Sandmeyer reactions. Part 3.[1] Estimation of absolute rate constants for the transfer of chloride ligands from Cu^{II} to 2-benzoylphenyl radical (Pschorr radical clock) and further investigations of the relative rates of transfer of chloride and water ligands to other substituted phenyl radicals

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Absolute rate constants have been estimated for the transfer of chloride ligands from $CuCl(OH_2)_5{}^+$, $CuCl_2(OH_2)_4$ and $CuCl_3(OH_2)_3{}^-$ to 2-benzoylphenyl radical in aqueous solution at ionic strength 5 mol dm^{-3} by comparison with its rate of cyclisation. The radical reacts with the monochlorocopper(II) complex with $k = (8.8 \pm 1.3) \times 10^6$ dm^3 mol^{-1} s^{-1}, but it does not discriminate between the di- and tri-chloro complexes, $k = (1.0 \pm 0.1_5) \times 10^8$ dm^3 mol^{-1} s^{-1}. Relative rate constants for the transfer of chloride and water ligands to a series of 2-, 3- and 4-substituted phenyl radicals have also been obtained; three copper complexes are implicated in chloride transfer for the conditions examined. Radicals with 3-and 4-substituents discriminate the monochlorocopper(II) complex from the two more highly chlorinated complexes, the discrimination increasing the more nucleophilic and reactive the radical. Radicals with strongly electron-withdrawing 2-substituents (CN, F) do not discriminate between any of the chlorocopper(II) complexes. A mechanistic rationale of the observations is proposed.

In the Sandmeyer reaction a diazonium ion is homolytically decomposed and substituted in a process catalysed by a copper redox cycle. In the traditional form of the reaction used for replacing the diazonium group by Cl, Br or CN, the solution of diazonium ion is added to a solution of the corresponding Cu^I salt in aqueous HCl, HBr or NaCN, as appropriate;[2] a Cu^I complex reduces the diazonium ion to produce an aryl radical, dinitrogen and a Cu^{II} complex which then oxidatively transfers a ligand to an aryl radical and the catalytic cycle is complete (see Scheme 1). In this mode of reaction the bulk of the copper resides in the Cu^I state and the Cu^{II} state is transient.

$$ArN_2{}^+ + Cu^ICl_2{}^- \longrightarrow Ar^\bullet + N_2 + Cu^{II}Cl_2$$

$$Ar^\bullet + Cu^{II}Cl_2 \longrightarrow ArCl + Cu^ICl$$

$$Cl^- + Cu^ICl \longrightarrow Cu^ICl_2{}^-$$

Scheme 1

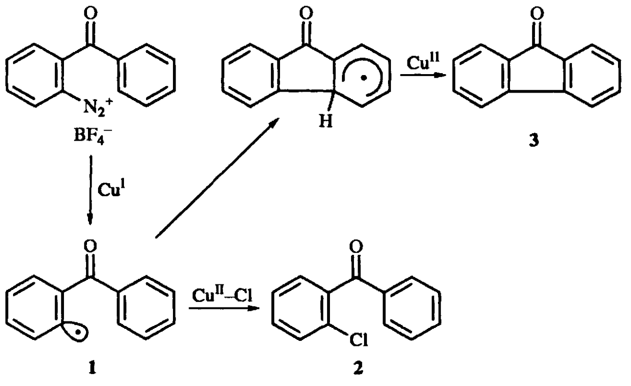
The Sandmeyer reaction may also be used to provide a homolytic route to phenols[3] in a variant where a water ligand (or OH^-) is transferred from the aquated Cu^{2+} ion. Here ligand transfer is slow in comparison with that of halide and a high concentration of the aquacopper(II) is required to ensure efficient interception of the aryl radicals. The bulk of the copper is thus maintained in the higher oxidation state. Since aquated Cu^+ is liable to aerial oxidation and disproportionation, the low concentration necessary for propagation of the reaction is maintained by suspended Cu_2O.

In a previous study[4] where we quantified the relative rates of chloride- and water-ligand transfer, diazonium tetrafluoroborates were dissolved in solutions of $CuSO_4$ to which varying quantities of NaCl were added and the catalytic cycle was initiated by addition of small amounts of ascorbic acid which produced the requisite Cu^I homogeneously *in situ* [eqn. (1)].

$$C_6H_8O_6 + 2Cu^{2+} \longrightarrow C_6H_6O_6 + 2H^+ + 2Cu^+ \quad (1)$$

Under these conditions several Cu^{II} species are available to compete for the aryl radicals. It was assumed that chlorocopper(II) complexes would transfer only chloride ligands and that the only species capable of transferring water was $Cu(OH_2)_6{}^{2+}$. Subsequent work[1] has shown this not to be the case: a sulfatocopper(II) complex occurs in solutions of $CuSO_4$ which transfers water at a rate which is less than that of simple aquated Cu^{2+}. [In calculating the concentrations of the various chlorocopper(II) complexes, no account was taken of the competing sulfate equilibrium.]

In this paper we report the estimation of absolute rates of chloride-ligand transfer from Cu^{II} complexes to the 2-benzoylphenyl radical clock (**1**) and a revised correlation analysis of the effects of aryl-radical substitution on the relative rates of water- and chloride-ligand transfer.



Scheme 2

Table 1 Stepwise and overall equilibrium constants for chlorocopper complexes

Copper(II) complexes			Copper(I) complexes				
	K_n^{II}/dm^3 mol^{-1} [a]	β_n^{II} [a]		K_n^{I}/dm^3 mol^{-1} [b]	β_n^{I} [b]	K_n^{I}/dm^3 mol^{-1} [c]	β_n^{I} [c]
$CuCl^+$	$K_1^{\text{II}} = 2.36$		CuCl	$K_1^{\text{I}} = 5 \times 10^2$		$K_1^{\text{I}} = 4.27 \times 10^3$	
$CuCl_2$	$K_2^{\text{II}} = 0.63$	$\beta_2^{\text{II}} = 1.49$	$CuCl_2^-$	$K_2^{\text{I}} = 2 \times 10^3$	$\beta_2^{\text{I}} = 1 \times 10^6$	$K_2^{\text{I}} = 36.3$	$\beta_2^{\text{I}} = 1.55 \times 10^5$
$CuCl_3^-$	$K_3^{\text{II}} = 0.46$	$\beta_3^{\text{II}} = 0.69$	$CuCl_3^{2-}$	$K_3^{\text{I}} = 1.0$	$\beta_3^{\text{I}} = 1 \times 10^6$	$K_3^{\text{I}} = 1.0$	$\beta_3^{\text{I}} = 1.55 \times 10^5$
$CuCl_4^{2-}$	$K_4^{\text{II}} = 0.08$	$\beta_4^{\text{II}} = 0.05$					

[a] Ref. 5. [b] Ref. 6. [c] Ref. 7.

