

The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XXX.¹ Chlorination of Triphenylene: Linear Free-energy Relationships in Chlorinations of Some Aromatic Hydrocarbons

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A study of the rates of chlorination of *p*-xylene, *m*-xylene, mesitylene, triphenylene, naphthalene, and phenanthrene by molecular chlorine in acetic acid, and of the proportions and nature of the products, allows a reassessment of the applicability of linear free-energy correlations with related data for other electrophilic reactions and with theoretical parameters. Similar relationships for the reactions of acidified hypochlorous acid in aqueous dioxan with a range of hydrocarbons are also discussed.

A number of authors have surveyed the applicability of linear free-energy correlations in the reactions of aromatic compounds with electrophiles.²⁻⁴ Chlorination by molecular chlorine has generally been included in the comparisons since Dewar and Mole's⁵ study, which included benzene, naphthalene, phenanthrene, and triphenylene. Partial rate factors, however, can be derived only approximately from these results, since the products were not fully characterised.

We have examined the substitution products derived from triphenylene and chlorine,⁶ and have established conditions under which chlorination can be effected by means of a positive chlorinating species.¹ We now report further experiments on the products from both

reactions; a number of aromatic substrates have been surveyed for chlorination by positive chlorine. The results allow linear free-energy relationships between these reactions and others, including comparisons with theoretical parameters, to be surveyed with fewer uncertainties than have been necessary until now.

EXPERIMENTAL

Most of the materials and methods have been described.^{1,6}

Spectra were recorded by use of a Unicam SP 800 u.v. spectrophotometer, a Varian T60 n.m.r. spectrometer, or a Perkin-Elmer 237 i.r. spectrophotometer, as appropriate. Microanalyses were performed by Dr. A. D. Campbell, University of Otago, Dunedin. For g.l.c., a Varian 1400 instrument with a flame-ionisation detector was used (5 ft × $\frac{1}{8}$ in column packed with 3% SE30; operating

¹ Part XXIX, P. B. D. de la Mare and L. Main, *J. Chem. Soc. (B)*, 1971, 90.

² L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

³ A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.

⁴ P. B. D. de la Mare and J. H. Ridd, 'Aromatic Substitution—Nitration and Halogenation,' Butterworths, London, 1958.

⁵ M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1957, 342.

⁶ R. Bolton, P. B. D. de la Mare, and L. Main, *J. Chem. Soc. (B)*, 1969, 170.

temperature initially 235°, programmed to rise at 2° min⁻¹. Authentic samples of triphenylene and its 1- and 2-chloro-derivatives were used to calibrate the chromatograms. 9,10-Dimethylphenanthrene had m.p. 143–145° (lit.,⁷ 143.5–144.5), λ_{\max} (cyclohexane) 225, 239, 249, 259, 265, 268, 274, 282, 288, 302, 323, 330, 339, and 353 nm ($\log_{10} \epsilon$ 4.37, 4.50, 4.67, 4.73, 4.71, 4.42, 4.34, 4.20, 4.02, 4.02, 2.50, 2.46, 2.62, and 2.59).

2-Chloro-1,3-dimethylbenzene (Koch-Light) was purified by fractional distillation; b.p. 186° at 760 mmHg, n_D^{20} 1.5274 (lit.,⁸ b.p. 184° at 750 mmHg, n_D^{20} 1.5268), ν_{\max} (CS₂) 588s, 706s, 768s, 914, 981, 1011m, 1034m, 1051s, 1111m, 1167, 1376s, 1409m, 1602, 1775, 1854, 1930, 2870, 2936s, 2967s, 2996s, and 3079m cm⁻¹. 4-Chloro-1,3-dimethylbenzene was prepared from 2,4-dimethylaniline; it had b.p. 186° at 754 mmHg, n_D^{20} 1.5235 (lit.,⁸ 185° at 740 mmHg, n_D^{20} 1.5235), ν_{\max} (CS₂) 628s, 723m, 806s, 871m, 923, 1051s, 1133, 1146m, 1168m, 1378s, 1609, 1747, 1819, 1887, 2876, 2936s, 2966s, 2995s, and 3035m cm⁻¹. 1-Chloronaphthalene (B.D.H.) was fractionally distilled; a middle fraction had b.p. 259° at 755 mmHg, n_D^{25} 1.6320, ν_{\max} (CS₂) 664s, 740, 765s, 790s, 807, 828m, 850, 971s, 1024m, 1063m, 1077m, 1146, 1205s, 1255m, 1355m, 1480s, 1484sh, 1595, and 3078m cm⁻¹. 2-Chloronaphthalene was prepared by the method of Jacobs *et al.*;⁹ repeated crystallisation from ethanol was needed to give a pure product, m.p. 60° (lit.,⁹ 61°), ν_{\max} (CS₂) 600m, 621, 639, 741s, 756, 765, 807s, 823, 850s, 863, 881m, 944m, 957, 984, 1077s, 1133m, 1195, 1350m, 1632m, and 3078m cm⁻¹.

