PERKIN 2

Sandmeyer reactions. Part 7.[1] An investigation into the reduction steps of Sandmeyer hydroxylation and chlorination reactions

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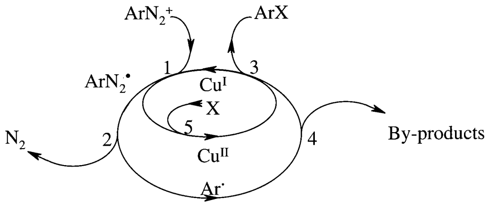
For Sandmeyer hydroxylation and chlorination in aqueous solution, the reduction steps have been investigated by means of correlation analyses of the effects of diazonium ion substitution on the rates of reduction. For simple hydroxylation, a change of behaviour between diazonium ions substituted by electron donor groups and those substituted by electron acceptor groups is interpreted as a change within an inner-sphere process from rate-determining electron transfer to rate-determining association of the reactants. By contrast, for citrate-promoted hydroxylation, a similar change in behaviour may be interpreted as a change between inner- and outer-sphere electron transfers. For chlorination, there is no mechanistic variation within the range of substituents examined but the pattern of behaviour is consistent with an inner-sphere mechanism. The various patterns of behaviour are rationalised in terms of the effects of diazonium ion substitution and catalyst ligation on the reduction potentials and self-exchange rates of the various reacting redox couples. Comparative correlation analyses of reductions and other electrophilic reactions of diazonium ions are used to support the arguments advanced in respect of Sandmeyer reduction steps. It is suggested that the Cu^I reductants react *via* a nucleophilic bridging ligand at the diazonium N_β to give transient *Z*-adducts which are the precursor complexes and that activation for electron transfer involves rotation about the N–N bond.

The general mechanism for a Sandmeyer reaction sequence is given in Scheme 1.[2,3] Reaction (1) is the one-electron reduction of the diazonium ion by a copper(I) complex. It is the rate determining step[4] and the rate has been shown to depend on substituents in the aryl ring and on the nature and number of ligands in the copper complex,[1,5,6] but its precise nature is uncertain. The precipitates often formed during synthetic procedure when solutions of diazonium salts and cuprous halides are mixed were widely believed to be copper(I)–diazonium complexes[7] but an X-ray crystallographic investigation demonstrated that, in the case of benzenediazonium bromide and CuBr at least, the precipitate is a simple salt, $PhN_2^+\ Cu_2Br_3^-$, which shows no evidence of bonding contact between the metal and the diazonium group.[8] Although complexes involving ligation of many transition metals by diazonium ions are known, none has been reported involving copper.[9] Reaction (1) might therefore proceed by either an outer-sphere mechanism or an inner-sphere mechanism in which the precursor complex has a fleeting existence.



Scheme 1

If the former, the product of the reduction step would be an aryldiazenyl radical, $ArN_2^\bullet$; if the latter, the successor complex formed upon electron transfer might decompose stepwise giving the diazenyl radical as an intermediate or, directly, giving dinitrogen and an aryl radical. The involvement of aryldiazenyl radicals in Sandmeyer reactions is thus presumed. When formed in alternative systems such as the homolysis of diazonium compounds in alkaline conditions,[10] of azo compounds[11,12] or of diazosulfides,[13] the reactions of aryldiazenyl radicals can be investigated. An upper limit for the rate constant for the fragmentation of phenyldiazenyl radical [reaction (2)] at 298 K has been measured[12] as $2 \times 10^8\ s^{-1}$ and most other estimates exceed $10^7\ s^{-1}$.[10,11]

However formed, the aryl radicals occurring in a Sandmeyer sequence may undergo a variety of fates. Useful reaction results from the transfer of a ligand X from a copper(II) complex giving ArX and returning the copper to the univalent state [reaction (3)] but, since aryl radicals are highly reactive species, other reactions may compete [reaction (4)]. The Sandmeyer sequence proper [reactions (1)–(3)] thus depends upon a catalytic cycle in copper. Copper(II) is labile in respect of the exchange of monodentate ligands (*e.g.* the lifetime for exchange of water on hexa-aquacopper(II) is *ca.* 10^{-9} s)[14] so the uptake of X by the catalyst [reaction (5)] is expected to be very rapid. Although there is a thermodynamically determined upper limit on the standard reduction potential of a reductant of diazonium ions (estimated by Galli[5] to be *ca.* 1 V), Sandmeyer reaction sequences are most efficient when the relevant Cu^{II}/Cu^I couple has a relatively high reduction potential for, in this circumstance, aryl radicals are produced relatively slowly and consumed relatively rapidly by the required sequence. Cyanodediazoniation exemplifies this well. Ligation by cyanide so stabilises copper(I) that, on mixing, Cu^{2+} and CN^-, the initially formed cyanocuprate(II) complexes have only a transient existence, decomposing to cyanogen and cyanocuprate(I).[15,16] Nevertheless, cyanocuprate(I) complexes are able to reduce diazonium ions and the cyanocuprate(II) complexes formed in the process then transfer cyanide ligands to aryl radicals produced concomitantly within their solvent cage.[1] Cyanogen formation, being a bimolecular process,[15,16] does not compete. Thus in Sandmeyer cyanation, the resting state of the catalyst is Cu^I and the Cu^{II} state has a transient caged existence only.

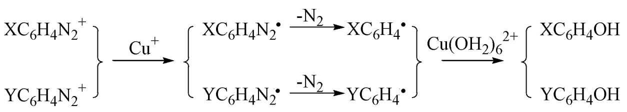
For halodediazoniations, the affinities of chloride and bromide ions for copper(I) are not such that these ions reduce Cu^{2+} and, in Sandmeyer reactions, their ligand transfers [reaction (3)] are slower than those of their cyano analogues. In this circumstance, aryl radicals can escape the solvent cage in which they are produced either to be lost to side-reactions or, in the presence of added alkenes, to be trapped in Meerwein reaction-products.[17–19] Galli[20,21] showed that the yields of Sandmeyer halogenation reactions are improved by having initial Cu(II) present in addition to Cu(I); the improvement occurs because the aryl radicals are not then restricted to ligand transfer only from co-produced halocuprate(II) complexes. Thus, in Sandmeyer halogenation the resting state of the catalyst is usually Cu^I but yields are improved by having significant initial amounts of Cu^{II} present too.

Hydroxydediazoniation is not one of the 'traditional' family of Sandmeyer reactions. It was Cohen and co-workers[22] who showed homolytic hydroxydediazoniation catalysed by copper ions to be feasible. Here, the catalytic copper couple is, in principle, $Cu^{2+}aq/Cu^{+}aq$ but, since $Cu^{+}aq$ is liable to aerial oxidation and disproportionation, experimentally, Cohen supplied Cu(I) as suspended Cu_2O. High concentrations of $Cu^{2+}aq$ are required if most radicals are not to be lost to side reactions because the transfer of water (or hydroxide) ligands to aryl radicals is comparatively slow. We have shown previously that water is transferred from $Cu(OH_2)_6^{2+}$ 400-fold less rapidly than chloride is transferred from the chlorocuprate(II) complexes occurring in Sandmeyer reaction conditions.[23,24] Thus for Sandmeyer hydroxylation, the resting state of the catalyst is Cu^{II} and Cu^I is transient. We have also discovered that coordination of the copper by citrate and certain other multi-dentate ligands promotes the catalytic cycle,[25] *i.e.* maximal yields of phenol can be obtained using a smaller concentration of copper when it is ligated by the non-transferrable ligand than when it is not so ligated. The effect of coordination of the catalyst by a multidentate ligand on the ligand transfer step will be addressed separately; in this paper some light is shed on the effect for the reduction step.

Results

(i) Relative rates of reduction in Sandmeyer hydroxylation and chlorination reactions

Since the reduction steps of Sandmeyer hydroxylation and chlorination reactions occur much faster than those of cyanation, direct measurement of absolute rate constants from the nitrogen evolution in the manner described in the foregoing paper[1] is not feasible. However, relative rates for either process can be obtained by carrying out competitive reductions of pairs of diazonium ions. An experimental procedure was devised in which a pair of substituted diazonium ions was dissolved in a suitable solution of Cu^{II} to which was added a very small amount of ascorbic acid (< 2 mol% relative to Cu^{II}) to initiate the reaction (Scheme 2). Ascorbate is known to reduce Cu^{2+} rapidly[26,27] whereas its reaction with diazonium ions is comparatively slow[28] and intermediate diazo-ether adducts may be isolated.[29] The initiation process is therefore more probably the reduction by ascorbate of Cu^{II} than reduction of diazonium ions; whatever the case, the small amounts of initiator used and the cycling of the catalyst ensure that the majority of diazonium ion reduction is effected by Cu^I.



Scheme 2

In order to ensure truly competitive reductions, reaction must cease before complete reduction of *both* diazonium ions—there must be an insufficiency of Cu^I. This presents something of a difficulty in Sandmeyer reactions where the catalytic cycle regenerates Cu^I in the ligand transfer step (Scheme 1) and, in an ideal system, the Cu^I concentration would remain constant after initiation with both reactions running to completion. In real systems, however, Cu^I may be lost through aerial oxidation[30] and side reactions which do not regenerate Cu^I and thus, provided a sufficiently small amount of ascorbic acid is added and the reactivities of the two diazonium ions are not too dissimilar, both reactions will be arrested before completion. What constitutes a sufficiently small amount of ascorbic acid varies with the pair of diazonium ions being compared. The Cu^{II} concentration is set high so as to optimise the ligand transfer step and ensure that the products of the reduction step (aryl radicals) are efficiently converted to Sandmeyer products, the amounts of which can be quantified by GC analysis.