Results

(*i*) Absolute rate constants for the transfer of Cu$^{\text{II}}$-chloride ligands to the 2-benzoylphenyl radical

Absolute rate constants for ligand-transfer processes may be determined by competing the ligand transfer against cyclisation and observing the relative amounts of ligand-transfer and cyclisation products. In this manner, we previously estimated [1] the gross rate of transfer of water from the hexaaquacopper(II) ion to be (1.47 ± 0.17) × 10^6 dm^3 mol^{-1} s^{-1}

Experimentally, 2-benzoylbenzenediazonium tetrafluoroborate (0.02 mol dm^{-3}), the precursor to **1**, was dissolved in 50 cm^3 of 0.3 mol dm^{-3} solutions of $Cu(NO_3)_2$ containing various concentrations of NaCl, the ionic strength of each solution being adjusted to 5 mol dm^{-3} with KNO_3 (see below). Homolysis was initiated by the rapid addition of 1 cm^3 of a solution of ascorbic acid (0.1 mol dm^{-3}), *i.e.* 10 mol percent of the diazonium ion concentration. The partitioning of copper between oxidation states is thus total [Cu$^{\text{II}}$] = 0.296 mol dm^{-3} and total [Cu$^{\text{I}}$] = 0.004 mol dm^{-3}.

In order to obtain values for the rates of chloride-ligand transfer, it is necessary to know the distribution of the various chlorocopper(II) complexes in solution under particular conditions. Ramette [5] has determined stability constants (Table 1) at ionic strength 5 mol dm^{-3} for the four weak complexes of Cu$^{\text{II}}$ with chloride, and we have adopted these. Our experimental procedure produces Cu$^{\text{I}}$ from initial Cu$^{\text{II}}$ in stoichiometric proportion to the initiating ascorbic acid used [eqn. (1)]. Cu$^{\text{I}}$ forms stronger complexes with chloride than does Cu$^{\text{II}}$, hence the chloride concentration available for forming Cl-transferring complexes with Cu$^{\text{II}}$ depends upon the amount of Cu$^{\text{I}}$ formed *in situ*. Ahrland and Rawsthorne [6] have obtained stability constants for three chlorocopper(I) complexes at ionic strength 5 mol dm^{-3} by solubility and potentiometric techniques (Table 1); there was no evidence for a fourth complex. Günter and Zuberbühler [7] have proposed different and more precise values for K_1^{I} and K_2^{I} from kinetic measurements made at the lower ionic strength of 0.2 mol dm^{-3} but we have adopted the values of Ahrland and Rawsthorne as the ionic strength at which they were determined is the same as that used by Ramette and our interest is in finding the distribution of species in mixtures containing both oxidation states of the metal. In fact, for the range of initial copper and chloride concentrations that we have employed, the calculated equilibrium concentration of chloride (the principal species used in our analysis, *vide infra*) is essentially the same whichever set of constants is used for Cu$^{\text{I}}$ complexes.†

If it is assumed that each chlorocopper(II) complex in solution can transfer chloride to the radical at a characteristic rate, the overall rate of production of 2-chlorobenzophenone (**2**), ArCl, from the radical Ar$^\bullet$, *i.e.* **1**, is given by eqn. (2), where k_n^{Cl} are rate

$$d[\text{ArCl}]/dt = \sum_{n=1}^{4} k_n^{\text{Cl}}[\text{Ar}^\bullet][\text{CuCl}_n^{(2-n)+}] \qquad (2)$$

constants corresponding to the particular chlorocopper(II) complexes.

In addition, **1** also cyclises to give fluorenone **3**, Fl, and the rate of this reaction is given by eqn. (3), where k^{C} is the rate constant for cyclisation. Hence, eqn. (4).

$$d[\text{Fl}]/dt = k^{\text{C}}[\text{Ar}^\bullet] \qquad (3)$$

$$\frac{d[\text{ArCl}]/dt}{d[\text{Fl}]/dt} = Q = \sum_{n=1}^{4} (k_n^{\text{Cl}}/k^{\text{C}})[\text{CuCl}_n^{(2-n)+}] \qquad (4)$$

Substitution of $[\text{CuCl}_n^{(2-n)+}]$ in terms of stability constants and the concentrations of composite ions gives eqn. (5).

$$Q = \sum_{n=1}^{4} (k_n^{\text{Cl}}/k^{\text{C}})\beta_n^{\text{II}}[\text{Cu}^{2+}][\text{Cl}^-]^n \qquad (5)$$

where $$\beta_n^{\text{II}} = \prod_{1}^{n} K_n^{\text{II}}$$

The material balance for Cu$^{\text{II}}$ gives: ‡

$$[\text{Cu}^{\text{II}}]_t = [\text{Cu}^{2+}] + \sum_{n=1}^{4} [\text{CuCl}_n^{(2-n)+}]$$

where $[\text{Cu}^{\text{II}}]_t$ is total Cu$^{\text{II}}$; again substituting $[\text{CuCl}_n^{(2-n)+}]$ in terms of stability constants and the concentrations of composite ions gives

$$[\text{Cu}^{\text{II}}]_t = [\text{Cu}^{2+}] + \sum_{n=1}^{4} \beta_n^{\text{II}}[\text{Cu}^{2+}][\text{Cl}^-]^n$$

whence $$[\text{Cu}^{2+}] = [\text{Cu}^{\text{II}}]_t/(1 + \sum_{n=1}^{4} \beta_n^{\text{II}}[\text{Cl}^-]^n) \qquad (6)$$

Elimination of $[\text{Cu}^{2+}]$ between eqns. (5) and (6) yields eqn. (7) which expresses *Q*, the relative rate of formation of the

$$Q = \frac{\sum_{n=1}^{4} (k_n^{\text{Cl}}/k^{\text{C}})\beta_n^{\text{II}}[\text{Cu}^{\text{II}}]_t[\text{Cl}^-]^n}{(1 + \sum_{n=1}^{4}\beta_n^{\text{II}}[\text{Cl}^-]^n)} \qquad (7)$$

ligand-transfer and cyclisation products, in terms of a single variable, the free chloride concentration. In the earlier work [4] it was assumed that the free chloride concentration remained approximately constant and that the ratio of reaction products equalled the relative rate at which these products formed. This seemed reasonable on the basis that, in the presence of sulfate, conversions of inorganic to organic chloride were relatively low and that ligand exchange rates on Cu$^{\text{II}}$ are rapid, hence

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† When [Cu$^{\text{II}}$] = 0.296 and [Cu$^{\text{I}}$] = 0.004 mol dm^{-3}, the correlation of the equilibrium chloride concentrations is given by: $[\text{Cl}^-]_{\text{A\&R}} = -0.0009 + 1.0025[\text{Cl}^-]_{\text{G\&Z}}$; $r^2 = 0.999\,99$.