Adducts from the Chlorination of Triphenylene.—Solutions of chlorine (500 ml; *ca.* 0.0104M) and triphenylene (500 ml; *ca.* 0.008M) in acetic acid were mixed and left at 25° until *ca.* 97% chlorine had reacted (*ca.* 30 h). The solvent was then removed under reduced pressure with minimal heating to leave the crude product as a cream solid (1.05 g). This was examined by ¹H n.m.r. spectroscopy, which revealed the presence of adducts of which the major component had two equivalent triplets (τ 4.07 and 4.92) in the region expected for alicyclic protons. A further singlet (τ 8.10) indicated the presence of acetoxy-adducts. I.r. spectroscopy showed the presence of carbonyl groups (ν_{\max} 1708 and 1722 cm⁻¹).

Treatment of the crude product with alcoholic sodium ethoxide in refluxing ethanol for 1 h gave material from which (as shown by ¹H n.m.r. spectroscopy) all the adduct material had been removed. G.l.c. of the product of dehydrochlorination showed the presence of much material of retention time greater than that of triphenylene and its monochloro-derivatives; similar peaks were observed in the chromatogram of the crude product, part of which clearly underwent thermal dehydrochlorination under these conditions.

For column chromatography, a slurry of n-hexane and deactivated silica gel (Riedel de Haen; 100 g) was de-aerated under vacuum. The products of chlorination (1 g) were dissolved in the minimum quantity of chloroform and mixed with a small amount of deactivated silica gel. Most of the chloroform was allowed to evaporate and the mixture was made into a slurry with n-hexane [eluant n-hexane-chloroform (90 : 10)]. Fractions (15–20 ml) were examined by t.l.c. on silica gel (Kieselguhr PF₂₅₄ and PF₃₆₆). The

spots were detected both by u.v. illumination and by iodine vapour. Although the small solubility of triphenylene and its derivatives reduced the sharpness of the separation, it was reasonably effective. Dichlorotriphenylene, the monochlorotriphenylenes, and triphenylene were eluted in that order in the first twelve fractions. A triphenylene tetrachloride was recovered in almost pure form from fractions 16 and 17. Fractions 18–21 contained other material which appeared as an undifferentiated spot on t.l.c. Later fractions contained this and other relatively unstable material.

The ¹H n.m.r. spectrum of fractions 16 and 17 in deuteriochloroform showed one adduct (>95%). It consisted of signals for aromatic protons [τ 1.39 (2H, m), 1.83 (2H, m), and 2.36 (4H, m)] consistent with a tetrahydrotriphenylene residue; and two apparent triplets (alicyclic) (τ 3.91 and 4.81). Scale expansion resolved the triplet at higher field into a quartet. As for naphthalene tetrachlorides,¹⁰ four of the possible triphenylene tetrachlorides involving addition to a single ring would have AA'XX' spectra with $J_{1,2} = J_{3,4}$, and the observed spectrum is very similar to that of naphthalene α -tetrachloride,¹⁰ but we were not able to detect unambiguously the presence of the outer satellite bands expected with $J_{1,2} = J_{3,4} = 3.7$ and $J_{2,3} ca. 12$ Hz.

The *tetrachloride*, m.p. 176° (from hexane-chloroform), had λ_{\max} (cyclohexane) 237, 243, 249, 255, 261, 264, 298, 308, 340, and 357 nm ($\log_{10} \epsilon$ 4.34, 4.36, 4.42, 4.62, 4.74, 4.60, 4.01, 4.00, 2.86, and 2.70) with shoulders at 223, 233, 273, and 280 nm, ν_{\max} (CS₂) 690s, 720s, 750s, 763s, 775s, 836m, 962m, 976w, 1053w, 1158m, 1233m, and 1346m cm⁻¹ (no significant absorption at 1700–1730 cm⁻¹) (Found: C, 58.2; H, 3.3; Cl, 38.2; C₁₈H₁₂Cl₄ requires C, 58.4; H, 3.3; Cl, 38.3%).

Dehydrochlorination of a portion of fraction 17 under the conditions already described gave an organic product from which all adduct had been removed. By g.l.c., it was shown that the main product comprised a mixture of dichlorotriphenylenes, including but not exclusively the dichlorotriphenylenes produced by direct reaction; the latter compounds appeared in fraction 8 mixed with much monochlorotriphenylene.

The ¹H n.m.r. spectra of fractions 18–21 showed that they contained the same triphenylene tetrachloride with increasing amounts of a second tetrachloride. The ¹H n.m.r. spectrum of this consisted of signals (all 1H) at τ 5.6 (q, 2-H), 4.8 (q, 3-H), 4.1 (d, 1-H), and 4.0 (d, 4-H); $J_{1,2}$ 3.0, $J_{2,3}$ 12.0, and $J_{3,4}$ 6.0 Hz. The equivalent weights of both fractions 17 and 21, determined by treatment with excess of ethanolic alkali and titration of the product with silver nitrate, showed that both were tetra- rather than dichlorides.