Hydroxylation. The reduction step of Sandmeyer hydroxylation was studied by measuring the amounts of the two phenols produced from the competitive reaction of two diazonium ions in aqueous solutions of $Cu(NO_3)_2$ as a function of the concentration of added ascorbic acid. Diazonium ions with substituents having similar net electronic effects were paired in order to avoid large disparity between the two phenol yields and hence the error in GC analysis. As an illustration, the competition between the unsubstituted benzenediazonium ion and its 4-chloro-derivative is displayed in Fig. 1. It can be seen that the diazonium ion bearing the net electron withdrawing substituent, Cl, is reduced the more rapidly and reacts to completion for lower initial concentrations of the initiator than the unsubstituted ion and that only at low ascorbic acid concentrations (< 3×10^{-4} mol dm^{-3}) is reaction truly competitive so that the difference in phenol yields reflects the difference in rates. All the competed pairs of diazonium ions behaved in similar ways (though were competitive over different ranges of ascorbic acid concentration) and all gave maximum yields of phenols around 80%. For kinetic analysis, only the phenol yields demonstrably falling within the competitive region were used.

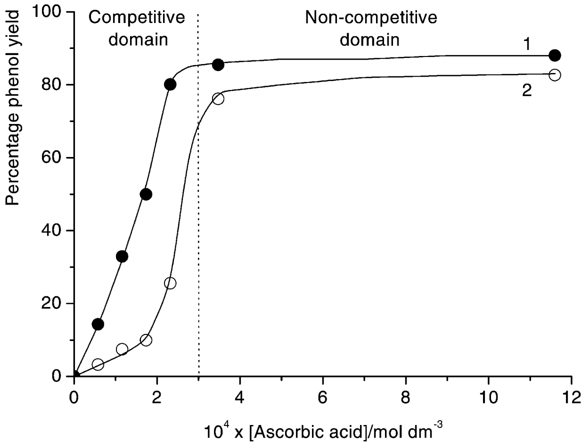


Fig. 1 Variation of percentage phenol yields from competitive Sandmeyer hydroxylations with the concentration of initiator used; plot 1, 4-chlorophenol; plot 2, phenol.

Kinetic analysis. For second order reduction steps of two competing diazonium ions $XC_6H_4N_2^+$ and $YC_6H_4N_2^+$ we have eqn. (6) and (7):

$$-d[XC_6H_4N_2^+]/dt = k_X[XC_6H_4N_2^+][Cu^+] \qquad (6)$$

$$-d[YC_6H_4N_2^+]/dt = k_Y[YC_6H_4N_2^+][Cu^+] \qquad (7)$$

Table 1 Percentage yields of phenols from the competitive reduction of 4-chloro- and unsubstituted benzenediazonium ions and derived relative reduction rate

10^4[Ascorbic acid]/mol dm^{-3}	Percentage yield 4-ClC$_6$H$_4$OH	Percentage yield C$_6$H$_5$OH	k_{Cl}/k_H[a]
0.58	14.26	3.20	4.73
1.16	32.86	7.43	5.16
1.74	49.92	9.94	6.61
2.32	80.05	25.51	5.47
			Mean 5.49 ± 0.80[b]

[a] Calculated as ln [100/(100−$\%_{4\text{-chlorophenol}}$)]/ln [100/(100−$\%_{\text{phenol}}$)], *cf.* eqn. (10). [b] The uncertainty is twice the standard error on the mean.

i.e.

$$-d[XC_6H_4N_2^+]/[XC_6H_4N_2^+] = k_X[Cu^+]dt$$

$$-d[YC_6H_4N_2^+]/[YC_6H_4N_2^+] = k_Y[Cu^+]dt$$

Integrating both between time limits of 0 and t gives eqn. (8) and (9):

$$\ln([XC_6H_4N_2^+]_0/[XC_6H_4N_2^+]_t) = k_X[Cu^+]t \qquad (8)$$

$$\ln([YC_6H_4N_2^+]_0/[YC_6H_4N_2^+]_t) = k_Y[Cu^+]t \qquad (9)$$

For competitive reactions, $[Cu^+]t$, though varying, is common to both at any instant hence elimination of $[Cu^+]t$ between eqn. (8) and (9) gives:

$$\frac{k_X}{k_Y} = \frac{\ln([XC_6H_4N_2^+]_0/[XC_6H_4N_2^+]_t)}{\ln([YC_6H_4N_2^+]_0/[YC_6H_4N_2^+]_t)}$$

If it is assumed that the phenol produced measures the diazonium ion which has reacted, eqn. (10) follows:

$$\frac{k_X}{k_Y} = \frac{\ln\{[XC_6H_4N_2^+]_0/([XC_6H_4N_2^+]_0 - [XC_6H_4OH])\}}{\ln\{[YC_6H_4N_2^+]_0/([YC_6H_4N_2^+]_0 - [YC_6H_4OH])\}} \qquad (10)$$

[In competitive rate studies the simple molar ratio of products is often taken to represent the relative rate constant. This is acceptable for competitive reactions of a single species such as occurs in radical clock experiments but, in experiments involving competition between different species which react at substantially different rates an integration over the competitive interval which gives a logarithmic ratio such as eqn. (10) is advisable].

Eqn.(10) indicates that the relative reduction rate of competing diazonium ions can be obtained from the percentage yields of the derived phenols: k_X/k_Y = ln [100/(100 − X%)]/ln [100/(100 − Y%)]. Table 1 gives the evaluation of k_{Cl}/k_H from the phenol yields shown in the competitive domain of Fig. 1.

The relative rates of reduction for other competed pairs of diazonium ions were obtained in like manner then, by serial multiplication where necessary, all were re-expressed relative to the rate for benzenediazonium ion itself. As a percentage of the mean values from competed pairs of diazonium ions, the uncertainties (twice the standard error on the mean) averaged 9%. In propagating error in the serial multiplications, we have therefore accorded each value an error of 10%. The rates of the reduction steps in Sandmeyer hydroxylation of substituted diazonium ions relative to that of the unsubstituted ion are given in Table 2. It is seen that the values span four orders of magnitude and those ions with electron withdrawing groups are reduced the more readily.

Citrate-promoted hydroxylation. Several mononuclear and binuclear citratocopper(II) complexes have been described which retain water or hydroxide ligands[31,32] and, on the assumption that such monodentate ligands may be transferable, the formation of phenols in this reaction is explicable. However, the nature of the reducing species formed by copper in the presence of trisodium citrate is uncertain. Although soft Cu^I is not expected to form strong complexes with ligands binding through hard oxygen atoms, the multi-dentate, anionic citrate ligand should bind in preference to water for coulombic and entropic reasons (the chelate effect) and hence influence its redox characteristics by comparison with the simple aquated ion. The polarographic half-wave potential of Cu^{2+} has been reported to be lowered in the presence of citrate[33] as have voltammetric peak potentials for sulfato-complexes of two different stoichiometries.[34] Competitive hydroxylations were run in the presence of trisodium citrate and at reduced copper concentration (see Experimental) but which, otherwise, were analogous to the simple hydroxylations described above and relative rate constants were found in the same way; these are given in Table 3. The values span two fewer orders of magnitude than those from simple hydroxylation but again indicate greater reactivity for those ions with electron withdrawing substituents.

Chlorination. Chloride ions bind to Cu^I much more strongly than do water molecules[30,35] and chloride ligands are transferred to aryl radicals by Cu^{II} much more rapidly than water ligands.[24] Consequently, addition of a suitable concentration of KCl to a solution of $Cu(NO_3)_2$ will ensure any copper(I) produced in it will occur as $Cu^ICl_2^-$ or $Cu^ICl_3^{2-}$ [35,36] and the product of Sandmeyer reaction will be the aryl halide. Reductions of pairs of diazonium ions were carried out as above but in the presence of KCl and the yields of aryl chlorides produced under demonstrably competitive conditions were used to evaluate relative rate constants. The results, given in Table 3, span five orders of magnitude and, as expected, show electron deficient ions to be reduced the more readily.

(ii) Correlation analysis of the relative rates of reduction of substituted diazonium ions

In this section is presented an analysis of the response to variation in substitution of the relative rates of reduction given in Tables 2 and 3. The logarithms of the relative rate constants were correlated using simple or multiple linear regression with single or dual substituent parameters as explanatory variables and with an intercept being allowed in each case. The simple substituent parameters σ_m, σ_p and σ_p^+ were taken from the compendium of Hansch, Leo and Taft[37] and σ^0 values were those of Wells, Ehrenson and Taft.[38] The dual substituent parameters, σ_I with one of σ_R^{BA}, σ_R^0, σ_R^+ or σ_R^-, were taken from the review of Ehrenson, Brownlee and Taft.[39] The results are summarised in Table 4. Correlations involving explanatory variables other than those indicated in the table were all poorer as judged in terms of the appropriateness of a linear correlation model or the precision of fit to such a model. The goodness of fit of data to a linear model is judged on the basis of the F-statistic and its significance, the magnitude of the standard deviation of the estimate, s, and by the use of Exner's

Table 2 Relative rate constants for the reduction of substituted diazonium ions by Cu^+aq

Substituent, X	k_{4X}/k_H	Substituent, X	k_{3X}/k_H
4-OMe	$(5.01 \pm 0.71) \times 10^{-3}$	3-Me	$(7.47 \pm 0.75) \times 10^{-1}$
4-OPh	$(4.95 \pm 0.70) \times 10^{-2}$	3-OMe	2.52 ± 0.25
4-Me	$(5.81 \pm 0.58) \times 10^{-2}$	3-Cl	16.4 ± 2.3
4-H	1.00 ± 0.10	3-H	1.00 ± 0.10
4-F	2.02 ± 0.20	$3\text{-}CF_3$	30.9 ± 5.7
4-Cl	5.49 ± 0.55	3-CN	49.5 ± 9.9
4-COMe	20.2 ± 3.5	$3\text{-}NO_2$	50.4 ± 10.1
$4\text{-}CO_2Et$	27.8 ± 3.9	$3,5\text{-bis-}CF_3$	116 ± 23
$4\text{-}CF_3$	56.2 ± 7.9		
4-CN	83.6 ± 14.5		
$4\text{-}NO_2$	110 ± 19		

