-atom attack on C_6H_5Cl,[8] $\log k_1(1\,000\ K)/dm^3\ mol^{-1}\ s^{-1} = 8.68$.

Before discussing the implications of the results, it is worthwhile to consider the mechanisms of desubstitution. As we have previously discussed,[8] desubstitution can be brought about either by addition and *ipso* substitution [(7), (8)] or by direct abstraction [(9), (10)]. These mechanisms operate to varying

$$X\cdot + H_2 \longrightarrow XH + H\cdot \qquad (8)$$

$$H\cdot + C_6H_5X \longrightarrow C_6H_5\cdot + HX \qquad (9)$$

$$C_6H_5\cdot + H_2 \longrightarrow C_6H_6 + H\cdot \qquad (10)$$

extents for the substituents investigated here. At one extreme, removal of OH occurs solely *via ipso* substitution.[7,8] Fluorine, on the other hand, is not displaced due to the high endothermicity of process (7) [$\Delta H_7(X = F) = +52\ kJ\ mol^{-1}$ at 1 000 K *]; in this case exothermic abstraction [$\Delta H_9(X = F)$ *ca.* $-47\ mol^{-1}$ †] is essentially the exclusive reaction.[8] We have evidence that both mechanisms contribute to chlorine removal, but that displacement is the primary pathway near 1 000 K.[3,8]

In the cases X = Cl, OH, addition of H (7*a*) is effectively irreversible,[8,10] so rates of desubstitution *via* this pathway correspond closely with rates of addition. Hydrogen addition to an unsubstituted ring site [equation (11)] is reversible and, as we have previously demonstrated,[8] does not contribute to desubstitution because of the slowness of H-migration relative to decomposition [(−11)].

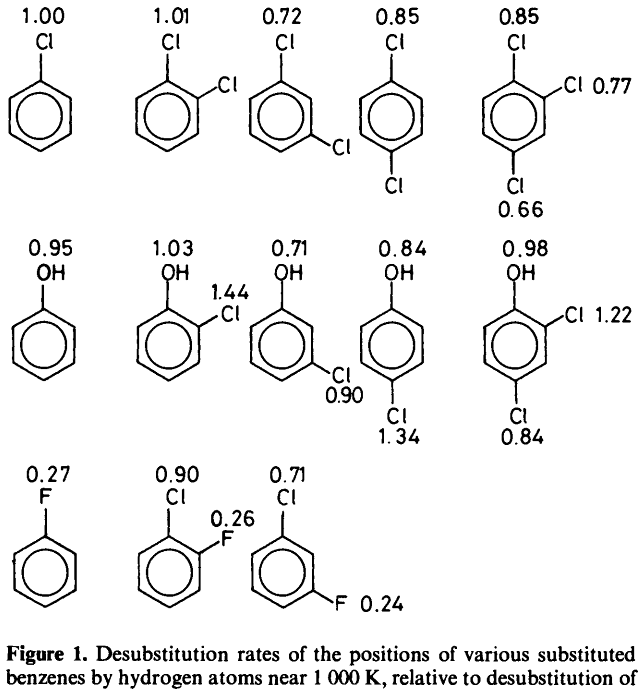

Figure 1. Desubstitution rates of the positions of various substituted benzenes by hydrogen atoms near 1 000 K, relative to desubstitution of chlorobenzene, for which $k(C_6H_5Cl) = 10^{8.68}\ dm^3\ mol^{-1}\ s^{-1}$ at 1 000 K (reference 8). Values are averaged results of the data in Tables 1–7. Data on monosubstituted benzenes were taken from reference 8.

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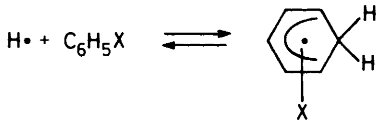
* Calculated from the data in references 11 and 12.

† At 1 000 K, taking an averaged value $H_f(C_6H_5^\cdot) = 319\ kJ\ mol^{-1}$;[13] other data from references 11 and 12.