Still later fractions (22–29) contained material less clearly characterised. They decomposed in air, or on evaporation, to give coloured materials, and their ¹H n.m.r. spectra had absorptions of intensities similar to those for the tetrachlorides in the aromatic and alicyclic regions. Absorptions around τ 8.0, expected for acetoxy-chlorides, were generally weaker than expected for a pure compound, or were absent in later fractions. It is likely that these fractions contained acetoxy-trichlorides and their products of decomposition, which may include trichlorodihydro-

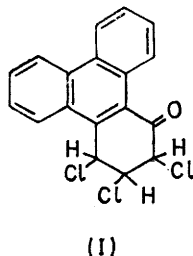
⁷ C. K. Bradsher and W. J. Jackson, jun., *J. Amer. Chem. Soc.*, 1954, **76**, 4140.

⁸ H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175.

⁹ T. L. Jacobs, S. Winstein, J. W. Ralls, and J. H. Robson, *J. Org. Chem.*, 1946, **11**, 27.

¹⁰ P. B. D. de la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *J. Chem. Soc. (B)*, 1966, 827.

triphenylene-1(2*H*)-ones (I) analogous to the related compounds obtained in the naphthalene series.¹¹ The i.r. spectrum was consistent with this; a moderately intense carbonyl absorption at 1708 cm⁻¹ had a wavenumber significantly lower than expected for a carbonyl group in an acetoxy-adduct.



In order to estimate the relative amounts of the different types of adduct produced, we employed a method used previously.¹⁰ Reaction of excess (1.5 g) of triphenylene in acetic acid (*ca.* 900 ml) with chlorine (1.00 × 10⁻³ mol) gave 0.72 × 10⁻³ mol of chloride by direct reaction, and a further 0.44 mol after alkaline dehydrochlorination of the organic portion of the product. From these results it can be calculated that chlorine (1 mol) reacts with triphenylene (0.78 mol) to give chlorotriphenylenes (0.56 mol), triphenylene tetrachloride (0.06 mol), and triphenylene acetoxy-trichloride (0.16 mol), it being assumed that these are the only products.

In determining the rate of chlorination of triphenylene in acetic acid, we followed the usual procedure. When part of the product is tetrachloride, formed from dichloride by rapid addition, the rate coefficient for initial attack on the hydrocarbon needs to be calculated by using a modified formula,¹² which in our case (since triphenylene was in considerable excess over chlorine) reduces to equation (1).

$$k_2 = 2.303 \log_{10} \{b/(b-x)\}/at(1+\alpha) \quad (1)$$

Here *a* and *b* are the initial concentrations of triphenylene and chlorine, *x* is the concentration of chlorine at time *t*, and α is the proportion of aromatic compound used up to form derivatives of tetrahydrotriphenylene, *viz.* 0.28. The mean value over three concordant determinations was then found to be 0.58 l mol⁻¹ min⁻¹ at 25°. Dewar and Mole's uncorrected value⁵ was 1.32 l mol⁻¹ min⁻¹; we regard our figure as more reliable.

The kinetics of the chlorination of triphenylene by acidified hypochlorous acid in 96% dioxan have been described elsewhere.¹ In this reaction, little addition (<10%) accompanies substitution, and we make no corrections to the rate coefficients to allow for this. The ratio of substitution products has now been determined for chlorination at 25° in this and in a number of other solvents, by using the analytical procedure based on i.r. spectroscopy also described elsewhere.⁶ Results are given in Table 1.

Products of chlorination of naphthalene by positive chlorine were examined by i.r. spectroscopy. 2-Chloronaphthalene absorbs strongly at 1077 cm⁻¹, whereas the absorption by 1-chloronaphthalene at the same wavelength and its adjacent absorption at 1063 cm⁻¹ are both much weaker. Since in our reaction mixtures 2-chloronaphthalene is the minor component, the ratio of heights of the peaks

¹¹ P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc. (C)*, 1967, 1586; P. B. D. de la Mare, S. de la Mare, and H. Suzuki, *J. Chem. Soc. (B)*, 1969, 429.

at these two wavelengths proved to be sensitive to small changes in composition. The reaction product (its concentration in carbon disulphide was adjusted to give approximately a standard concentration of chloronaphthalenes) was compared with mixtures of known composition.

TABLE 1
Ratio of chlorotriphenylenes formed in the chlorination of triphenylene at 25°

Reagent	Solvent	Added electrolytes	Ratio 1-chloro to 2-chloro
Cl ₂	HOAc ^a		73 : 27
Cl ₂	CHCl ₃		64 : 36
Cl ₂	MeNO ₂		56 : 44
Cl ₂	96% Dioxan	0.75M-HClO ₄	89 : 11
ClOH ₂ ^{+b}	96% Dioxan	0.50M-HClO ₄	86 : 14
ClAgCl ^{+b}	96% Dioxan	0.50M-HClO ₄ 0.002M-AgClO ₄	85 : 15

^a Ref. 6. The ratio was unchanged by the method of work-up. ^b See ref. 1 for a discussion of the nature of the reagents.