Table 3 Relative rate constants for the reduction by citrato- and chloro-copper(I) complexes of various 4-substituted benzenediazonium ions

Substituent	Citratocopper(I) k_{4X}/k_H	Chlorocopper(I) k_{4X}/k_H
4-OMe	0.0785 ± 0.0111	0.00529 ± 0.00075
4-OPh	0.249 ± 0.035	0.0525 ± 0.0074
4-Me	0.342 ± 0.034	0.0655 ± 0.0066
4-H	1.00 ± 0.10	1.00 ± 0.10
4-F	1.37 ± 0.14	2.69 ± 0.27
4-Cl	1.99 ± 0.20	10.7 ± 1.1
4-COMe	2.74 ± 0.47	42.2 ± 7.3
$4\text{-}CO_2Et$	3.31 ± 0.47	78.6 ± 11.1
$4\text{-}CF_3$	4.31 ± 0.75	74.5 ± 10.5
4-CN	5.57 ± 0.96	579 ± 100
$4\text{-}NO_2$	8.06 ± 1.40	1700 ± 290

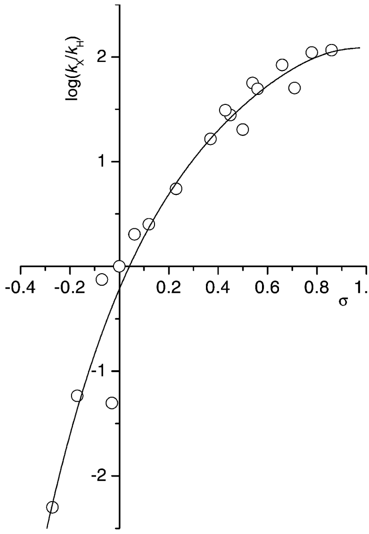


Fig. 2 Curved Hammett plot for the rate determining reduction step in Sandmeyer hydroxylation of 3- and 4-substituted benzenediazonium ions.

parameter ψ which facilitates comparisons between correlations differing in size of data set or degrees of freedom.[40,41]

Hydroxylation. Fig. 2 shows the Hammett plot of the relative rates of reduction during Sandmeyer hydroxylation (*cf.* Table 2). The plot exhibits both curvature and scatter and clearly a linear model is not appropriate for the correlation of the complete data set which includes points for both 3- and 4-substituents. The use of σ_p^+ in place of σ_p for 4-substituents having +I or +M effects reduces the curvature somewhat but a linear model is still not appropriate. (In Table 4 no standard deviations of the estimate, *s*, intercept, or regression coefficients, ρ, are quoted where the trend-line of the data points is curved and a linear model is inappropriate, *e.g.* entries 1 and 2). The application of multiple linear regression to a data set requires the separation of data for differently positioned substituents because inductive (I) and mesomeric (M) effects combine in proportions which are position-dependent. Preliminary to the application of multiple linear regression, entries 3 and 4 report simple regressions for the subset of eleven 4-substituted diazonium ions. Comparison of entries 3 and 4 shows that the use of σ_p^+ in place of σ_p for the 4-substituents having +I or +M effects in the reduced data set improves the correlation but it is still not precise, $0.10 < \psi < 0.20$ representing only 'fair' goodness of fit.[41] Nor does multiple linear regression using σ_I with σ_R^+ as explanatory variables improve the fit (compare entries 5 and 4). Evidently, the variation in the 11-point subset is not explained satisfactorily in terms of any single combination of inductive and resonance effects which applies to the whole subset. However, if the data are further subdivided, the six points for those 4-substituents having +I or +M effects (and including H) are precisely accommodated by multiple linear regression using σ_I with σ_R^+ as explanatory variables (entry 6, Fig. 3) and there is no significant intercept. The five points for the 4-substituents having −I and −M substituents are not correlated on the same line but, taken as a group, they are correlated by σ_I alone (entry 7, Fig. 3); no admixture of resonance character (*i.e. via* any scale of σ_R) is statistically significant. The quality of the correlation is only 'fair' but no worse than that of entry 5. The variation of the 11-point subset is thus better described by further subdivision of the subset than otherwise. We note at this juncture that the susceptibility to inductive effects, ρ_I, differs between the two subsets of 4-substituents and also that the correlation line of the −I and −M subset shows a significant intercept.

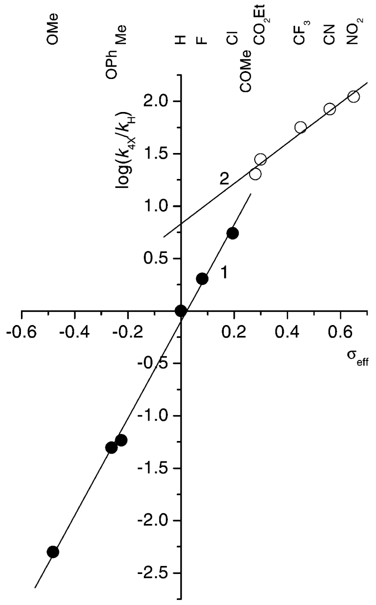


Fig. 3 Plots of log (k_{4X}/k_H) *versus* the effective substituent constant, σ_{eff}, for the reduction step in Sandmeyer hydroxylation of 4-substituted benzenediazonium ions; plot 1, $\sigma_{eff} = (\sigma_I + 0.74\sigma_R^+)$; plot 2, $\sigma_{eff} = \sigma_I$.

Entry 8 in Table 4 gives the results of multiple linear regression applied to the data for the subset of 3-substituents which spans the full range of electronic characteristics. The more precise fit of the majority of points is obtained if those for the $3\text{-}NO_2$ and $3,5\text{-bis-}CF_3$ substituents are excluded from the correlation (entry 9, Fig. 4); the intercept is not significantly different from zero. Entry 10 correlates the data for the $3\text{-}CF_3$, 3-CN, $3\text{-}NO_2$ and $3,5\text{-bis-}CF_3$ substituents with σ_I in a manner comparable with entry 7 and it also includes the intercept of the latter entry as a data-point (see Discussion).

Citrate-promoted hydroxylation. Entries 11 to 17 in Table 4 report correlations for the data set of eleven 4-substituted

Table 4 Correlation analysis of the logarithms of the relative rate constants for the reduction steps in Sandmeyer reactions

Entry	Substituents	Explanatory variables	n^a	$R^{2\,b}$	F^c	$F_{\text{signif}}{}^d$	ψ^e	s^f	Intercept c	Regression coefficients ρ	ρ_I	ρ_R
Hydroxylation												
1	3 and 4	σ_m or σ_p	17	0.909	150.07	3.26×10^{-9}	0.321					
2	3 and 4	σ_m, σ_p or $\sigma_p{}^+$	17	0.938	226.30	1.86×10^{-10}	0.265					
3	4, all	σ_p	11	0.923	107.21	2.68×10^{-6}	0.307					
4	4, all	σ_p or $\sigma_p{}^+$	11	0.971	304.88	3.00×10^{-8}	0.188	0.264	0.423 ± 0.187	2.816 ± 0.322		
5	4, all	σ_I and $\sigma_R{}^+$	11	0.970	130.89	7.73×10^{-7}	0.203	0.285	-0.133 ± 0.410		3.362 ± 0.965	2.774 ± 0.481
6	4, +I & +M	σ_I and $\sigma_R{}^+$	6	0.996	396.32	2.32×10^{-4}	0.098	0.092	-0.100 ± 0.221		4.626 ± 0.673	3.408 ± 0.405
7	4, −I & −M	σ_I	5	0.974	114.30	1.75×10^{-3}	0.208	0.058	0.834 ± 0.269		1.915 ± 0.543	
8	3, all	σ_m	8	0.925	74.11	1.35×10^{-4}	0.316					
9	3, Me to CN	σ_I and $\sigma_R{}^{BA}$	6	0.996	337.40	2.94×10^{-4}	0.089	0.068	0.040 ± 0.152		2.906 ± 0.385	0.687 ± 0.363
10	3, CF_3 to $(CF_3)_2$	σ_I	5	0.990	286.17	4.50×10^{-4}	0.135	0.054	0.855 ± 0.153		1.370 ± 0.258	
Citrate-promoted hydroxylation												
11	4, all	σ_p	11	0.899	79.91	9.02×10^{-6}	0.351					
12	4, all	σ_p or $\sigma_p{}^+$	11	0.924	109.79	2.42×10^{-6}	0.305					
13	4, all	σ_I and $\sigma_R{}^+$	11	0.966	112.65	1.38×10^{-6}	0.216	0.130	-0.084 ± 0.187		1.389 ± 0.440	1.186 ± 0.220
14	4, +I & +M	σ_I and $\sigma_R{}^+$	6	0.996	399.12	2.29×10^{-4}	0.089	0.042	0.000 ± 0.100		1.992 ± 0.306	1.585 ± 0.184
15	4, −I & −M	σ_I	5	0.971	102.09	2.06×10^{-3}	0.220	0.036	0.141 ± 0.168		1.135 ± 0.357	
16	4, −I & −M with H	σ_I	6	0.979	187.23	1.65×10^{-4}	0.177	0.050	0.045 ± 0.116		1.328 ± 0.270	
17	4, −I & −M with H, F & Cl	σ_I	8	0.489	5.75	5.34×10^{-2}	0.825					
Chlorination												
18	4, all	σ_p	11	0.947	160.12	4.89×10^{-7}	0.254					
19	4, all	σ_p or $\sigma_p{}^+$	11	0.967	260.13	6.00×10^{-8}	0.201	0.341	0.282 ± 0.241	3.359 ± 0.471		
20	4, all	σ_I and $\sigma_R{}^+$	11	0.992	508.78	3.70×10^{-9}	0.105	0.175	-0.096 ± 0.251		4.443 ± 0.591	3.223 ± 0.295
21	4, +I & +M	σ_I and $\sigma_R{}^+$	6	0.999	1186.4	4.49×10^{-4}	0.045	0.057	-0.035 ± 0.135		5.069 ± 0.415	3.592 ± 0.250
22	4, −I & −M	σ_I	5	0.874	20.72	1.99×10^{-2}	0.561	0.281	0.493 ± 1.310		3.983 ± 2.784	