Table 7. Rate data for conversion of 2,4-dichlorophenol.[a]

Experiment	Products/mmol h^{-1} [b] DCLPH	*o*-DCLPH	*p*-CLPH	*m*-DCLBZ	PH	CLBZ	BZ	Rate constants[c] $k_{OH}/k_{\beta}/k_{\delta}$	k_{OH}/k_1	$k_{2o}[H^{\bullet}]/s^{-1}$
1[d,e]	3.80	0.412	0.573	0.510	0.0900	0.101	4.94	1.13/1.37/1	0.97	0.0197
2[d,f]	3.37	0.399	0.593	0.482	0.0868	0.111	4.81	1.09/1.46/1	1.00	0.0207
3[d,g]	2.95	0.456	0.663	0.577	0.136	0.172	5.01	1.10/1.42/1	0.98	0.0272

[a] Tubular flow reactor (233 × 0.45 cm), effective volume = 37.0 cm^3. [b] DCLPH = 2,4-dichlorophenol, *o*-CLPH = *o*-chlorophenol, *p*-CLPH = *p*-chlorophenol, *m*-DCLBZ = *m*-dichlorobenzene, PH = phenol, CLBZ = chlorobenzene, BZ = benzene. [c] k_{OH}, k_{β}, and k_{δ} are the respective rate constants for removal of OH from the 1-position and Cl from the 2- and 4-positions of DCLPH, k_1 is the average value required to match the observed quantities of PH and CLBZ when relative rates for mono- and di-substituted benzenes are taken as those given in the Scheme. [d] Inflows (mmol h^{-1}): 2,4-DCLPH = 5.90, BZ = 5.88. [e] T = 995 K, H_2 = 252 mmol h^{-1}, t = 6.10 s. [f] T = 1 001 K, H_2 = 262 mmol h^{-1}, t = 5.94 s. [g] T = 1 010 K, H_2 = 256 mmol h^{-1}, t = 6.00 s.



(11)

Substituent Effects on Dechlorination.—Effect of Cl. In general, rates of substituent removal decrease slightly as the degree of ring chlorination increases (Figure 2). Rate differences are limited, however, with the smallest rate constant for chlorine removal in the series C_6H_5Cl, *o-,m-,p-*$C_6H_4Cl_2$, 1,2,4-$C_6H_3Cl_3$ being *ca.* 2/3 that of the largest. These results are in line with the electrophilic nature of $H^{\bullet}$.[14] The relative position of Cl also plays a significant role: *ortho*-Cl has little effect on the desubstitution rate, *meta*-Cl is the most deactivating, and *para*-Cl shows intermediate behaviour.

The *ortho*/*para* directing effect of Cl on electrophilic addition of $H^{\bullet}$ is similar to that found with addition of $^{\bullet}OH$ to the C–Cl sites of dichlorobenzenes at 563 K.[15] The extrapolated pattern for OH addition at 1 000 K, $k_o\!:\!k_m\!:\!k_p$ = 1.56:1:1.29, is close to that found here, $k_o\!:\!k_m\!:\!k_p$ = 1.40:1:1.18.* The most significant difference is that, on a per-site basis, OH appears to add equally fast to C_6H_5Cl and *m*-$C_6H_4Cl_2$, while addition of $H^{\bullet}$ is clearly retarded by *meta*-Cl.

When more than one Cl is present, there is an additive effect on the rate of dechlorination. Thus partial rate factors $f_{o,m,p} = k_{o,m,p}/2k_1$ can be derived from the dichlorobenzene series data (f_o = 1.01, f_m = 0.72, f_p = 0.85). Then, if each position of trichlorobenzene is considered to be affected by two substituents, the measured relative rates (±4%) can be calculated by multiplying the appropriate f values: for the 1-position $k(\text{calc})/k_1 = f_of_p$ = 0.86 (observed k/k_1 = 0.85); for the 2-position, $k(\text{calc})/k_1 = f_of_m$ = 0.73 (observed k/k_1 = 0.76); for the 4-position, $k(\text{calc})/k_1 = f_mf_p$ = 0.61 (observed k/k_1 = 0.65).

Effect of OH. *o*- and *p*-OH clearly facilitate displacement of Cl, whereas *m*-OH slightly retards it. In 2,4-dichlorophenol, removal of 4-Cl (f = 0.84) is somewhat slower than the value derived (0.96) by multiplying the f-values for *p*-chlorophenol (1.34) and *m*-$C_6H_4Cl_2$ (0.72). On the other hand, 2-Cl (f = 1.22) is displaced faster than calculated: 1.44 × 0.72 = 1.04. The exact reasons for these 'deviations' are unclear and we refrain from speculation here.