Appropriate checks were made to establish that there was no interference from naphthalene or from minor by-products, and that the procedure of extraction and recovery did not alter significantly the isomeric proportions. The ratio of 1-chloronaphthalene to 2-chloronaphthalene for chlorination by hypochlorous acid in 95% dioxan containing 0.5M-perchloric acid with and without 0.001M-silver perchlorate was thus found to be 95 : 5.

A similar method was used for examination of the products of chlorination of *m*-xylene; the strong absorptions of 2-chloro-1,3-dimethylbenzene at 706 cm⁻¹ and of 4-chloro-1,3-dimethylbenzene at 723 cm⁻¹ were observed. Allowance had to be made for weak absorption by *m*-xylene at 723 cm⁻¹ if the latter compound was present in more than *ca.* five-fold excess; we found that if, in a recorded spectrum of a mixture, the absorption of *m*-xylene at 689 cm⁻¹ was more than twice as strong as that of 4-chloro-1,3-dimethylbenzene, it was necessary to remove some of the *m*-xylene by careful evaporation before the analysis was carried out. Brown and Stock⁸ used a similar method, based on the bands at 765 and 803 cm⁻¹. Results are given in Table 2.

TABLE 2
Ratio of chloro-1,3-dimethylbenzenes found in the chlorination of *m*-xylene at 25°

Reagent	Solvent	Added electrolytes	Ratio 4-chloro to 2-chloro
Cl ₂	HOAc ^a		77 : 23
Cl ₂	96% Dioxan	0.50M-HClO ₄	78 : 22
ClOH ₂ ^b	96% Dioxan	0.50M-HClO ₄	66 : 34
ClAgCl ^{+b}	96% Dioxan	0.50M-HClO ₄	65 : 35

^a Ref. 8. ^b See ref. 1 for a discussion of the nature of the reagents.

DISCUSSION

Most of our studies of chlorination by molecular chlorine refer to acetic acid as solvent. We have, however, made a few measurements in 96% dioxan for comparison with results for chlorination by positive chlorine, and to establish the extent to which this change in solvent affects the response of the rate to change in

¹² P. B. D. de la Mare and J. S. Lomas, *Rec. Trav. chim.*, 1967, 86, 1082.

structure. In this solvent, as in acetic acid,¹³ we expect the rate to be quite sensitive to the presence of, or change in, the concentration of added electrolytes, so we have made the measurements in the presence of added lithium perchlorate or perchloric acid; the latter was always present in the reaction involving positive chlorine. Results are included in Table 3, which summarises also the values from the literature for chlorination in acetic acid used in the following discussion.

TABLE 3

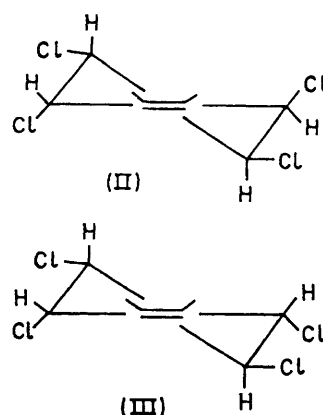
Rate coefficients for chlorination of some aromatic compounds by molecular chlorine at 25°

Compound	k_2 (l mol ⁻¹ min ⁻¹) in HOAc	k_2 (l mol ⁻¹ min ⁻¹) in 96% dioxan with 0.35M-HClO ₄	k_2 (l mol ⁻¹ min ⁻¹) in 96% dioxan with 0.40M-HClO ₄
		Benzene	0.000092 ^a
<i>p</i> -Xylene	0.19 ^a	0.17 ^b	
Triphenylene	0.58 ^b		
Naphthalene	3.0 ^c	5.0 ^b	10.0 ^b
<i>m</i> -Xylene	17.2 ^a	23 ^b	
Phenanthrene	26 ^a		
Mesitylene	2820 ^e		

^a Ref. 8. ^b This investigation. ^c Ref. 12; *cf.* 4.4, uncorrected for adduct-formation (S. F. Mason, *J. Chem. Soc.*, 1959, 1233). ^d Ref. 13. ^e Ref. 27.