[a] No. of data points. [b] R is the correlation coefficient. [c] $F = R^2(n - m)/[(1 - R^2)(m - 1)]$ where $(m - 1)$ is the number of explanatory variables. [d] The significance of F is greater the lower the value of F_{signif}. [e] $\psi = [n(1 - R^2)/(n - m)]^{1/2}$; goodness of fit criteria: $\psi < 0.02$, very good; $0.02 < \psi < 0.1$, good; $0.1 < \psi < 0.2$, fair; $0.2 < \psi < 0.5$, poor (*cf.* refs. 40, 41). [f] Standard deviation of the estimate.

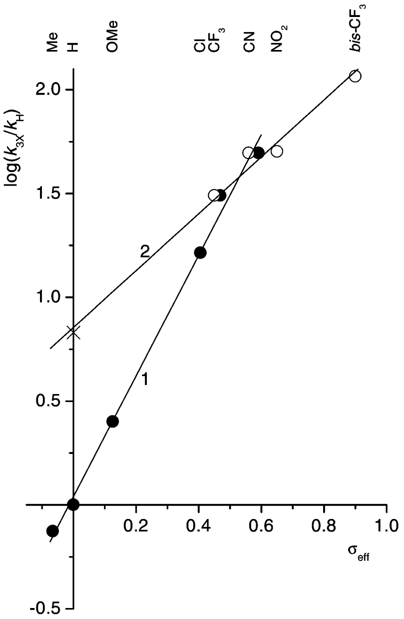


Fig. 4 Plots of log (k_{3X}/k_H) *versus* the effective substituent constant, σ_{eff}, for the reduction step in Sandmeyer hydroxylation of 3-substituted benzenediazonium ions; plot 1, $\sigma_{\text{eff}} = (\sigma_I + 0.24\sigma_R{}^{BA})$; plot 2, $\sigma_{\text{eff}} = \sigma_I$; × marks the intercept of plot 2 in Fig. 3.

diazonium ions. The findings parallel those for the same ions when reduced under simple hydroxylation conditions: correlations in terms of σ_p or σ_p with $\sigma_p{}^+$ for +I and +M substituents (entries 11 and 12) produce curves for which a linear model is inappropriate. Multiple linear regression using σ_I and $\sigma_R{}^+$ gives a fit of the full data set which is 'fair' (entry 13) but subdivision of the set according to the electronic characteristics of the substituents improves the precision for the +I and +M substituents, including H (entry 14 and Fig. 5) and the −I and

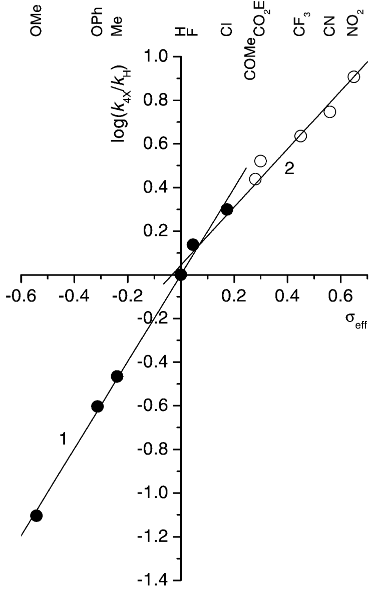


Fig. 5 Plots of log (k_{4X}/k_H) *versus* the effective substituent constant, σ_{eff}, for the reduction step in citrate-promoted Sandmeyer hydroxylation of 4-substituted benzenediazonium ions; plot 1, $\sigma_{\text{eff}} = (\sigma_I + 0.79\sigma_R{}^+)$; plot 2, $\sigma_{\text{eff}} = \sigma_I$.

−M substituents are again best correlated by σ_I alone (entry 15, Fig. 5). As for simple hydroxylation, the variation in the dependent variable for citrate-promoted hydroxylation is best accounted for by subdivision of the 11-point set according to the nature of the substituents. The range of log (k_{4X}/k_H) values for citrate-promoted hydroxylation is narrower than that for simple hydroxylation and the intercept for entry 15 is small and appears not to be significantly different from zero; indeed, the precision of correlation of the data for −I and −M substituents is improved if the datum for H is included with them (entry 16). At first sight, it would appear that if it were valid to include H with the −I and −M substituents, it would be necessary also to include the data for F and Cl as these groups exert net electron withdrawing effects intermediate in magnitude between H and the −I and −M substituents; however, these halogens do not correlate with H and the −I and −M substituents (entry 17) (see Discussion).

Chlorination. Entries 18–22 of Table 4 summarise correlations for the set of eleven 4-substituted diazonium ions. Here the pattern of behaviour is rather different from that found for the two hydroxylations. As for them, the simple Hammett plot is curved (entry 18) and correlation is improved by using σ_p^+ for the +I and +M substituents (entry 19) but multiple linear regression using σ_I and σ_R^+ now gives 'good' correlation of the whole data set (entry 20, Fig. 6). If the +I and +M groups are taken separately, their correlation using σ_I and σ_R^+ is improved (compare entries 20 and 21) but the −I and −M substituents are not then adequately correlated as a separate subset by σ_I (entry 22) nor is any scale of σ_R statistically significant in correlating the subset. We conclude that the variation within the 11-point data set for chlorination is best accounted for by retaining the integrity of the set over the full range of substituent character.

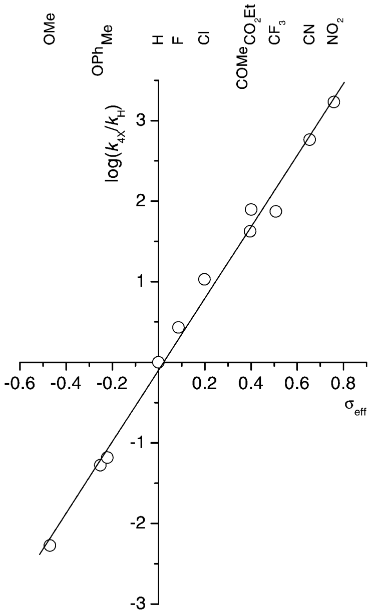


Fig. 6 Plot of log (k_{4X}/k_H) *versus* the effective substituent constant, σ_{eff}, for the reduction step in Sandmeyer chlorination of 4-substituted benzenediazonium ions, $\sigma_{eff} = (\sigma_I + 0.72\sigma_R^+)$.

Discussion

(i) The curved Hammett plot for simple Sandmeyer hydroxylation

Different origins for 'downward concavity' in a Hammett plot can be envisaged according to the reaction concerned. For the particular case of Fig. 2, the plot is constructed from analyses of products which are not directly formed in the actual rate determining step but which arise from a subsequent fast step (ligand transfer) where aryl radicals are trapped. Curvature might conceivably occur if the trapping efficiency were to vary significantly across the substituent sequence so that the apportioning of aryl radicals between phenolic products and by-products varied. Water (or hydroxide) transfer is the slowest of the Sandmeyer ligand transfers and electron deficient radicals react the least rapidly;[24] furthermore, the success of the competition experiments used to obtain the results requires sufficient side-reaction to arrest the catalytic cycle. There is therefore the potential for curvature in Fig. 2 to occur trivially as an analytical artefact. In order to minimise this possibility, we used a concentration of Cu^{2+} that was sufficient to ensure that, given an efficient catalytic cycle, each conversion of diazonium ion to phenol would be maximised: outside the competitive domain, reactant accountability as phenol exceeded 80% for the 4-substituted series and 70% for the 3-substituted series. In view of this, we are confident that the curvature in Fig. 2 is due to underlying mechanistic cause and not artefact. The finding that the data used in constructing the figure are amenable to correlation analysis supports this conclusion.

(ii) Summary of substituent effects

In Results (ii) the best fittings of experimental relative rate constants (k_X/k_H) to eqn. (11) were identified.

$$\log (k_X/k_H) = \rho_I\sigma_I + \rho_R\sigma_R + c \qquad (11)$$

In every case requiring two explanatory variables, c proved to be zero within experimental error (*cf.* Table 4, entries 6, 9, 14 and 20). Hence, if $\lambda = \rho_R/\rho_I$,

$$\log (k_X/k_H) = \rho_I[\sigma_I + \lambda\sigma_R] = \rho_I\sigma_{eff} \qquad (12)$$

where σ_{eff} is the effective substituent parameter. In three cases ρ_R (and hence λ) proved to be zero (*cf.* Table 4, entries 7, 10 and 15).