‡ It is assumed that the proportions of Cu$^{\text{I}}$ and Cu$^{\text{II}}$ remain constant over the duration of the reaction; essentially all Cu$^{\text{I}}$ is as chloro complexes which are not rapidly autoxidised.[7]

maintaining the essential constancy of ligand-transferring complexes over the duration of the reaction. Here such an assumption is no longer valid: in the absence of sulfate the concentrations of chlorocopper(II) complexes are higher than in its presence and, consequentially, the ratios of chlorinated products to any other products arising from the same aryl radical increase much more rapidly in the absence of sulfate than in its presence. As a result, the range of initial chloride concentrations that is utilisable practically (the constraint being that the product ratios should be conveniently measurable by GC without undue error) is reduced in the absence of sulfate. This, together with the sequestration of Cl^- by Cu^I, ensures that, when low initial chloride concentrations that are comparable with that of the diazonium ion are used, they cannot be presumed to be constant over the duration of the reaction. The relative rate constants in the right hand side of eqn. (7) cannot therefore be evaluated accurately by assuming that Q is equal to the observed product ratio, R_{obs} = [chlorobenzophenone]/[fluorenone]. Eqn. (7) is not readily integrated over time, so our procedure has been first to approximate R_{obs} to Q and to fit R_{obs} to the right hand side of eqn. (7) by non-linear regression and then use the estimates of k_n^{Cl}/k^C so obtained as the starting values in computer simulations of the reaction where, by trial and error, these initial values were adjusted until a satisfactory coincidence of observed and simulated product ratios was obtained.

In Table 2 are given total and corresponding equilibrium chloride concentrations for solutions where the total concentrations of Cu^{II} and Cu^I are 0.296 and 0.004 mol dm^{-3}, respectively, together with the observed product ratios, R_{obs}.

The fitting of R_{obs} to equilibrium chloride concentrations according to the four-term expression of eqn. (7) produces values of k_2^{Cl}/k^C and k_4^{Cl}/k^C which are negative and with large standard errors, and hence are without physical significance. However, even at the highest concentration of chloride used the equilibrium concentration of $CuCl_4^{2-}$ is very low, amounting to less than 0.05 mol percent of the total concentration of possible chloride-transferring species; we therefore disregard this minor complex. Fitting R_{obs} to the first three terms of eqn. (7) also produces a negative value for k_2^{Cl}/k^C, the regression program accommodating a slight inflection, presumably an artefact, evident at low chloride values in the plot of R_{obs} *versus* equilibrium chloride concentrations (Fig. 1).

The regression was therefore constrained to assign a positive value to k_2^{Cl}/k^C in three ways: by according equal relative rate constants to all three complexes, or to $CuCl^+$ and $CuCl_2$, or to $CuCl_3^-$ and $CuCl_2$. The first way gave a poor account of the data, the predicted curve exhibiting the wrong curvature; the second way gave a slightly better account of the data than the third (correlation coefficients 0.997 and 0.993, respectively) but for reasons that will emerge we choose the latter, the fitting expression being eqn. (8); the continuous line of Fig. 1 represents this expression. The multiples of β_2^{II} and β_3^{II} in the numerator of eqn. (8) account statistically for the fact that $CuCl_2$ has two transferable chlorides and $CuCl_3^-$ has three.

Although $CuCl_3^-$ is a rather minor species, amounting to 1.9 mol percent of the Cl-transferring species at the highest chloride concentration employed, it cannot be ignored: a fitting of the data to only the first two terms of eqn. (7), with or without discrimination between them, gives poorer correlation than does eqn. (8). The preliminary value of k_1^{Cl}/k^C obtained from eqn. (8) is (9.1 ± 2.7) and that of $k_{2.3}^{Cl}/k^C$ is (123 ± 9), where the quoted uncertainties are the standard errors.

Table 2 Total and equilibrium[a] chloride concentrations (mol dm^{-3}) and observed product ratios, R_{obs} for competitive Sandmeyer chlorination and Pschorr cyclisation of 2-benzoylphenyl radical

$[Cl^-]_t$	$10[Cl^-]_{eq}$	R_{obs}	$[Cl^-]_t$	$10[Cl^-]_{eq}$	R_{obs}
0.025	0.102	0.274	0.250	1.502	2.350
0.050	0.250	0.504	0.275	1.665	2.684
0.075	0.401	0.769	0.300	1.830	3.569
0.100	0.553	0.993	0.325	1.995	3.585
0.125	0.707	1.075	0.350	2.162	4.654
0.150	0.863	1.387	0.375	2.330	5.177
0.175	1.021	1.436	0.400	2.499	—
0.200	1.180	1.801	0.425	2.669	6.813
0.225	1.340	2.010	0.450	2.840	6.726

[a] Calculated using the chlorocopper(II) stability constants of Ramette[5] and chlorocopper(I) stability constants of Ahrland and Rawsthorne[6] for solutions containing total $[Cu^{II}]$ = 0.296 and total $[Cu^I]$ = 0.004 mol dm^{-3}.

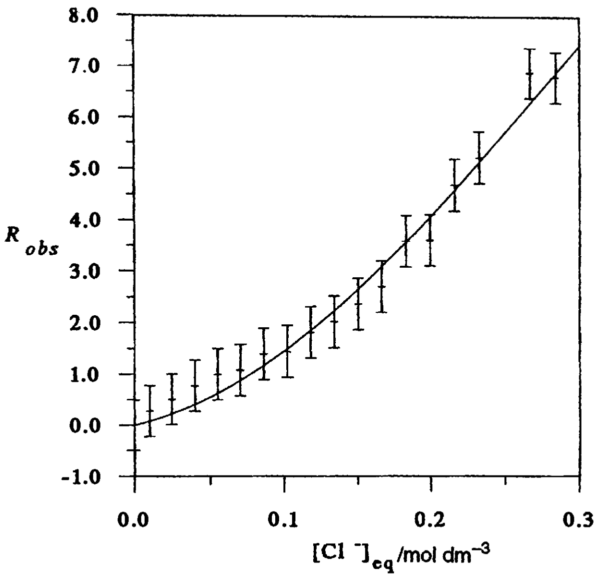


Fig. 1 Variation of the product ratio, R_{obs} = [2-chlorobenzophenone]/[fluorenone], as a function of equilibrium chloride concentration for competitive Sandmeyer and Pschorr reactions of 2-benzoylphenyl radical. Error bars correspond to the standard error of the set of R_{obs} values.