Adducts from Triphenylene.—As with naphthalene,¹⁰ several adducts are formed in the chlorination of triphenylene; together they comprise *ca.* 28% of the aromatic compound used up in the chlorination. The acetoxy-trichlorides are less stable than those derived from naphthalene; they resemble more closely in their behaviour on attempted isolation the unstable acetoxy-chlorides derived from phenanthrene.¹⁴ The polychlorides, however, are reasonably stable and can be isolated by chromatography. The main component possibly is a compound analogous in structure to naphthalene α -tetrachloride. Its u.v. spectrum, resembling closely that of 9,10-dimethylphenanthrene, eliminates from consideration any tetrachlorides formed by attack on two aromatic rings, and its ¹H n.m.r. spectrum indicates an AA'XX' structure. One of the possibilities is (II) (like naphthalene α -tetrachloride; aromatic residue not shown). Accompanying this, and eluted later from the chromatogram, is a second tetrachloride. This, like naphthalene δ -tetrachloride,¹⁰ has all its hydrogen atoms in different magnetic environments; and the spectrum can be treated by first-order analysis, in which the large coupling constant, since it is associated with the quartets, must be a 2,3-coupling. The structure is then defined by the remaining couplings to be (III), analogous with that of the δ -isomer of naphthalene tetrachloride. Heterolytic paths for chlorination leading to these tetrachlorides are presum-

ably analogous to those involved in the similar chlorination of naphthalene.



The dichlorotriphenylenes produced by dehydrochlorination of these compounds are a mixture of at least two components, as is the case for the naphthalene tetrachlorides.¹⁵ They should be substituted in one ring, in contrast with some of the compounds expected by direct dichlorination of triphenylene. In agreement with this, early fractions from the column chromatogram showed (g.l.c.) the presence of fractions both of the same and of different retention times.

Correlations involving Overall Reactivities.—The results given in Table 3 for molecular chlorination, together with those reported earlier for reactions involving positive chlorine,¹ and values given by Mackor *et al.*¹⁶ for basicities, can be put together as logarithms of relative reactivities (which themselves are proportional to free energies) as in Table 4.

TABLE 4

Data for linear free-energy relationships

Hydrocarbon	Basicity constant HF/BF ₃ (ref. 16)	Logarithms of relative reactivities			
		Cl ₂ HOAc	Cl ₂ 96% dioxan	ClOH ₂ ⁺ 96% dioxan	ClAgCl ⁺ 96% dioxan
<i>p</i> -Xylene	0	0	0	0	0
Triphenylene	1.1	0.48		0.28	0.34
Naphthalene	1.7	1.20	1.47	0.74	0.81
<i>m</i> -Xylene	2.5	1.95	2.13	0.97	1.04
Mesitylene	5.3	4.18			2.14

There is obviously a close correspondence between the results for the two reactions which provide positive chlorine, despite the difference between the nature of the solvation of the electrophile. Comparison can also be made with the result available for chlorination by acidified hypochlorous acid in water.¹⁷ The partial rate factors for chlorination of toluene under these conditions (f_o 134; f_m 4; f_p 82) lead to a predicted value of $\log_{10} k_2(m\text{-xylene})/\log_{10} k_2(p\text{-xylene}) = 1.27$; the mean value obtained in 96% dioxan is 1.00. The rate,

¹³ P. B. D. de la Mare, A. Singh, E. A. Johnson, R. Koenigsberger, J. S. Lomas, V. Sanchez de Olmo, and A. M. Sexton, *J. Chem. Soc. (B)*, 1969, 717.

¹⁴ P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 1961, 5285; P. B. D. de la Mare and R. Koenigsberger, *ibid.*, 1964, 5327.

¹⁵ P. B. D. de la Mare, R. Koenigsberger, and J. S. Lomas, *J. Chem. Soc. (B)*, 1966, 834.

¹⁶ E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, 1958, 54, 66; 186.

¹⁷ P. B. D. de la Mare, J. T. Harvey, M. Hassan, and S. Varma, *J. Chem. Soc.*, 1958, 2756.

therefore, appears to respond less in the latter solvent, a result which implies a slightly lower reaction constant (ρ) for the reaction. This constant can be calculated from Figure 1, for the reaction attributed to ClAgCl^+ , as -5.5 if the ρ value for molecular chlorine is -10.0 , (*cf.* ref. 2; data in ref. 4 give a value of -9.6). The value for positive bromine¹⁸ is -6.2 . We thus confirm,

large effects. The correlation with basicity as measured by reaction with boron trifluoride and hydrogen fluoride is also reasonably good but not perfect.

Correlations with Theoretical Parameters.—Benzene reacts too slowly for satisfactory rate measurements under our conditions, so for correlations of reactivity with theoretical parameters we have used *p*-xylene as the

TABLE 5
Partial rate factors for chlorination by positive chlorine (ClAgCl^+)¹ in 96% dioxan at 25°, and some related theoretical parameters

Hydrocarbon	Position	$2 + \log_{10} (k_2 F/n)$	Localisation energy L_r^+ with $-\Delta\alpha_s = 0.45$	$\Sigma\pi_{rr}\Delta\alpha_s$ with $-\Delta\alpha_s = 0.25$	$\pi_{rr}\Delta\alpha_s$ with $\Delta\alpha_r = 1.25$	$\Sigma\pi_{rr}\Delta\alpha_s + \pi_{rr}\Delta\alpha_r$ with $\Delta\alpha_s = -0.25, \Delta\alpha_r = 1.25$
<i>p</i> -Xylene	<i>a</i>	1.63	2.39	0.037	0.497	0.534
Triphenylene	1	1.72	2.38		0.533	0.533
Triphenylene	2	0.97	2.48		0.507	0.507
Naphthalene	1	2.42	2.30		0.554	0.554
Naphthalene	2	1.14	2.48		0.507	0.507
<i>m</i> -Xylene	2	2.81	2.24	0.078	0.497	0.575
<i>m</i> -Xylene	4	2.78	2.24	0.065	0.497	0.562
Mesitylene	<i>a</i>	3.89	2.09	0.104	0.497	0.601