For Sandmeyer hydroxylation eqn. (13)–(17) give the best account of the experimental data:

4-substituents (+I or +M and including H),

$$\begin{aligned}\log (k_{4X}/k_H) &= (4.63 \pm 0.67)\sigma_I + (3.41 \pm 0.40)\sigma_R^+ \\ &= (4.63 \pm 0.67)[\sigma_I + (0.74 \pm 0.14)\sigma_R^+] \qquad (13)\end{aligned}$$

4-substituents (−I or −M),

$$\log (k_{4X}/k_H) = (1.91 \pm 0.54)\sigma_I + (0.83 \pm 0.27) \qquad (14)$$

3-substituents (Me to CN),

$$\begin{aligned}\log (k_{3X}/k_H) &= (2.91 \pm 0.38)\sigma_I + (0.69 \pm 0.36)\sigma_R^{BA} \\ &= (2.91 \pm 0.38)[\sigma_I + (0.24 \pm 0.13)\sigma_R^{BA}] \qquad (15)\end{aligned}$$

3-substituents [CF_3 to 3,5-$(CF_3)_2$],

$$\log (k_{3X}/k_H) = (1.37 \pm 0.26)\sigma_I + (0.85 \pm 0.15) \qquad (16)$$

The definition of eqn. (16) is discussed later.

For citrate-promoted hydroxylation the best equations are (17) and (18):

4-substituents (+I or +M and including H),

$$\begin{aligned}\log (k_{4X}/k_H) &= (1.99 \pm 0.31)\sigma_I + (1.58 \pm 0.18)\sigma_R^+ \\ &= (1.99 \pm 0.31)[\sigma_I + (0.79 \pm 0.15)\sigma_R^+] \qquad (17)\end{aligned}$$

4-substituents (−I or −M),

$$\log(k_{4X}/k_H) = (1.13 \pm 0.36)\sigma_I + (0.14 \pm 0.17) \quad (18)$$

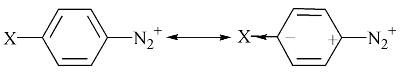
For Sandmeyer chlorination the experimental data are best described solely by eqn. (19):

all 4-substituents

$$\begin{aligned}\log(k_{4X}/k_H) &= (4.44 \pm 0.59)\sigma_I + (3.22 \pm 0.29)\sigma_R{}^+ \\ &= (4.44 \pm 0.59)[\sigma_I + (0.72 \pm 0.12)\sigma_R{}^+] \quad (19)\end{aligned}$$

Correlation analysis has thus allowed *two* distinct types of relative rate behaviour to be discerned; one is dependent solely on the inductive effects of substituents whereas the other depends additionally on their mesomeric effects. For 4-substituted diazonium ions in both simple and promoted hydroxylation and for 3-substituted diazonium ions in simple hydroxylation, the effects of the most strongly electron withdrawing substituents on the relative reaction rate are due to their inductive effects alone and are independent of their mesomeric effects ($\sigma_{eff} = \sigma_I$). By contrast, in both hydroxylations and chlorination the effects of 4-substituents with +M effects are measured by $\sigma_{eff} = [\sigma_I + (0.75 \pm 0.08)\sigma_R{}^+]$; the dependence on $\sigma_R{}^+$ implies that the reactivity perturbed by the 4-substituents is strongly influenced by their capacity for electron donation to the π-system to which they are attached. For 3-substituents in simple hydroxylation, the effects of +M substituents and the weakly electron withdrawing substituents are measured by $\sigma_{eff} = [\sigma_I + (0.24 \pm 0.13)\sigma_R{}^{BA}]$. The lower value of λ and the change of scale of σ_R found for 3-substituents by comparison with the similar 4-substituents no doubt reflect the reduced conjugation in the 3-substituted series between the substituent and the diazonium function.

The finding that the value of ρ_I in eqn. (13) is larger than its value in eqn. (15) indicates that the relative rates of the 4-substituted diazonium ions show a greater susceptibility to inductive effects than those of the 3-substituted ions despite the substituent being at a greater distance from the diazonium function. This is well precedented and the I_π effect, *i.e.* the inductive polarisation of the π-electrons of the substituted ring (*cf.* **1** and **2**) is invoked in explanation.[38] The finding that $\rho_{I(para)} > \rho_{I(meta)}$ may be construed as evidence that the π-system of the diazonium ions is particularly important for the reactivity being perturbed by substituent effects.



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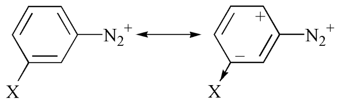

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(iii) Reduction mechanism

If Fig. 2 were to relate to an outer-sphere electron transfer to diazonium ions by aquacopper(I), the curvature could imply that the rates of reduction of ions with electron withdrawing substituents approach the diffusion-controlled limit. We consider this is unlikely to be the case from the following application of the Marcus cross-relation:[42]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (20)$$

$$\ln f_{12} = (\ln K_{12})^2/4\ln(k_{11}k_{22}/Z^2) \quad (21)$$

where k_{12} is the second order rate constant for an outer-sphere electron transfer between species 1 and 2, K_{12} is the equilibrium constant for the same reaction, k_{11} and k_{22} are the respective self-exchange rate constants of the reactant species and Z is the collision frequency (*i.e.* 10^{11} s^{-1}).

The standard reduction potentials of the couples $Fe^{III}(EDTA)^-/Fe^{II}(EDTA)^{2-}$ and $Cu^{2+}aq/Cu^+aq$ are similar (0.12 and 0.159 V *vs.* NHE, respectively)[43,44] and consequently the reductions of any given species by $Fe^{II}(EDTA)^{2-}$ and Cu^+-aq are expected to have similar free energy changes of reaction and hence similar values of K_{12}. However, the respective self-exchange rates of the couples $Fe^{III}(EDTA)^-/Fe^{II}(EDTA)^{2-}$ and $Cu^{2+}aq/Cu^+aq$ are *ca.* 3×10^4 dm^3 mol^{-1} s^{-1} and 1×10^{-5} dm^3 mol^{-1} s^{-1},[45,46] eqn. (20) and (21) thus lead to the expectation that, in an outer-sphere process, $Fe^{II}(EDTA)^{2-}$ should reduce a given substrate more rapidly than aquacopper(I).

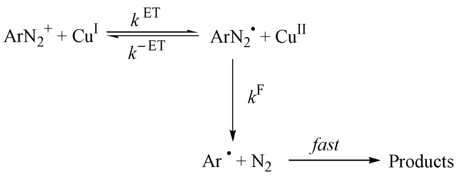
Previously, we have measured absolute rate constants for the outer-sphere reduction of a series of 4-substituted diazonium ions by $Fe^{II}(EDTA)^{2-}$ at pH 9 and have correlated these by eqn. (22).[47]

$$\log(k_{4X}/k_H) = 1.74(\sigma_I + 0.78\sigma_R{}^+) \quad (22)$$

Although an absolute rate constant for the reduction for 4-nitrobenzenediazonium ion was not directly measurable owing to the limitations of the EPR technique employed, eqn. (22) and the value of 1.8×10^5 dm^3 mol^{-1} s^{-1} measured for k_H may be used to derive for it a value of 3.9×10^6 dm^3 mol^{-1} s^{-1} which is 3 to 4 orders of magnitude below the diffusion-controlled rate. It is very improbable therefore that the curvature in Fig. 2 arises because diazonium ions with electron withdrawing substituents, such as 4-nitrobenzenediazonium ion, are reduced by aquacopper(I) in an outer-sphere process at rates approaching the diffusion-controlled limit.

The curvature of Fig. 2 thus suggests the possibility of a change in rate-determining step within a multi-step mechanism and the resolution of the relative rate data for both 3- and 4-substituted diazonium ions into two distinct correlations [eqn. (13) with (14) and eqn (15) with (16)] provides confirmation. In both series, the diazonium ions with substituents capable of electron donation and the unsubstituted ion undergo reactions with rate determining steps which are different from those of ions having electron withdrawing substituents. The intercepts in eqn. (14) and (16) occur because the correlated substituted ions react with rate determining steps different from that of the parent ion with which they are compared.

Although an outer-sphere reduction is envisaged as a one-step electron transfer process within an encounter complex of the reactants, such a process is not necessarily excluded for the reduction of diazonium ions by the evidence of two different rate determining steps within the reaction series. For example, it remains possible that if an aryldiazenyl radical, $ArN_2{}^\bullet$, were to be formed *reversibly* in the reduction, its fragmentation to nitrogen and an aryl radical might conceivably become rate determining in cases where electron transfer is fast, *i.e.* for ions with electron withdrawing substituents (Scheme 3).



Scheme 3

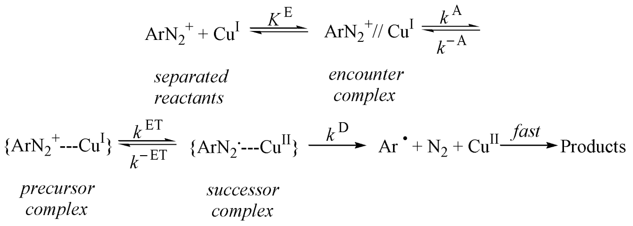
With the notation given in Scheme 3, application of the steady state hypothesis to $ArN_2{}^\bullet$ gives eqn. (23).

$$\text{Rate} = k^F k^{ET}[ArN_2{}^+][Cu^I]/(k^{-ET}[Cu^{II}] + k^F) \quad (23)$$

It is evident that for rate determining fragmentation of the diazenyl radical ($k^{F} \ll k^{-ET}[Cu^{II}]$) the rate is inversely proportional to $[Cu^{II}]$ whereas for fast diazenyl radical fragmentation ($k^{F} \gg k^{-ET}[Cu^{II}]$) the rate is independent of $[Cu^{II}]$. By competitively reducing a pair of diazonium ions which do not have the same rate determining steps, the effect of changing $[Cu^{II}]$ should be to change their relative rate. No significant increase in the relative rate for the 4-CO_2Et/4-Cl pair (from 5.5 when $[Cu^{II}] = 0.3$ mol dm^{-3}) was observed when $[Cu^{II}]$ was halved nor was any significant decrease observed in the relative rate of the 4-CF_3/4-Cl pair (from 10.3 when $[Cu^{II}] = 0.3$ mol dm^{-3}) when $[Cu^{II}]$ was doubled. There is thus no evidence for any involvement of rate determining diazenyl radical fragmentation. The conclusion from the results for simple Sandmeyer hydroxylation is that, whatever the nature of the two rate determining steps discovered, they are not consistent with the reduction by Cu^{+}aq of diazonium ions with electron donating substituents occurring *via* an outer-sphere process which becomes non-rate determining for ions with electron withdrawing substituents. The reduction must consequently occur by an inner-sphere process, *i.e.* one involving the formation of an intermediate which facilitates electron transfer.