Having obtained these preliminary values from the fitting of R_{obs} by eqn. (8), computer simulations of the reaction were carried out in which the partitioning of Ar$^{\bullet}$ between chlorinated and cyclised products was modelled. The value of k^C employed was 8 × 10^5 s^{-1} as previously found.[1] If values of k_1^{Cl}, k_2^{Cl} and k_3^{Cl} obtained from this figure and the above preliminary magnitudes were used, the production of ArCl was underestimated since eqn. (8) assumes constancy of $[Cl^-]$ whereas, as discussed above, this concentration declines significantly over the course of the reaction and hence the real Cl-transfer rates, particularly that determined by k_1^{Cl} which is predominant at low chloride concentrations, are higher than the preliminary estimates imply. In the simulations the equivalence of k_2^{Cl} and k_3^{Cl}

$$R_{obs} = \frac{[Cu^{II}]_t\{(k_1^{Cl}/k^C) \times K_1^{II} \times [Cl^-] + (k_{2.3}^{Cl}/k^C) \times (2 \times \beta_2^{II} \times [Cl^-]^2 + 3 \times \beta_3^{II} \times [Cl^-]^3)\}}{(1 + \sum_{n=1}^{3} \beta_n^{II}[Cl^-]^n)}$$

$$= \frac{0.296\{(k_1^{Cl}/k^C) \times 2.36[Cl^-] + (k_{2.3}^{Cl}/k^C) \times (2.98[Cl^-]^2 + 2.07[Cl^-]^3)\}}{(1 + 2.36[Cl^-] + 1.49[Cl^-]^2 + 0.69[Cl^-]^3)} \quad (8)$$

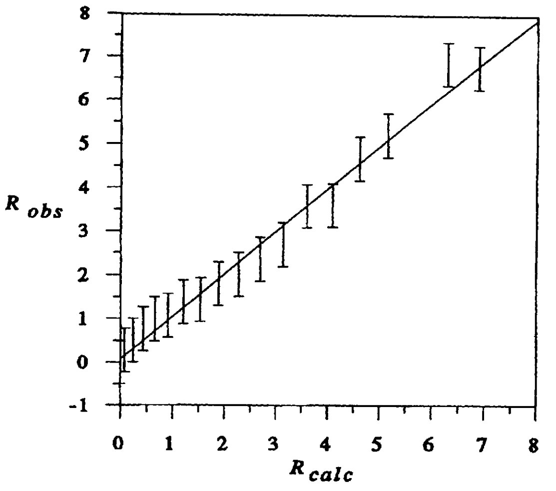


Fig. 2 Correlation of observed and calculated product ratios for competitive Sandmeyer and Pschorr reactions of 2-benzoylphenyl radical. Error bars correspond to the standard error of the set of R_{obs} values.

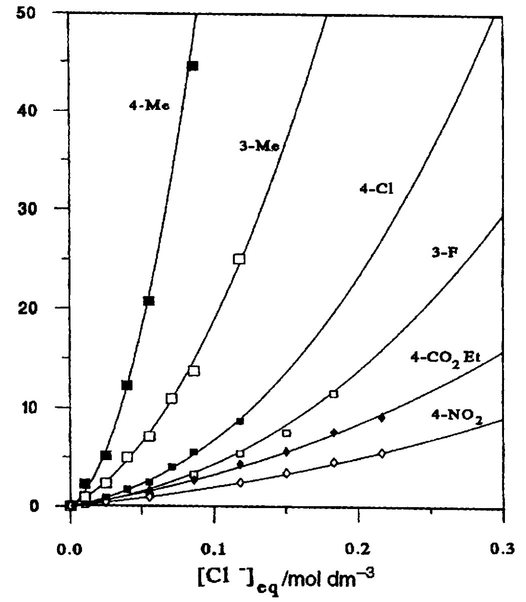


Fig. 3 Variation of competitive Sandmeyer product ratios, S_{obs} = [ArCl]/[ArOH], as a function of equilibrium chloride concentration for representative 3- and 4-substituted phenyl radicals. Discrete points are experimental values and the continuous lines their fitting by eqn. (12).

(*i.e.* values statistically corrected for the number of transferable Cl ligands) found for the preliminary estimates was retained. Fig. 2 shows the correlation of experimental R_{obs} values with calculated values obtained by such simulation using the constants: $k_1^{Cl} = (8.8 \pm 1.3) \times 10^6$ dm^3 mol^{-1} s^{-1} and $k_{2.3}^{Cl} = (1.0 \pm 0.1_5) \times 10^8$ dm^3 mol^{-1} s^{-1}. In view of the indirect way in which the rate constants have been obtained, the uncertainties quoted correspond to an estimated error of 15% of the value; this compares with an 11% uncertainty ascribed previously to the value of k^C upon which these estimates are based. We propose these as the best estimates of the absolute rate constants for Cl-ligand transfer from chlorocopper(II) complexes to the 2-benzoylphenyl radical. Using these figures, relative rate constants $k_1^{Cl}/k^C = 11.0$ dm^3 mol^{-1} and $k_{2.3}^{Cl}/k^C = 125$ dm^3 mol^{-1} may be reconstituted for comparison with the preliminary values. We shall return later to the lack of discrimination between $CuCl_2$ and $CuCl_3^-$ by the radical clock. Simulation indicated that the mono-, di- and tri-chlorocopper(II) complexes were responsible for 17.4, 69.3 and 13.3%, respectively, of the chloride-ligand transfer for the highest initial chloride concentration of 0.45 mol dm^{-3}, confirming the conclusion from curve fitting that the minor third complex is not negligible.

(ii) Correlation analysis of relative rates of chloride- and water-ligand transfer from copper(II) complexes to substituted aryl radicals

A series of 3- and 4-substituted diazonium tetrafluoroborates was decomposed in solutions of 0.3 mol dm^{-3} $Cu(NO_3)_2$ containing varying amounts of sodium chloride. For these experiments ionic strengths were adjusted with KNO_3 to 1.32 mol dm^{-3}, the value formally attained at the highest concentration of chloride used. Despite the lower ionic strength, we have continued to use Ramette's stability constants; Carlsson and Wettermark[8] have quoted values for K_1^{II} and K_2^{II} of 2.3 and 0.72 dm^3 mol^{-1}, respectively, at an ionic strength of 1 mol dm^{-3} (1 mol dm^{-3} $HClO_4$) which are not materially different from Ramette's values. It was felt that variations in K_n^{II} values as a consequence of medium change would be comparable with the uncertainties in the values.

By using a similar procedure to that described in (*i*) we have obtained relative rate constants for the transfer of chloride and water ligands to a series of substituted phenyl radicals. In a system free of sulfate or other interfering counterions, the rate of water-ligand transfer is given by eqn. (9) where k^{OH} is the rate constant for water-ligand transfer. Combination of eqn. (2), now applied to aryl radicals in general, with eqn. (9) gives eqn. (10).

$$d[ArOH]/dt = k^{OH}[Ar^\bullet][Cu^{2+}] \qquad (9)$$

$$\frac{d[ArCl]/dt}{d[ArOH]/dt} = V = \sum_{n=1}^{4} (k_n^{Cl}/k^{OH})[CuCl_n^{(2-n)+}]/[Cu^{2+}] \qquad (10)$$

Substitution of $[CuCl_n^{(2-n)+}]$ in terms of stability constants and the concentration of composite ions, and cancellation of terms, gives eqn. (11).

$$V = \sum_{n=1}^{4} (k_n^{Cl}/k^{OH})\beta_n^{II}[Cl^-]^n \qquad (11)$$

Because chloride concentrations vary over the duration of the reaction, again the observed product ratio, S_{obs}, is inadequate as a measure of V but again may be used to obtain a preliminary estimate of relative rate constants.