^a All unsubstituted positions are equivalent.

for chlorine over a considerably wider range of reactivity and in a second solvent of widely different ionising power, that the positive halogenating species derived from chlorine and bromine have transition states for electrophilic substitution requiring ρ values of *ca.* 6, whereas the molecular reagents give much higher values.

Figure 1 illustrates that there is a reasonably good but not perfect linear free-energy relationship between

reference compound, when equation (2) is appropriate

$$\log_{10} (k_2 F/n) = \log_{10} f_r + c \quad (2)$$

Here F is the fraction of attack occurring at an r -type position, n is the number of equivalent such positions, and f_r is the partial rate factor for substitution at a single such position. Values are given in Table 5.

In making these calculations, the value of F has been taken to be the percentage of the relevant isomer found in the products of substitution. We have discussed in earlier papers (*cf.* ref. 20) the uncertainties resulting from this procedure. It can be justified only if attack on each position in a single hydrocarbon divides in similar proportion between substitution and addition. To the extent to which this is not true, an error is introduced into the partial rate factors, the maximum possible being dependent on the amount of addition. In our case, we have shown¹ that this could be up to about 10 units %, which would affect the partial rate factors for the major products only slightly in free-energy terms, but could have a significant influence on the minor products. There is no way of which we are aware to remove this uncertainty; use of any other assumption is equally arbitrary. The fact that product proportions have been shown to be very little affected by the method of work-up gives some confidence to our assumptions.

A number of different sets of theoretical reactivity indices are available³ for unsubstituted aromatic compounds; for extension to methyl-substituted derivatives, it is necessary to make allowance for the electron-releasing properties of this group. We have chosen here to explore the correlation between our rate data for positive chlorination and (a) localisation energies and (b) charge densities.

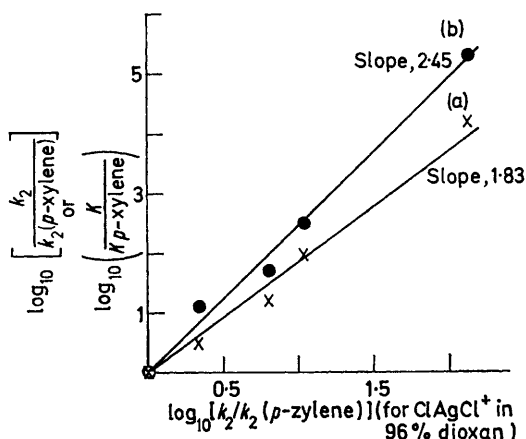


FIGURE 1 Relationship between rate of positive chlorination (ClAgCl^+) and (a) rate of molecular chlorination ($\text{Cl}_2\text{-AcOH}$), (b) basicity constant (HF/BF_3 , ref. 16)

the overall rate for molecular chlorination in acetic acid and the overall rate for positive chlorination in 96% dioxan. That molecular chlorination also is not much affected by the change in solvent from 96% dioxan to acetic acid is evident from Table 4, though it is now known¹⁹ that more extensive solvent changes can have

¹⁸ P. B. D. de la Mare and I. C. Hilton, *J. Chem. Soc.*, 1962, 997.

¹⁹ L. M. Stock and A. Himoe, *J. Amer. Chem. Soc.*, 1961, **83**, 4605.

²⁰ P. B. D. de la Mare and E. A. Johnson, *J. Chem. Soc.*, 1963, 4076.

(a) *Localisation Energies*.—For the unsubstituted compounds, we use the localisation energies L_r^+ given by Streitwieser.³ For the polymethylbenzenes, we have used equation (3) given by Longuet-Higgins²¹ for the

$$\Delta E_\pi = -c_{rs}{}^2 \Delta \alpha_s \quad (3)$$

change in localisation energy resulting from the presence of an inductive substituent at a position s , $\Delta \alpha_s$ being the change in coulomb integral of a carbon atom s and c_{rs} being a coefficient obtained by simple rules given by Coulson and Longuet-Higgins.²² From this, we get equation (4). We have treated $\Delta \alpha_s$ as an adjustable

$$\begin{aligned} L_r^+ &= L_r^+ (\text{parent molecule}) - \Sigma \Delta E_\pi \\ &= L_r^+ (\text{parent molecule}) + \Sigma c_{rs}{}^2 \Delta \alpha_s \end{aligned} \quad (4)$$

parameter; and sought to obtain the most satisfactory correlation with the reactivities. A value of $\Delta \alpha_s$ of