Although little is known of the species responsible for reduction in the citrate-promoted hydroxylation, the lower reduction potentials observed[33,34] for the Cu^{II}/Cu^{I} couple in the presence of citrate than in its absence are consistent with the presence of citrate resulting in a more powerful reductant. If reduction rates increase with a falling reduction potential of the reductant, the citratocopper(I) should reduce diazonium ions faster than aquacopper(I) and the diminished selectivity observed for reactions in the citrate-containing system is thus consistent with the reactivity–selectivity principle. The substituent-dependent pattern of behaviour reflected by eqn. (17) and (18) parallels that reflected by eqn. (13) and (14); evidently, increased absolute rates of reduction in the citrate-containing system do not affect the occurrence of a behavioural change at the same position in the substituent sequence as occurs for simple hydroxylation and the citratocopper(I) reductant, like Cu^{+}aq, is inferred to reduce diazonium ions which are substituted by electron donating groups by an inner-sphere mechanism (see later).

Scheme 4 illustrates an inner-sphere reduction mechanism for diazonium ions. The reactant species form an encounter complex, the concentration of which will depend on the diffusive characteristics of the particular species and their ionic charges; substitution in the diazonium ions is not expected to be important for the encounter process. The components of the encounter complex then associate to produce the precursor complex.[48] This process, involving bond formation, *is* expected to be susceptible to substituent effects. Electron transfer, which is also expected to be susceptible to substituent effects in the diazonium moiety, occurs when vibrational excitation takes the precursor complex to a state which is also accessible to the successor complex, *i.e.* the complex formed by the reacting species after electron transfer. The latter complex then dissociates in a process expected to be substituent dependent.



Scheme 4

In principle, any of the three steps—formation of the precursor complex, activation to enable electron transfer proper, or dissociation of the successor complex—might be the overall rate determining step. Application of the steady state hypothesis to the precursor and successor complexes of Scheme 4, using the notation shown in the scheme, results in eqn. (24).

$$\text{Rate} = K^{E}k^{A}k^{ET}k^{D}[ArN_2^{+}][Cu^{I}]/(k^{D}k^{-A} + k^{D}k^{ET} + k^{-ET}k^{-A}) \quad (24)$$

As Cu^{II} undergoes rapid ligand exchange,[14] the rate of dissociation of the successor complex comprising Cu^{II} and a diazenyl radical, itself liable to rapid fragmentation,[12] is expected to be fast and irreversible with the consequence that electron transfer is irreversible. Eqn. (24) is thus simplified to eqn. (25).

$$\text{Rate} = \{K^{E}k^{A}k^{ET}/(k^{-A} + k^{ET})\}[ArN_2^{+}][Cu^{I}] \quad (25)$$

When $k^{ET} \ll k^{-A}$, electron transfer is rate determining and eqn. (25) is simplified to eqn. (26):

$$\text{Rate} = (K^{E}k^{A}k^{ET}/k^{-A})[ArN_2^{+}][Cu^{I}] \quad (26)$$

and when $k^{ET} \gg k^{-A}$, association to form the precursor complex is rate determining and eqn. (25) is simplified to eqn. (27):

$$\text{Rate} = K^{E}k^{A}[ArN_2^{+}][Cu^{I}] \quad (27)$$

The change in rate determining step uncovered by the correlation analysis for diazonium ion reduction during simple Sandmeyer hydroxylation is thus identified as being between electron transfer and association of the reactants to form the precursor complex.

In order to assign the correlations found for simple hydroxylation [eqn. (13) and (14)] to the appropriate rate determining step, we note again that they have disparate gradients and that both are positive. If it is *assumed* that eqn. (13) relates to rate determining electron transfer, it follows from eqn. (26) that the observed relative rate constants, k_{4X}/k_{H}, correlated by eqn. (13) correspond to $(k^{A}k^{ET}/k^{-A})_{X}/(k^{A}k^{ET}/k^{-A})_{H}$ (K^{E} cancels being independent of substitution) and the gradient of eqn. (13) is hence $(\rho_{I}^{ET} + \rho_{I}^{A} - \rho_{I}^{-A})$. The relative rate constants correlated by eqn. (14) correspond to $k^{A}_{X}/(k^{A}k^{ET}/k^{-A})_{H}$ since H falls in the subset of substituents for which rate determining electron transfer has been assumed. However, $k^{A}_{X}/(k^{A}k^{ET}/k^{-A})_{H} = (k^{A}_{X}/k^{A}_{H}) \times (k^{-A}_{H}/k^{ET}_{H}) = (k^{A}_{X}/k^{A}_{H}) \times P$, where $P > 1$ since the condition $k^{ET} < k^{-A}$ holds generally when electron transfer is rate determining; $\log_{10} P$ is identified as the intercept of eqn. (14). The gradient of eqn. (14) is thus ρ_{I}^{A} which is positive, *i.e.* association to form the precursor complex from the encounter complex is assisted by inductively electron withdrawing substitution in the diazonium ion. It follows that the reverse process will be assisted by the opposite electronic character and that ρ_{I}^{-A} is hence expected to be negative. Electron transfer from Cu^{I} to the diazonium moiety within the precursor complex will be assisted by electron withdrawing substituents making ρ_{I}^{ET} positive. The gradient of eqn. (13), $(\rho_{I}^{ET} + \rho_{I}^{A} - \rho_{I}^{-A})$, is therefore the sum of three positive terms whereas that of eqn. (14) equals only one of these terms. The assumption that eqn. (13) relates to rate determining electron transfer thus requires eqn. (13) to have a gradient larger than eqn. (14); this accords with observation and so validates the initial assumption. [The contrary assumption that eqn. (13) relates to rate determining association fails because it requires electron transfer to become rate determining only for the most electron withdrawing substituents which is nonsensical.]

(iv) Electron transfer as the rate determining step

A similar analysis may be applied to the case of citrate-promoted hydroxylation and the results compared to obtain insight into how the promotion of the reduction step is derived. With reference to eqn. (14) and (18), the values of ρ_I^A are similar for both hydroxylations, (1.91 ± 0.54) and (1.13 ± 0.36) for the simple and citrate-promoted processes, respectively. Evidently the promotional effect does not reside in any greatly changed sensitivity to substituent variation on the part of the relative rates at which the precursor complexes are formed from the encounter complexes. The gradients of eqn. (13) and (17) correspond to the respective values of $(\rho_I^{ET} + \rho_I^A - \rho_I^{-A})$ for the two hydroxylations. Since the values of ρ_I^A are similar, the difference in gradients must correspond mainly to differences in the values of $(\rho_I^{ET} - \rho_I^{-A})$. As the values of ρ_I^A do not differ greatly between the two hydroxylations, the same might reasonably be presumed for ρ_I^{-A} and hence the difference in gradients of eqn. (13) and (17) is inferred to stem essentially from differences in ρ_I^{ET}. We have seen that the intercepts of eqn. (14) and (18) are given by their respective values of $\log_{10} P = \log_{10} (k^{-A}_H/k^{ET}_H)$; a small intercept in eqn. (18) is thus consistent with a much greater value of k^{ET}_H relative to k^{-A}_H in the case of promoted hydroxylation. Generalising across the range of substitution, the evidence therefore supports the inference that the origin of the effect that citrate ligation of the copper catalyst has on the reduction step of Sandmeyer hydroxylation is *via* increased rates of electron transfer with an associated reduction in selectivity.

For simple hydroxylation, $\rho_I^A = (1.91 \pm 0.54)$ [eqn. (14)] and since $-\rho_I^{-A}$ is a positive number it follows that $(\rho_I^A - \rho_I^{-A}) > (1.91 \pm 0.54)$. When electron transfer is rate determining [eqn. (13)] the observed gradient, ρ_I, is (4.63 ± 0.67) *i.e.* $\rho_I = (4.63 \pm 0.67) = (\rho_I^{ET} + \rho_I^A - \rho_I^{-A})$, hence, $\rho_I^{ET} < [(4.63 \pm 0.67) - (1.91 \pm 0.54)] = (2.72 \pm 0.86)$.