Observed product ratios, [ArCl]/[ArOH] = S_{obs}, were approximated to V and fitted to eqn. (11) by non-linear regression. As in (*i*) above, the fitting expression was simplifed to terms for three complexes [eqn. (12)], the second and third

$$S_{obs} = (k_1^{Cl}/k^{OH}) \times 2.36 \times [Cl^-] + (k_{2.3}^{Cl}/k^{OH})\{2 \times 1.49 \times [Cl^-]^2 + 3 \times 0.69 \times [Cl^-]^3\} \qquad (12)$$

reacting at the same rate when corrected statistically for the number of transferable ligands. Although the role of the third complex was minor {simulations indicating that the trichlorocopper(II) complex effected 5.3% of chloride ligand to the 4-nitrophenyl radical at $[Cl^-]_t$ = 0.35 mol dm^{-3} and 3.5% to 4-methylphenyl radical at $[Cl^-]_t$ = 0.15 mol dm^{-3}}, neglect of the third complex gave a poorer account of the data and significantly changed the rate constants for the remaining complexes. Fig. 3 shows, for a selection of aryl radicals, the variation of S_{obs} as a function of equilibrium chloride

Table 3 Relative rate constants for chloride and water ligand transfer to substituted phenyl radicals

Substituent	$k_1^{\mathrm{Cl}\,a}$	$k_{2,3}^{\mathrm{Cl}\ a}$	$(k_1^{\mathrm{Cl}}/k^{\mathrm{OH}})_{\mathrm{corr}}{}^b$	$(k_{2,3}^{\mathrm{Cl}}/k^{\mathrm{OH}})_{\mathrm{corr}}{}^b$
4-Me	1.2×10^8	2.3×10^9	490	9388
H	5.5×10^7	8.0×10^8	225	3265
4-Cl	1.8×10^7	2.0×10^8	73.5	816
4-CO_2Et	1.5×10^7	4.0×10^7	61.2	163
4-CF_3	8.5×10^6	6.0×10^7	34.7	245
4-CN	8.3×10^6	2.3×10^7	33.9	93.9
4-NO_2	9.0×10^6	2.1×10^7	36.7	85.7
3-Me	6.0×10^7	5.0×10^8	245	2041
3-Cl	1.8×10^7	1.9×10^8	69.4	775
3-F	1.3×10^7	1.1×10^8	53.1	449
3-CN	1.2×10^7	4.4×10^7	49.0	180
3-NO_2	1.1×10^7	3.8×10^7	44.9	155

[a] Chloride ligand transfer rate constants obtained by reaction simulation to reproduce observed product ratios, k^{OH} being set at 1.47×10^6 dm^3 mol^{-1} s^{-1}. [b] Statistically corrected relative rate constants reconstituted from simulated chloride transfer rates and $k^{\mathrm{OH}}{}_{\mathrm{corr}} = 2.45 \times 10^5$ dm^3 mol^{-1} s^{-1}.

concentration (Table 2) and the continuous lines show the fittings of these data points by eqn. (12). Fig. 3 also demonstrates the significant effect of the substitution upon S_{obs}, the selectivity in preference of chloride over water ligands increasing as the substituent becomes more electron donating.

In Table 3 are presented the values of k_1^{Cl} and $k_{2,3}^{\mathrm{Cl}}$ which simulate S_{obs} on the assumption that, for each aryl radical, $k^{\mathrm{OH}} = 1.47 \times 10^6$ dm^3 mol^{-1} s^{-1}, *i.e.* the gross value appropriate to water transfer to the 2-benzoylphenyl radical (**1**), and values of $(k_n^{\mathrm{Cl}}/k^{\mathrm{OH}})_{\mathrm{corr}}$, *i.e.* values derived from the simulations and corrected for the numbers of both Cl and H_2O ligands. The assumption that the aquacopper(II) ion transfers water to all the aryl radicals at the same rate as it transfers to **1**, implies the neglect of any substituent effect on water transfer. The values of k_n^{Cl} are thus lower estimates since any actual substituent effect on water transfer is expected to be an increase in the transfer rate as the electron donating character of the substituent increases, just as the data show occurs in greater degree for chloride transfer (see below). The values of $(k_1^{\mathrm{Cl}}/k^{\mathrm{OH}})_{\mathrm{corr}}$ for the least reactive radicals show that chloride-ligand transfer occurs more than 30 times more readily than water transfer. This observation, together with the excellent fit of the data by eqn. (12) (Fig. 3), justifies the initial assumption that chloro complexes transfer only chloride: any *water* transfer by *chloro* complexes is negligible.

Fig. 4 represents Hammett plots of $\log(k_1^{\mathrm{Cl}}/k^{\mathrm{OH}})_{\mathrm{corr}}$ and $\log(k_{2,3}^{\mathrm{Cl}}/k^{\mathrm{OH}})_{\mathrm{corr}}$. Hammett σ constants were used for all substituents except 4-Me where σ^+ gives the better fit.[9] The use of other σ constants, either simple or bisected, gave no improvement to the correlation of the data. The equations of the lines of Fig. 4 are:

$$\log(k_1^{\mathrm{Cl}}/k^{\mathrm{OH}})_{\mathrm{corr}} = 2.27 - 1.08\sigma \qquad r^2 = 0.915 \quad (13)$$

$$\text{and} \quad \log(k_{2,3}^{\mathrm{Cl}}/k^{\mathrm{OH}})_{\mathrm{corr}} = 3.35 - 1.87\sigma \qquad r^2 = 0.944 \quad (14)$$

The positive intercepts reflect the greater ease of chlorination than hydroxylation of the unsubstituted phenyl radical in the Sandmeyer reaction and the larger intercept for the di- and tri-chlorocopper(II) complexes shows that these complexes chlorinate the phenyl radical more readily than does the monochloro complex.

It is readily shown that the gradient of a Hammett plot for a series of relative rate constants (ρ^{rel}) is equal to the difference between the ρ values for the two series of constants compared in the relative constants. Thus for the present cases, $\rho_n^{\mathrm{rel}} = (\rho_n^{\mathrm{Cl}} - \rho^{\mathrm{OH}})$. Our evaluations of k_n^{Cl} have assumed ρ^{OH} to be zero, *i.e.* that water ligand transfer occurs at the same rate for all the aryl radicals. The implication of this assumption is that the gradients of the lines of Fig. 4 represent ρ_n^{Cl}, the values for chloride ligand transfer from the various chlorocopper(II) complexes. If such an assumption is an oversimplification and $\rho^{\mathrm{OH}} \neq 0$, the negative values observed for $\rho_n{}^{\mathrm{rel}}$ can arise in two algebraic circumstances: either (*a*) $|\rho_n^{\mathrm{Cl}}| > |\rho^{\mathrm{OH}}|$ with ρ_n^{Cl} negative, or (*b*) $|\rho_n^{\mathrm{Cl}}| < |\rho^{\mathrm{OH}}|$ with ρ^{OH} positive. The nature of the ligand transfer is oxidative with respect to the aryl radicals and reductive with respect to the Cu$^{\mathrm{II}}$ complexes. Hence faster rates for each type of ligand transfer are to be expected for the more nucleophilic aryl radicals (*i.e.* for those with the more electron donating substituents) and for the more strongly oxidising Cu$^{\mathrm{II}}$ complexes. Experimental observation therefore accords with algebraic circumstance (*a*) and, if ρ^{OH} is non-zero, it is expected to be small and negative.