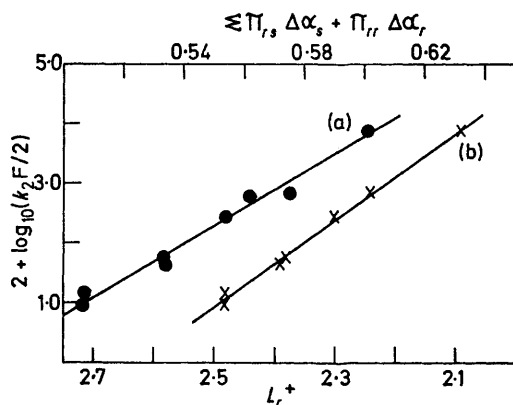


FIGURE 2 Relationship between rate of chlorination by positive chlorine (ClAgCl^+) and theoretical parameters based on (a) charge densities and (b) localisation energies

—0.45, which is in reasonable agreement with those of some other studies (ref. 3, p. 133) gives approximately the best fit, with a formal correlation coefficient of 0.997 and a formal standard deviation of 2.2%. The relationship is represented graphically in Figure 2, and can be seen to be quite good, over a reactivity range of 10^3 ; worst agreement is for the minor component of substitution in naphthalene, where uncertainty resulting from assumptions concerning the accompanying addition is greatest, and even here the discrepancy is no more than 0.1 logarithmic units.

(b) *Charge Densities*.—The quantity that we have used for correlation here is $\pi_{rr}\Delta\alpha_r + \Sigma\pi_{rs}\Delta\alpha_s$. The first term of this equation implies adoption of the concept that the self-atom polarisability π_{rr} , of a ring carbon atom partly determines its reactivity,²¹⁻²³ and that the effect of the electrophile is to change the electron density, which is unity for even alternant hydrocarbons, by an amount $\pi_{rr}\Delta\alpha_r$. The value of $\Delta\alpha_r$ will depend on the nature and distance of the electrophile. This term takes account of

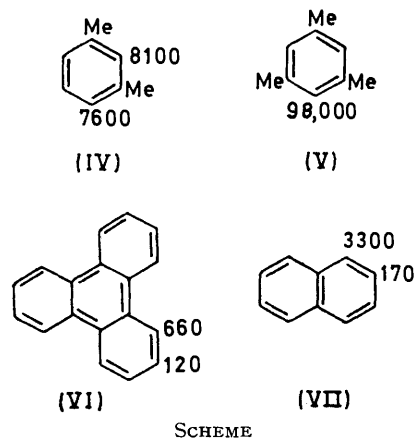
²¹ H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 283; *Proc. Roy. Soc.*, 1951, *A*, **207**, 121.

²² C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **192**, 16.

differences between ring systems and positions within an unsubstituted ring system. The term $\pi_{rs}\Delta\alpha_s$ takes account of the influence of the substituent on the charge density around the ring. A treatment of this kind has been used for correlation of the rates of bromination of the dimethylnaphthalenes by Berliner and his co-workers²⁴ with some success. We have used values of π_{rr} given by Streitwieser,³ and those of π_{rs} given by Coulson and Longuet-Higgins.^{21,22} Effects of methyl groups are considered to be independent and additive, as in the former treatment.

The best fit with the partial rate factors depends on the ratio of $\Delta\alpha_r : \Delta\alpha_s$ being —5.0. In Table 5 we have included values of $\Sigma\pi_{rs}\Delta\alpha_s + \pi_{rr}\Delta\alpha_r$ for $-\Delta\alpha_s = 0.25$ and $\Delta\alpha_r = 1.25$, which give the most satisfactory agreement with partial rate factors for chlorination by positive chlorine. The formal correlation coefficient is 0.990, and the formal standard deviation is 5.1%. The results are represented graphically in Figure 2; by inspection, the fit is not as good as that for correlation with localisation energies.

In principle, it might be thought that extrapolation of the graphs in Figure 2 to the appropriate theoretical value for benzene would enable evaluation of the constant term in equation (2), and hence of partial rate factors relative to benzene. But it has been noted (see ref. 24) that in such correlations with theoretical parameters the value for benzene often lies at too low a reactivity. A better evaluation of this constant is probably to be derived from the partial rate factors for chlorination of toluene by positive chlorine in water;¹⁷ by application of the additivity principle to these values, $\log_{10} f_r$ for *p*-xylene should be 2.73, so that the constant should be —3.10. This value leads, subject to the provisos already mentioned, to the partial rate factors for chlorination by positive chlorine (ClAgCl^+)¹ (Scheme). These are



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probably quite satisfactory relative values, though there is some additional uncertainty in their absolute magnitudes.

²³ H. H. Greenwood and R. McWeeney, *Adv. Phys. Org. Chem.*, 1966, **4**, 73.