It follows from eqn. (26) that ρ_R in eqn. (13) equals $(\rho_R^{ET} + \rho_R^A - \rho_R^{-A})$. The finding that σ_I is the only required explanatory variable in eqn. (14) indicates the association process to be independent of the mesomeric effects of substituents and the principle of microscopic reversibility requires that its reverse should also be independent of such effects, *i.e.* $\rho_R^A = \rho_R^{-A} = 0$. The value of ρ_R in eqn. (13) therefore corresponds to ρ_R^{ET}. For the electron transfer process in the simple hydroxylation of 4-substituted diazonium ions we hence deduce the inequality (28), where, since the value of ρ_I^{ET} is an upper limit, the value of λ^{ET}, *i.e.* (1.25 ± 0.42), is a lower limit.

$$\begin{aligned}\log (k_{4X}/k_H)^{ET} &< (2.72 \pm 0.86)\sigma_I + (3.41 \pm 0.40)\sigma_R^+ \\ &< (2.72 \pm 0.86)[\sigma_I + (1.25 \pm 0.42)\sigma_R^+] \qquad (28)\end{aligned}$$

Analogous reasoning with respect to citrate-promoted hydroxylation results in the inequality (29)

$$\begin{aligned}\log (k_{4X}/k_H)^{ET} &< (0.86 \pm 0.47)\sigma_I + (1.58 \pm 0.18)\sigma_R^+ \\ &< (0.86 \pm 0.47)[\sigma_I + (1.84 \pm 1.03)\sigma_R^+] \qquad (29)\end{aligned}$$

Although the uncertainties on the values of λ^{ET} estimated for the two hydroxylation processes are large, the values themselves are larger than 1, indicating the electron transfer process to be strongly influenced by the mesomeric effects of substituents. The explanatory variable needed to represent the +M effects of substituents (σ_R^+) suggests that, in the transition state for electron transfer, the lone pairs of the +M substituents interact strongly with the π-system to which they are attached and, the stronger this interaction, the more difficult it is for the diazonium moiety to accept the electron.

Just as the expressions (28) and (29) were found for electron transfers to 4-substituted diazonium ions, we can argue from eqn. (15) and (16)† to deduce a corresponding expression for the 3-substituted series.

We obtain the inequality (30):

$$\begin{aligned}\log (k_{3X}/k_H)^{ET} &< (1.54 \pm 0.46)\sigma_I + (0.69 \pm 0.36)\sigma_R^{BA} \\ &< (1.54 \pm 0.46)[\sigma_I + (0.45 \pm 0.27)\sigma_R^{BA}] \qquad (30)\end{aligned}$$

We note that $\rho_{I(meta)} < \rho_{I(para)}$ for the electron transfer step consistent with the similar finding for the overall ρ_I values; as expected, $\rho_{R(meta)} < \rho_{R(para)}$.

The relative rates of reduction during Sandmeyer chlorination do not exhibit evidence of a change in rate determining step and the single correlation observed [eqn. (19)] is consistent with electron transfer as the rate determining step over the entire range of substituents considered. The finding that eqn. (19) has the same algebraic form as eqn. (13) supports this suggestion. Indeed, the two equations appear to be identical within the indicated uncertainties. This must be fortuitous; they cannot apply to the same actual reaction as they encompass different ranges of substitution and the former involves mixed chlorocuprate reductants. At the chloride concentration of our experiments (0.3 mol dm^{-3}) only the less chlorinated couples are important[35,36] and a self-exchange rate of 20 dm^3 mol^{-1} s^{-1} has been estimated for the predominant of these ($Cu^ICl_2^-/Cu^{II}Cl_2$).[49] The ratio of self-exchange rates of $Cu^ICl_2^-/Cu^{II}Cl_2$ and $Cu^+aq/Cu^{2+}aq$[46] is hence $20/(1 \times 10^{-5}) = 2 \times 10^6$. Thus, if aquacopper(I) were to reduce a given substrate in an *outer-sphere* process, the Marcus cross-relation implies the effect of introducing two chloride ligands on the intrinsic barrier to electron transfer should be to increase the reduction rate by a factor of up to 2×10^6. However, the chloride ligation also raises the standard reduction potential of the reductant. This attenuates the rate at which the dichloro-complex will reduce a particular substrate, relative to the rate of the aqua-complex, by a factor of $\exp(F\Delta E^{\ominus}/RT)$ where $\Delta E^{\ominus}$ is the difference in their standard reduction potentials, F and R are, respectively, the Faraday and gas constants and T is the absolute temperature. Inserting values, the factor is $\exp[9.469 \times 10^4 \times (0.159 - 0.50)/8.314 \times 298] = 2.2 \times 10^{-6}$. The effect of the chloride ligation on reduction potential in diminishing the relative rate of reduction would be to negate its effect in reducing the intrinsic barrier to outer-sphere electron transfer. It follows from this reasoning that if, as we observe, the aquacopper(I) complex does not reduce diazonium ions in an outer-sphere process, the dichlorocuprate is also unlikely to do so. Yandell[49] has suggested that the self-exchange rate constant for $Cu^+aq/Cu^{2+}aq$ is 5.2 dm^3 mol^{-1}, much larger than the value of 1×10^{-5} dm^3 mol^{-1} obtained by Sutin and co-workers.[46] Such a large value would imply that the rate-enhancing effect of the chloride ligation on the intrinsic barrier to outer-sphere electron transfer would be small and greatly off-set by its detrimental effect on reduction potential. The available evidence thus favours an inner-sphere reduction step in the Sandmeyer chlorination reaction which remains rate determining across the whole range of substituents examined.

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† Eqn. (16) was derived somewhat differently from the other correlations on account of the few data and their narrow range. Because they occur near the intersection of the lines given by eqn. (15) and (16) (*cf.* Fig. 4) the points for 3-CF_3 and 3-CN are accommodated equally well by both equations and we note also that eqn. (16) and eqn. (14) are expected to have an intercept in common, *i.e.* $\log_{10} (k^{-A}_H/k^{ET}_H)$. We therefore used data for 3-CF_3, 3-CN, 3-NO_2, 3,5-bis-(CF_3) and the intercept found for eqn. (14) in evaluating regression coefficients for eqn. (16); error in $\log (k_{3,5\text{-}(CF_3)_2}/k_H)$ was minimised by competing decomposition of the 3,5-bis(trifluoromethyl)benzenediazonium ion against diazonium ions in both the 3- and 4-substituted series (substituent parameter additivity was assumed for the disubstituted diazonium ion). An attempt to extend the range of the data set by including 3,5-dinitrobenzenediazonium ion failed; no phenolic products were produced from its decomposition in the same conditions as the other diazonium ions, only tarry products being obtained.

Table 5 Comparative correlation analysis of selected electrophilic reactions of diazonium ions

Entry	Reaction	Ref.	Best correlation	$\lambda = \rho_R/\rho_I$	n[a]	R^2[b]	F[c]	F_{signif}[d]	ψ[e]	s[f]
	Anion addition to β-N[g]									
1	OH^-	50	$2.86\sigma_p$	1	6	0.993	580.4	1.76×10^{-5}	0.102	0.098
2	CN^-	50	$2.35\sigma_p$	1	6	0.996	912.3	7.16×10^{-6}	0.077	0.064
3		50	$3.65\sigma_p$	1	6	0.997	1476.3	2.74×10^{-6}	0.067	0.081
4	$PhSO_2^-$	51	$2.13\sigma_I + 2.70\sigma_R^{BA}$	1.27	6	0.992	193.3	6.72×10^{-4}	0.126	0.098
5		51	$3.64\sigma_I + 3.42\sigma_R^{BA}$	0.94	6	1.000	5734.8	4.23×10^{-6}	0.000	0.028
	Azo-coupling									
6	1-Naphtholate (i)[g]	52	$3.99\sigma_I + 2.75\sigma_R^+$	0.69	6	0.999	1341.7	3.73×10^{-5}	0.045	0.081
7	(ii)[h]	52	$4.29\sigma_I + 0.68\sigma_R^+$	0.16	6	0.998	705.9	9.76×10^{-5}	0.063	0.081
8	1-Naphtholate-4-sulfonate (i)[g]	52	$4.00\sigma_p$	1	5	0.976	120.3	1.62×10^{-3}	0.200	0.300
9	(ii)[h]	52	$4.04\sigma_I + 1.39\sigma_R^o$	0.34	6	1.000	15668.8	9.37×10^{-7}	0.000	0.016
10	2-Naphthylamine-6-sulfonate (i)[g]	53	$4.03\sigma_I + 2.50\sigma_R^+$	0.62	5	0.999	1763.5	5.67×10^{-4}	0.050	0.058
11	(ii)[h]	53	$4.30\sigma_I + 1.32\sigma_R^{BA}$	0.30	5	0.999	1074.3	9.30×10^{-4}	0.050	0.059
	Electron transfer[g]									
12	Polarographic $E_{1/2}$: sulfolane	54	$0.225\sigma_p^+$/V, $3.80\sigma_p^+$	1	9	0.973	254.1	9.28×10^{-7}	0.186	0.030
13	nitromethane	55	$(0.317\sigma_I + 0.198\sigma_R^+)$/V, $5.36\sigma_I + 3.35\sigma_R^+$	0.62	5	0.999	1558.0	6.41×10^{-4}	0.050	0.008
14	Decamethylferrocene, MeCN	56	$3.25\sigma_p$	1	5	0.982	164.4	1.02×10^{-3}	0.173	0.099
15	$Fe(CN)_6^{4-}$, pH 7, H_2O	56	$4.56\sigma_p$	1	7	0.991	541.2	2.73×10^{-6}	0.112	0.192
16	$ArN_2^+/ArN_2^•$ exchange	56	$5.97\sigma_p$	1	7	0.991	575.4	2.35×10^{-6}	0.128	0.244
17	$Fe(EDTA)^{2-}$, pH 9, H_2O	47	$1.74\sigma_I + 1.37\sigma_R^+$	0.78	5	0.997	349.8	2.85×10^{-3}	0.087	0.037
18	TMPD, pH 4.5, H_2O	57	$1.99\sigma_I + 1.05\sigma_R^+$	0.53	7	0.975	77.2	6.37×10^{-4}	0.209	0.131
19	PhCHOH radical, H_2O	58	$0.59\sigma_p^+$	1	5	0.974	110.2	1.84×10^{-3}	0.208	0.075
20	Semiquinone radical anion, pH 7, H_2O	59	$2.38\sigma_I + 2.50\sigma_R^{BA}$	1.05	6	0.992	193.6	6.70×10^{-4}	0.126	0.080
21	Hydroquinone anion, pH 7, H_2O	60	$3.09\sigma_I + 4.10\sigma_R^o$	1.33	7	0.996	468.9	1.80×10^{-5}	0.083	0.110
22	Phenothiazine, acidified MeCN	61	$2.39\sigma_I + 5.03\sigma_R^o$	1.53	4[i]	0.998	320.5	3.95×10^{-2}	0.089	0.045
23	Cu^+_{aq}, H_2O (i)[g]		$< 2.72\sigma_I + 3.41\sigma_R^+$	1.25	6					
24	(ii)[h]		$< 1.54\sigma_I + 0.69\sigma_R^+$	0.45	6					
25	$CitratoCu^I$, H_2O		$< 0.86\sigma_I + 1.58\sigma_R^+$	1.84	6[i]					

[a–f] See corresponding footnotes to Table 4. [g] 4-Substituted diazonium ions. [h] 3-Substituted diazonium ions. [i] Minimal data set but significance acceptable.