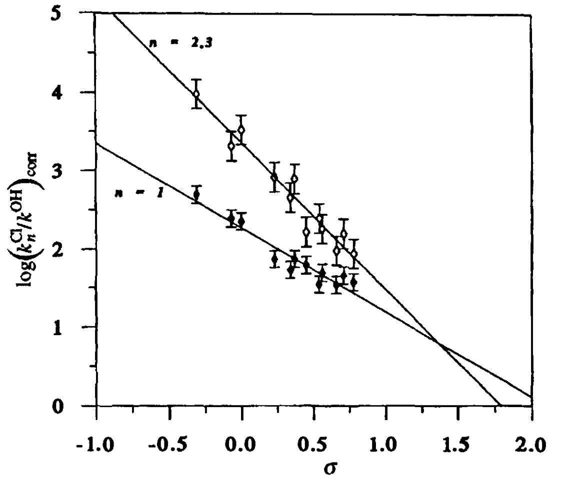


Fig. 4 Hammett plots for relative ligand-transfer rates to substituted phenyl radicals from chloro- and aqua-copper(II) complexes. Error bars represent the standard errors of the data sets.

Whatever uncertainty surrounds the substituent dependence, or otherwise, of k^{OH}, this is eliminated in the difference between eqns. (13) and (14). Eqn. (15) indicates that the transfer of a

$$\log(k_{2,3}^{\mathrm{Cl}}/k_1^{\mathrm{Cl}})_{\mathrm{corr}} = 1.08 - 0.79\sigma \qquad (15)$$

chloride ligand to the 4-nitrophenyl radical ($\sigma = 0.78$) occurs more readily from the di- and tri-copper(II) complexes than from the monochloro complex by a factor of 2.5:1 and that this selectivity increases to 18.4:1 for the 4-methylphenyl radical ($\sigma^+ = -0.31$). The selectivity of chloride-ligand transfer to aryl radicals thus increases as the reactivity of the radicals increases and so represents a failure of the reactivity–selectivity principle.

Although differences in selectivity for chlorocopper(II) complexes are apparent among the 3- and 4-substituted radicals [*cf.* eqn. (15)], none is unselective; however, selectivity is observed to decline the more electron withdrawing the substituent. An *ortho* substituent, on account of its proximity to the radical centre, might conceivably exert a substituent effect on ligand-transfer reactions larger than 3- or 4-substituents; we consequently examined the behaviour of 2-cyano- and 2-fluorophenyl radicals which were chosen to maximise the electron withdrawing power of the substituent for minimal steric and conformational effects. Interestingly, both proved to be non-discriminating between all three chlorocopper(II) complexes, S_{obs} being fitted by eqn. (16), [*cf.* eqn. (12)]. The preliminary

$$\begin{aligned} S_{\mathrm{obs}} &= (k_{1,2,3}^{\mathrm{Cl}}/k^{\mathrm{OH}})\{K_1^{\mathrm{II}} \times [\mathrm{Cl}^-] + 2 \times \beta_2^{\mathrm{II}} \times [\mathrm{Cl}^-]^2 + \\ &\quad 3 \times \beta_3^{\mathrm{II}} \times [\mathrm{Cl}^-]^3\} \\ &= (k_{1,2,3}^{\mathrm{Cl}}/k^{\mathrm{OH}})\{2.36 \times [\mathrm{Cl}^-] + 2 \times 1.49 \times [\mathrm{Cl}^-]^2 + \\ &\quad 3 \times 0.69 \times [\mathrm{Cl}^-]^3\} \qquad (16) \end{aligned}$$

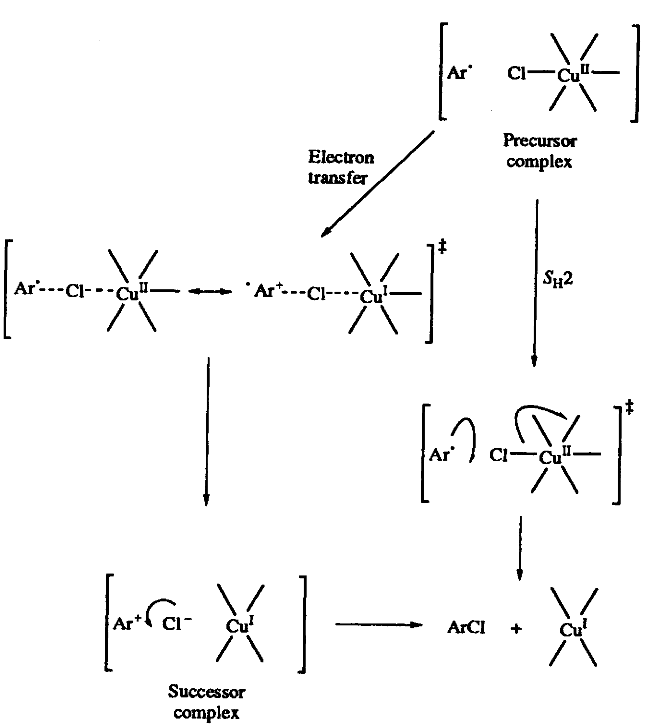
values of ($k^{\rm Cl}_{1,2,3}/k^{\rm OH}$) obtained from eqn. (16) were (14.5 ± 0.1) for the 2-cyanophenyl radical and (3.4 ± 0.1) for the 2-fluorophenyl radical, where the indicated uncertainties are the standard errors. Assuming $k^{\rm OH} = 1.47 \times 10^6$ dm^3 mol^{-1} s^{-1}, these values give $k^{\rm Cl}_{1,2,3} = 2.1 \times 10^7$ and 5.0×10^6 dm^3 mol^{-1} s^{-1}, respectively for the two radicals. The former value was marginally adjusted to 2.3×10^7 dm^3 mol^{-1} s^{-1} as a consequence of simulation experiments but the latter value required no adjustment.

Discussion

Our results show that, for the range of initial chloride concentrations employed, the transfer of chloride ligands to aryl radicals in general, is effected by three chlorocopper(II) complexes. With a given copper complex, radical reactivity depends upon substitution, electron-donating substituents producing the higher reactivity. The more reactive of the investigated radicals (*e.g.* 4-Me, 3-Me) discriminate the monochlorocopper(II) complex from the other two complexes (which react at the same rate when statistical allowance is made for their numbers of transferable ligands) and the degree of discrimination declines as the reactivity of the radical falls; the least reactive radicals (2-CN, 2-F) do not discriminate between any of the three complexes. Where the reactivity of copper complexes is distinguished, the higher reactivity is associated with the greater degree of chlorination.