²⁴ J. B. Kim, C. Chen, J. K. Krieger, K. R. Judd, C. C. Simpson, and E. Berliner, *J. Amer. Chem. Soc.*, 1970, **92**, 910.

It is possible to treat the results for molecular chlorination in a similar way; here, partial rate factors can be determined directly, since the rate of chlorination of benzene has been established⁸ as $9.2 \times 10^{-5} \text{ l mol}^{-1} \text{ min}^{-1}$, a value which accords with our²⁵ value ($7.5 \times 10^{-5} \text{ l mol}^{-1} \text{ min}^{-1}$) when allowance is made²⁵ for the solvent

rather than linear. Significant dipolar interaction between the terminal chlorine atom and the developing positive charge would then give an enhancement of the rate of addition; this enhancement would be most marked for cases in which *cis*-addition was most significant. If this interpretation is correct, it must have an

TABLE 6

Data relating to the chlorination of triphenylene, naphthalene, and phenanthrene by molecular chlorine in acetic acid at 25°

	Triphenylene		Naphthalene	Phenanthrene
k_2 (rel) (Benzene = 1)	6300		32,600	280,000
Total substitution (%)	72		66	35
Total addition (%)	28 ^a		34 ^a	65
Total acetoxy-chloride (%)	20 ^a		13 ^a	17
Position	1	2	1	9
Substitution (%)	53	19	66 ^b	34.3 ^c
Partial rate factor (normal assumptions)	4.6×10^3	1.7×10^3	4.9×10^4	9.7×10^5
$\log_{10} f_r$	3.66	3.23	4.69	5.98
Possible range (d) of $\log_{10} f_r$	3.52—3.71	3.08—3.47	4.51—4.69	5.53—5.92
L_r^+ (Benzene = 2.54)	2.38	2.48	2.30	2.30

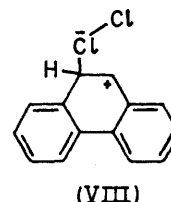
^a Tetrachloride or acetoxy-trichloride. ^b Assumed no 2-substitution; only 5% was found for positive chlorination. ^c Ref. 13. ^d By using the extreme assumptions for F [equation (2)] for triphenylene, 0.53—0.81 (1-position), 0.19—0.47 (2-position); for naphthalene, 0.66—1.00; for phenanthrene, 0.343—0.993; see text.

effect of the high concentration of benzene used in our measurement.* Additive effects in the chlorination of alkylbenzenes have been discussed extensively by us and by others,^{4,8,27} so we will confine ourselves here to a comparison of triphenylene, naphthalene, and phenanthrene.

Relevant data are summarised in Table 6. The correlation between localisation energies and rate of molecular chlorination is poor, even over the range of structures considered here. Removal of benzene from the comparison improves the correlation slightly, but leaves it still poor. As to interference from the concomitant addition through alteration in the proportions of products, the most extreme assumptions that can be made concerning the effect on the partial rate factors would be alternatively to exclude addition from or to assign all the addition to one particular position; and these extremes give the ranges indicated in Table 6. Even this does not allow the possibility of a satisfactory correlation; we note particularly the relatively large difference in rate of chlorination of naphthalene and phenanthrene, despite the fact that the localisation energies, as well as some other reactivity indices,³ for 1-substitution in the former and 9-substitution in the latter are the same.

Although the concomitant addition does not seem to interfere significantly with linear free-energy relationships through altering the proportions of products, it is possible that it exerts an influence through making a significant contribution to the ease of overall interaction of the electrophile with the aromatic substrate. We have proposed elsewhere¹⁴ that the intermediate leading to *cis*-addition might for phenanthrene have the geometry shown in (VIII), with the $\overset{+}{\text{Ar}}-\overset{-}{\text{Cl}}-\text{Cl}$ system angular

influence on the rate of 9-chlorination of phenanthrene, for example, involving at least a power of ten.



The effect of solvent on the orientation of chlorination of triphenylene was shown in Table 1. The changes are not easily interpretable. It is clear that significant variations occur, and that these are not directly related to the overall reaction rate; since chlorination in chloroform is slower, and in nitromethane is faster, than in acetic acid, whereas in both chloroform and in nitromethane there is more 2-substitution than in acetic acid. We have noted similar irregularities in the effect of solvent on the ratio of addition to substitution in chlorination of phenanthrene.¹³ It seems likely that the solvent may play a part by way of specific effects of solvation on the exact geometry and fate of the intermediate (VIII).

Our results show that specific influences of solvent can have an influence on the partial rate factor for triphenylene more important than that resulting from primary steric hindrance to 1-substitution. They confirm our earlier conclusion⁶ that such steric hindrance must be unimportant for reagents having smaller steric requirements than the nitronium ion.

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* Other values in the literature^{5,26} are in our view less satisfactory.

²⁵ P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 1958, 1519.

²⁶ R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, 1957, **79**, 4348.

²⁷ E. Baciocchi and G. Illuminati, *Gazzetta*, 1962, **92**, 89.