It should be kept in mind, however, that proper interpretation of small rate differences requires knowledge about the enthalpy and entropy contents of the four states involved (two starting compounds and two transition states). When multiple substituents are present on a benzene ring, the free energies of formation of various isomers may be significantly different: from equilibration and *trans*-substitution studies at 300 K on halobenzenes, toluenes *etc.*,[16] partial equilibrium factors have been derived and may be translated into free energies of interaction. For example, *o*-Cl destabilizes bromine in ClC_6H_4Br, relative to that in C_6H_5Br, by 10.5 kJ mol^{-1}, whereas *m*- and *p*-Cl each have a destabilizing effect of only 4 kJ mol^{-1}.[16] On the other hand, *m*-C_2H_5 stabilizes C–Br by 1.1 kJ mol^{-1}.[17] In as much as such (de)stabilizing effects may be different in the transition states, the observed rate differences are not out of line. At 1 000 K, for example, a relative rate of 1.2 corresponds to a net activation energy difference of *ca.* 1.5 kJ mol^{-1}.

Effect of F. In accordance with its electronegative character, *m*-F retards dechlorination; *o*-F has only a limited effect.

Substituent Effects on Dechlorination Pathways.—As already mentioned, conversions ArCl ⟶ ArH involve *ipso* addition of $H^{\bullet}$, and, for C_6H_5Cl, to a smaller extent, also involve direct abstraction of Cl. The relative rate, k_7/k_9, may depend to some extent on further substitution. Since the transition states are comparable (*i.e.* relatively early in the reaction sequence, some positive charge development at the ring carbon) it may be argued that effects of substitution on both rates should be similar and, thus, that displacement will remain the major mode of Cl removal. This is with the caveat, however, that rates of F-abstraction appear to be little affected by ring substitution (*vide infra*), which could indicate that abstraction of Cl becomes relatively more important.

In any case, a Hammett-type plot of f *vs.* σ_m, σ_p, or $\mathscr{F}$ values[18] for dechlorination can be made in the usual way. Figure 2 shows such plots for the rate of chlorine removal from *m-,p-*disubstituted benzenes. The ρ values (−0.2 to −0.4) are similar to that previously found for *ipso* substitution of monosubstituted benzenes at 1 000 K, (ρ *ca.* −0.3).[8] Since ρ = −0.3 at 1 000 K could correspond to ρ = −1.0 at 300 K, the dependence is much stronger than that observed for H(T) addition to *m-,p-*positions of C_6H_5X (ρ = −0.3 at 313 K).[19] A stronger dependence may reflect the fact that addition of H to $[^{\delta+}C\text{–}Cl^{\delta-}]$ carbon atoms is likely to involve a more polar transition state than addition to a C–H site.

The quality of the correlation in Figure 2 is surprisingly good, much better than that obtained in previous gas-phase studies of H-addition to aromatics.[8,14] In contrast with previous work, however, the present data are both site-specific and unperturbed by varying steric effects at the reactive carbon. This may in part explain the better correlation. Still, in the room temperature liquid-phase study of H(T) addition to the *m-,p-*positions of C_6H_5X,[19] only a marginal correlation was observed. In view of this, our limited data, and the somewhat undefined nature of the reaction (addition/abstraction ratio), the quality of the correlation should be treated with caution.

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* These results assume, of course, that displacement is the dominant dechlorination pathway.

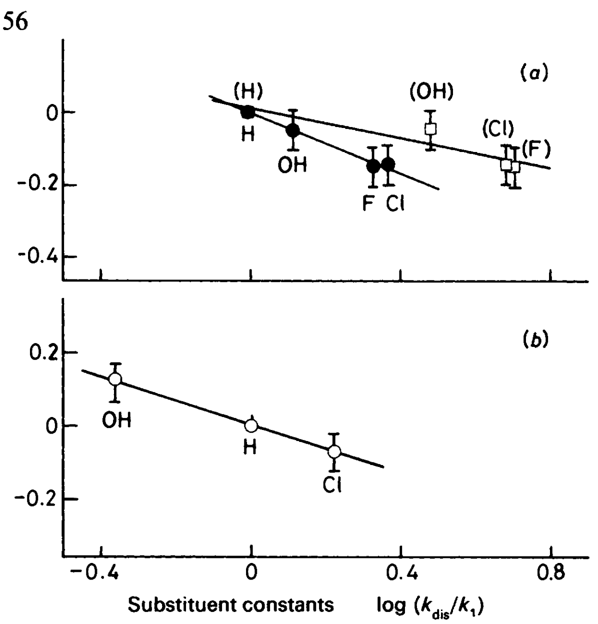

Figure 2. Hammett-type plot of partial rate factors for dechlorination *f* *vs.* substituent constants for *m*-,*p*-substituted chlorobenzenes $\rho(\sigma_m) = -0.41$; $\rho(\sigma_p) = -0.33$; $\rho(\mathscr{F}) = -0.21$. (*a*) ●, σ_m; □, $\mathscr{F}$. (*b*) ○, σ_p.