The almost unique capacity of Cu$^{\rm II}$ to furnish ligand-transferring species in the Sandmeyer and related reactions[10] strongly suggests an inner-sphere mechanism for the ligand-transfer step. Such a process involves the initial association of an aryl free radical with a Cu$^{\rm II}$ complex to form a bimolecular precursor complex, the detailed nature of which is uncertain. There is evidence that alkyl radicals are oxidised by Cu$^{\rm II}$ *via* transient organo-Cu$^{\rm III}$ species,[11-14] (implying radical attack on the metal centre); if similar intermediates should intervene in the present reaction, the observation of Cl-ligand transfer by $\rm CuCl(OH_2)_5^+$ would necessitate the preferred retention of Cl in the derived organo-Cu$^{\rm III}$ intermediate in order to allow subsequent reductive elimination of ArCl. However, without direct spectroscopic evidence such as supports the involvement of organo-Cu$^{\rm III}$ in alkyl radical oxidation, there is little to suggest the involvement of Cu$^{\rm III}$ intermediates in aqueous Sandmeyer reactions [although Cohen[15] has invoked arylcopper(II) and diarylcopper(III) intermediates to account for observations made on the decomposition of diazonium ions by Cu$^{\rm I}$ in largely non-aqueous conditions].

On the other hand, the formation of the precursor complex might involve attack by the aryl radical on a *ligand* rather than the metal: interaction of the radical's singly occupied orbital (SOMO) with the σ^* orbital of a metal-ligand bond would at once weaken the metal-ligand attachment and associate the radical with a particular ligand; the ligand transfer might thus resemble an $S_{\rm H}2$ displacement (Scheme 3).



Scheme 3

Alternatively, if the ligand is not so smoothly detached, vibration within the precursor could take it to a geometry where its potential energy surface intersects that of an isoelectronic configuration comprising a phenyl cation associated with a Cu$^{\rm I}$ complex.[16] At this instant, electron transfer could occur producing an excited successor complex which relaxes with loss of ligands from copper as the coordination number changes from 6 to 4; the nucleophile would thus be delivered directly from the coordination sphere of the metal to the aryl cation within the solvation shell of the successor complex. The activation of the precursor complex to the transition state for electron transfer would be facilitated by greater oxidising power of the Cu$^{\rm II}$ moiety and by electron-donating substitution in the aryl ring since each affects the energy of an orbital in the postulated SOMO-σ* interaction. The description of the Sandmeyer product-determining transition state in terms of radical attack on a ligand rather than directly upon the metal thus may have elements of both the 'organic' $S_{\rm H}2$ mechanism and the 'inorganic' mechanism of electron transfer *via* a bridging ligand.

We have related qualitatively the differences in reactivity between the different copper complexes [reflected in the different gradients of eqns. (13) and (14)] to the oxidising powers of the corresponding chlorocopper(II) complexes; the relation can be made explicit in terms of standard reduction potentials. Elementary half-cell considerations[17] show that the standard reduction potential, $E_n^\ominus$, of a chlorocopper complex couple, $\rm CuCl_n^{(2-n)+}/CuCl_n^{(1-n)+}$, is given by eqn. (17) where $E_0^\ominus$ is the standard reduction potential for the couple $\rm Cu^{2+}/Cu^+$.[18] Hence, since for the chloro complexes of copper, $\beta_n^{\rm I} \gg \beta_n^{\rm II}$

$$\begin{aligned} E_n^\ominus &= E_0^\ominus - 0.059 \log(\beta_n^{\rm II}/\beta_n^{\rm I}) \\ &= 0.16 - 0.059 \log(\beta_n^{\rm II}/\beta_n^{\rm I}) \end{aligned} \qquad (17)$$

(Table 1), it is largely the values of $\beta_n^{\rm I}$ which determine the reduction potentials. Ahrland and Rawsthorne[6] report $\beta_3^{\rm I} = \beta_2^{\rm I}$; consequently, the calculated standard reduction potentials for the couples $\rm CuCl_2/CuCl_2^-$ and $\rm CuCl_3^-/CuCl_3^{2-}$ are similar: 0.50 and 0.52 V, respectively, when derived from their figures, and the value for the couple $\rm CuCl^+/CuCl$ is 0.30 V. Thus the ratio of the gradients of eqns. (14) and (13) (*i.e.* $\rho_2^{\rm Cl}/\rho_1^{\rm Cl} = 1.7$) is consistent with the ratio of reduction potentials of the corresponding complexes, and the lack of discrimination by radicals between the two higher complexes (*i.e.* $\rho_3^{\rm Cl}/\rho_2^{\rm Cl} = 1$) occurs because the two complexes have essentially the same reduction potential.

Substituents in the aryl ring do not conjugate directly with the SOMO of the radical but 4-substituents in particular are expected, nevertheless, to exert an influence particularly where electron-transfer character is important. Calculations[19] indicate that the π-system of phenyl cation is strongly polarised owing to the high electronegativity of C(1); electron-donating substitution capable of facilitating such π-polarisation in the transition state for electron transfer will thus accelerate the

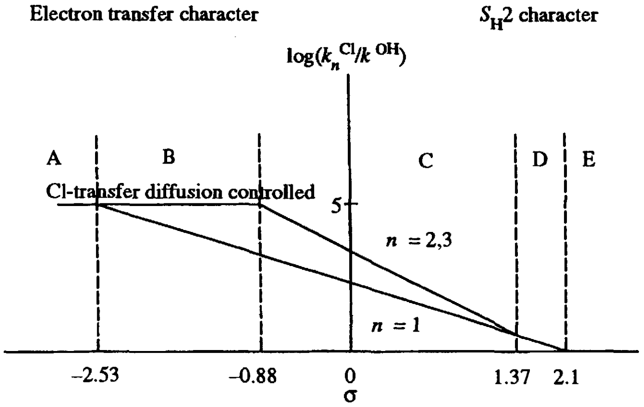


Fig. 5 Domains of aryl radical behaviour for competitive Sandmeyer chlorination and hydroxylation defined by extrapolation of Hammett plots

reaction. Our results show (Table 3) that the range of reactivity over the substituent interval NO_2 to Me is greater for 4-substituents than for 3-substituents as would be expected from such a suggestion. The observations on both the effect of increased chlorination of the copper complexes and of substituent variation in the aryl radicals confirm that greater reactivity is associated with a greater degree of electron-transfer character in the transition states for chloride-ligand transfer.

A gradation between electron-transfer character and S_H2 character in the transition states of the reactions studied may account for the observed failure of the reactivity–selectivity principle. For a ligand transfer which resembles S_H2 displacement, there need be no great separation of charges in the transition state but, by contrast, when the transition state has electron-transfer character the separation of charge will be considerable, the Franck–Condon principle requiring movement of the electron to be rapid in comparison with nuclear movement. Consider the electron-transfer mode for the reaction of an aryl radical with each of the relevant chlorocopper(II) complexes.

$$Ar^{\bullet} + CuCl^+ \longrightarrow [Ar^+\cdots Cl\cdots Cu]^{\ddagger} \longrightarrow ArCl + Cu^+$$

$$Ar^{\bullet} + CuCl_2 \longrightarrow [Ar^+\cdots Cl\cdots CuCl^-]^{\ddagger} \longrightarrow ArCl + CuCl$$

$$Ar^{\bullet} + CuCl_3^- \longrightarrow [Ar^+\cdots Cl\cdots CuCl_2^{2-}]^{\ddagger} \longrightarrow ArCl + CuCl_2^-$$

For the monochlorocopper(II) complex, cationic charge is conserved from reactants through the transition state to products; for the dichloro complex, both the reactants and products are neutral but there is charge separation in the transition state; for the third complex anionic charge is conserved between reactants and products but charge separation increases in the transition state. We suggest the increased polarity of the transition states derived from the higher complexes, relative to that derived from the monochloro complex, accounts for the failure of the reactivity–selectivity principle in this series of reactions; Pross[20] has described how the principle may fail when a transition state acquires attributes which are not intermediate between those of reactants and products, due to the admixture of excited-state character.

The limiting behaviour of aryl radicals reacting with chlorocopper(II) complexes can be understood in terms of Fig. 5 in which the Hammett plots of Fig. 4 are set in a broader context, allowing the definition of five domains of radical behaviour.

Domain A. This contains radicals for which chloride-ligand transfer from *all* complexes is diffusion controlled [in view of the value of k^{OH} adopted, this should happen for $\log(k_n^{Cl}/k^{OH})_{corr}$ values of *ca.* 5]; owing to the extremely negative σ-range of this domain, it is likely that such behaviour will remain hypothetical.

Domain B. Here, reaction with the higher complexes is diffusion controlled but that with the monochlorocopper(II) complex is substituent-dependent. This may be typified by 4-methoxyphenyl radical which failed to correlate with other radicals;[4] if so, amino-substituted phenyl radicals would be expected to behave similarly.

Domain C. This contains most of the radicals of the present study. It is limited by the onset of diffusion-controlled chlorination by the more reactive complexes, at one extreme, and the loss of discrimination by aryl radicals between the chloride environments in all complexes (*i.e.* at σ *ca.* 1.4) at the other.

Domain D. This includes radicals which do not discriminate between the chloride environments of the various chlorocopper(II) complexes but do distinguish such chloride ligands from the water ligands of the aquacopper(II) ion; the 2-cyano- and 2-fluoro-phenyl radicals may be representative of this class though lack of reliable σ values for *ortho* substituents precludes certainty. It is likely that all points to higher σ values than the intersection of the Hammett plots will lie on a single (lower) line. The point at which this meets the abscissa (at a notional σ value of 2.1), is where radicals would cease to discriminate between chloride in any of the chloro complexes and *water* in the aquacopper(II) ion.

Domain E. This would contain any radicals which failed to distinguish chloride and water ligands. The σ-ranges of domains D and E indicate that they may be accessible to investigation by use of radicals with suitable multiple electron-withdrawing substitution.

Conclusions

A pattern of behaviour for phenyl radicals, in general, reacting with chlorocopper(II) complexes has been discerned and an explanatory mechanism proposed. Chloride-ligand transfer occurs with variable degrees of S_H2 and electron-transfer character dependent upon the particular chlorocopper(II) complex and upon substitution in the radical, the electron-transfer mode being favoured the more strongly oxidising the copper complex and the more nucleophilic the radical. 2-Benzoylphenyl radical has been used as a radical clock to obtain absolute rate constants for chloride ligand transfer. Since reactions of phenyl radicals are substituent-dependent, the values obtained cannot be taken as *the* chloride ligand transfer rate constants in the way that the rate constants found by using reactions of hex-5-enyl radical are characteristic for primary alkyl radicals.[21] Nevertheless, 2-benzoylphenyl radical is typical of the range of radicals studied. Its rate constants for reaction with chlorocopper(II) complexes are similar to those inferred from relative rates for 3-fluorophenyl or 4-ethoxycarbonylphenyl radicals.

Experimental

Materials

Diazonium tetrafluoroborates were prepared and purified as described previously from the corresponding commercially available amines.[1,4] All other materials were commercial materials used as supplied.

Sandmeyer reactions

The general procedure was to take 50 cm^3 of a stock solution of $Cu(NO_3)_2$ in water (0.3 mol dm^{-3}) and to dissolve in it appropriate quantities of solid NaCl and KNO_3 (for adjustment of ionic strength), the increment in volume being neglected. To the vigorously stirred solution was added 0.001 mol of the appropriate diazonium salt and, when it had dissolved, 1 cm^3 aqueous ascorbic acid solution (0.1 mol dm^{-3}) was added rapidly. Evolution of dinitrogen was immediate and organic products separated. Ethyl acetate (25 cm^3) was added together with a standard solution in the same solvent of a suitable internal standard for GC analysis. The mixture was then transferred to a tap funnel, separated and the organic layer analysed directly. Reactant accountabilities typically exceeded 80%.

The conditions of analysis varied with the analyte. Products from 2-benzoylphenyl radical were quantified, using dibenzofuran as internal standard, an Alltech Econocap Carbowax capillary column operated either at 180 °C for 2 min with ramping at 6° min^{-1} to 240 °C, or isothermally at 220 °C; products from 2-cyanophenyl radical were analysed on the same column operated isothermally at 240 °C, using 1,4-dichlorobenzene as the internal standard and those from 2-fluorophenyl radical were analysed on a J&W DB225 capillary column with the same internal standard. Packed columns were used for the analysis of products from 3- and 4-substituted phenyl radicals: a 1% DEGA on Gaschrome Q column (1 min at 130 °C ramping at 16° min^{-1} to 185 °C) was employed to quantify the products from 3- and 4-cyanophenyl and 3- and 4-nitrophenyl radicals using 1,4-dichloro- or 1,4-dibromo-benzene, as appropriate, as internal standard; mixtures from the remaining 3- and 4-substituted radicals were analysed by means of a 10% SE 30 on Gaschrome Q column with the same internal standards; dependent on the analyte, the column was held at either 120 °C or 160 °C for 3 min and then ramped at 16° min^{-1} to 250 °C.

Curve-fitting and simulations

The curve-fitting of experimental product ratios to equilibrium free chloride concentrations was carried out using the nonlinear regression data analysis program ENZFITTER.[22] Reactions were simulated by means of the kinetic simulation program SIMULA initially supplied by Professor D. J. Waddington and modified for PC operation by Dr A. C. Whitwood. In all simulations the reduction of the diazonium ion was made to be rate-determining with the rate constant set at an arbitrary value of 5×10^4 dm^3 mol^{-1} s^{-1} for each reducing species, the point of interest being the subsequent faster product-determining partitioning of the aryl radicals so produced between ligand transfers and cyclisation as appropriate. The cyclisation rate constant of the 2-benzoylphenyl radical ($k^C = 8.0 \times 10^5$ s^{-1}) was the fiducial value against which ligand transfers were gauged.

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