Substituent Effects on Dehydroxylation.—If the desubstitution rate of phenol is assigned a value of 1, the relative dehydroxylation rates of *o*-,*m*-,*p*-chlorophenols become 1.08, 0.75, and 0.88, respectively. These results are near those obtained for *o*-,*m*-,*p*-dichlorobenzenes when using the dechlorination rate of C_6H_5Cl as a standard, *k*(relative, per site) = 1.01, 0.72, and 0.85. The effect of Cl on dehydroxylation is thus very similar to that observed on dechlorination.

ortho-OH and -Cl lead to higher desubstitution rates than when these groups are in the *para*-position (Figure 1). This could indicate a certain amount of rate acceleration due to steric relief in the transition state, but it may also simply be a reflection of the π-electron densities. *ab initio* calculations by Hehre *et al.*[20] on monosubstituted benzenes suggest that, for resonance-donating substituents, *ortho*-π-electron populations are larger than those of the *para*-position. For relatively unhindered groups, therefore, effects stemming from steric relief may be unimportant, although at present an unambiguous interpretation is not possible.

Effect of Cl *on Defluorination.*—The rate of fluorine removal is little affected by Cl-substitution on the ring. The measured relative defluorination rates for fluorobenzene and *o*-,*m*-chlorofluorobenzene are 1, 0.96 ± 0.16, and 0.89 ± 0.16, respectively.

These results do not stem from direct competition reactions and our data are therefore not precise enough to determine exact differences; nonetheless, it appears that substituent effects are smaller for this reaction. We are unable to directly compare this result with other abstractions by $H^\bullet$ from sp^2 hybridized carbon, as there seem to be no other studies reported in the literature.

We may, however, make comparison with abstractions of H from substituted benzenes by Cl[21] and OH[22] radicals. In the former case, at 563 K, rates of hydrogen abstraction decreased by a factor 4.6 (per available H) when going from C_6H_6 to C_6H_5Cl. Some selectivity was also observed, with $k_m/2k_p = 1.33$. Extrapolated to 1 000 K (by assuming results are due only to enthalpy differences), these become $k(C_6H_6)/k(C_6H_5Cl) = 2.4$, $k_m/2k_p = 1.17$. Such rate differences have been traced to the stability of the resulting *o*-,*m*-,*p*-substituted phenyl radicals.[21] Abstraction of H by $Cl^\bullet$ is endothermic, however, [ΔH(1 000 K) *ca.* +39 kJ mol^{-1}] and will involve a very late transition state. By comparison, exothermic fluorine abstraction [ΔH(1 000 K) *ca.* −47 kJ mol^{-1}] entails a much earlier transition state in which the phenyl-radical-like properties are much less developed. Hence, the stabilities of the resulting phenyl radicals are expected to have little effect on the reaction rate.

Abstraction of H from benzenes by OH is more similar in that it is also exothermic [ΔH(1 000 K) *ca.* −30 kJ mol^{-1}]. At 563 K, $k(C_6H_6)/k(C_6H_5Cl) = 2.5$, $k_m/2k_p = 1.2$,[22] which extrapolates to $k(C_6H_6)/k(C_6H_5Cl) = 1.7$, $k_m/2k_p = 1.1$ at 1 000 K. The relatively low selectivity ($k_m/2k_p$ values) observed in H-abstraction is similar to that observed here with abstraction of F. The primary difference is that the rate of fluorine abstraction is little affected when going from C_6H_5F to *o*-,*m*-ClC_6H_4F, while abstraction of H from C_6H_6 and C_6H_5Cl is markedly different. This may reflect the greater exothermicity of fluorine abstraction as well as differences in transition-state structures.

Implications with Respect to Hydrogenolysis.—The present results show that the rate of chlorine removal from benzenes by hydrogen atoms is only mildly affected by other ring substituents. For the studied compounds, per-site dechlorination rate constants are 0.66–1.44 times that of chlorobenzene. Rates were slightly increased by electron donation to the addition site and decreased by electron withdrawal. Presuming equal pre-exponential factors, the differences correspond to activation energies for hydrogen-atom addition which are within 3.5 kJ mol^{-1} of that for C_6H_5Cl.

Since the substituents we have examined vary widely in their electronic properties (Figure 2) it is unlikely that very different results would be obtained with other groups. It therefore appears that rate differences in dechlorination of aromatics should be minor and thus that hydrogenolysis should prove effective irrespective of the details of the compound structure.

Acknowledgements

Financial support was given by the Dutch Ministry of Housing, Physical Planning, and the Environment (VROM).

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Paper 9/01229J
Received 23rd *March* 1989
Accepted 2nd *October* 1989