(v) Comparative correlation analyses of electrophilic reactions of diazonium ions

Preparatory to addressing the nature of the association process it occurred to us to enquire whether correlation analysis which enables patterns characteristic of the type of process to be recognised, would allow distinction between inner- and outer-sphere reduction processes for diazonium ions. Data sets from the literature of selected electrophilic reactions of diazonium ions were subjected to correlation analysis and the findings, given in Table 5, judged by the same criteria as those in Table 4. Of necessity, some of the original data sets have been reduced because of the unavailability of Taft dual substituent parameters for a few of the substituents used and because consideration is restricted to mono-substituted systems. Data for 3-substituents were also removed which ensured that comparisons between single and dual parameter correlations for subsets relating to 4-substituents are more reliably made but, where there were sufficient 3-substituted diazonium ions to constitute an adequate subset for treatment, these were analysed separately. The correlations are compared in terms of ρ_I for when a dual parameter expression gives the best account of the data, ρ_I is the coefficient of the effective substituent parameter [$\sigma_{eff} = (\sigma_I + \lambda\sigma_R)$]; when a single explanatory variable gives the best account of a data set, λ ($= \rho_R/\rho_I$) is given as 1 since Hammett's $\sigma_p = (\sigma_I + \sigma_R^{BA})$, $\sigma_p^+ = (\sigma_I + \sigma_R^+)$ *etc.*

Entries 1 and 2 relate to the rates of addition of OH^- and CN^- to the β-nitrogen atom of 4-substituted diazonium ions to give *Z*-azo-adducts.[50] The latter nucleophile adds reversibly and entry 3 applies to the equilibrium constants. Similarly, entries 4 and 5 relate to the addition rates and equilibrium constants for the reversible association of 4-substituted diazonium ions with benzenesulfinate anions.[51] The reaction constants for the equilibria are, of course, larger than those for the corresponding addition rates owing to the contribution from the reaction constants of the reverse steps. It is evident from entries 1 to 5 that rates of addition of simple anionic nucleophiles at $N_β$ of diazonium ions are characterised by $\lambda \geq 1$ and ρ_I of magnitude 2.5 ± 0.4.

Entries 6 to 11 relate to azo-coupling reactions of substituted diazonium ions with naphthalenic substrates. Entry 8 is the only correlation in the group best described in terms of a single substituent parameter but this correlation is considerably less precise than the others and Štěrba and co-workers[52] noted aberrant behaviour of the 4-cyano- and 4-nitrobenzenediazonium ions; unfortunately, exclusion of these points results in a data set too small for the dual parameter treatment. However, the precise correlations of the other entries in the group show that the reaction of $N_β$ of the diazonium ions with these aromatic π-systems is characterised by reaction constants of about 4, that the coupling rates are more susceptible to the inductive effects of 3-substituents than those of 4-substituents [*i.e.* $\rho_{I(meta)} > \rho_{I(para)}$], and that substituents' mesomeric effects are less important than their inductive effects ($\lambda < 1$) especially, as expected, for 3-substituted series (entries 7, 9 and 11). Most of the correlations involve σ_R^+ as the descriptor of resonance effects which is unsurprising as σ^+, from which it is derived, was defined for electrophilic aromatic substitution;[62] those which do not involve σ_R^+ refer to 3-substituted series where the extent of conjugation is reduced relative to the 4-substituted series. The different ranges of ρ_I and λ values evident between two classes of reaction of diazonium ions, both involving electron-pair donation to $N_β$, led to the hope that inner- and outer-sphere electron transfer processes might be distinguishable in terms of correlation analysis.

Entries 12 to 22 are all concerned with single electron transfers to diazonium ions from a variety of donors and entries 23 to 25 inclusive give, for comparison, the limiting correlations of the inner-sphere electron transfers from Cu^I deduced in this paper [inequalities (28)–(30)]. Entry 12 relates to the correlation of polarographic half-wave potentials, $E_{1/2}$, found for diazonium ions in sulfolane solution by Elofson and Gadallah[54] who plotted values for fourteen 3- and 4-substituted diazonium ions *versus* σ, or $\sigma_p{}^+$ for 4-substituents having +M effects. We find that for the reduced set of nine 4-substituted diazonium ions that we have considered, the best correlation is also obtained using σ or $\sigma_p{}^+$, as appropriate, and with negligible change in the reaction constant. In order to obtain a dimensionless gradient for comparability with other reaction constants given in Table 5 we divide the gradient of 0.225 V by $(RT\ln 10)/F$, *i.e.* 0.0592 V and obtain 3.80. There is a considerable scatter in this data set by comparison with entry 13 which relates to a more recent polarographic investigation of diazonium ions in nitromethane solution.[55]

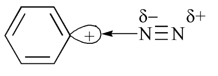
Entries 14 and 15 relate to reductions of diazonium ions where the Fe$^{\text{II}}$ reductants were chosen by Doyle and co-workers,[56] on account of their being substitution inert, to react by outer-sphere mechanisms. The absolute rates of reduction found for these two reductants and their known self-exchange rates were used to extract, *via* the Marcus cross-relation [eqn. (20) and (21)], self-exchange rates for diazonium/diazenyl couples, $ArN_2{}^+/ArN_2{}^•$ (entry 16). In doing so, Doyle's group took the $E_{1/2}$ values of entry 12 to represent standard reduction potentials; furthermore, because their rate constant for 4-methoxybenzenediazonium ion did not correlate well with $E_{1/2}$ for the ion (0.14 V), they inferred the latter to be incorrect and adopted a value of 0.24 V. In fact, the $E_{1/2}$ values found for solution in sulfolane[54] are correlated with those in nitromethane[55] by the expression $E_{1/2}{}^{\text{sulf}} = (0.994E_{1/2}{}^{\text{nitro}} + 0.112)$ from which it can be inferred that Elofson and Gadallah's value of $E_{1/2}$ in sulfolane was, probably, essentially correct. For these reasons, the value of the reaction constant of entry 16 must be treated with circumspection.

Nevertheless, the reaction constant for $ArN_2{}^+/ArN_2{}^•$ self-exchange can be inferred to be large as follows. The Leffler index,[63] α, relates the free energy change of activation for a reaction, $\Delta G^‡$, to the overall free energy change of reaction, ΔG^o, *via* $\alpha = d\Delta G^‡/d\Delta G^o$, where α may take values between 0 and 1. The reaction constant for a set of rate data is given by $\rho^{\text{rate}} = d(\log_{10} k)/d\sigma = -(RT\ln 10)^{-1}d\Delta G^‡/d\sigma$ and that for the corresponding overall reactions considered as formal equilibria is $\rho^{\text{equil}} = d(\log_{10} K)/d\sigma = -(RT\ln 10)^{-1}d\Delta G^o/d\sigma$ whence it follows that $\rho^{\text{rate}} = \alpha\rho^{\text{equil}}$, *i.e.* for a reaction series, the upper limit on the reaction constant for forward rates is determined by the reaction constant for the equilibria. The upper limit on reaction constants relating to the rates of outer-sphere reduction of diazonium ions to aryldiazenyl radicals is therefore determined by the reaction constant for the overall reduction of diazonium ions to diazenyl radicals. For a self-exchange, the rates of the forward (f) and backward (b) steps are equal and both participants bear the same substituent. Hence, for a set of self-exchanges such as those in $ArN_2{}^+/ArN_2{}^•$,

$$\rho^{\text{exch}} = (\rho_f{}^{\text{rate}} - \rho_b{}^{\text{rate}}) = [\rho_f{}^{\text{rate}} - (-\rho_f{}^{\text{rate}})] = 2\rho_f{}^{\text{rate}} = 2\alpha\rho^{\text{equil}} = \rho^{\text{equil}}, \qquad (34)$$

since the symmetry requires α to be 0.5. The reaction constant for self-exchange rates should therefore equal that for overall reduction. From this reasoning it follows that *either* the $E_{1/2}$ values of entry 12 are not valid measures of standard reduction potentials as their adjusted reaction constant (3.80) is not larger than *all* the reaction constants for outer-sphere reduction rates: that for reduction by ferrocyanide (4.56) exceeds it; *or*, ferrocyanide does not react by an outer-sphere mechanism. Assuming that reduction by ferrocyanide *does* occur by an outer-sphere process, the reaction constant for self-exchange must exceed 4.56. It is likely, therefore, that over the range of substituent character from 4-MeO to 4-NO$_2$ the self-exchange rates of diazonium ions probably span at least five orders of magnitude although their absolute values remain uncertain. The adjusted reaction constant for $E_{1/2}$ values found in nitromethane (5.36) suggests that values interpolated from the data of entry 13 may be better estimates of standard reduction potentials than those of entry 12.

The large span of exchange rate constants indicates a requirement for a substantial structural and orbital reorganisation on receipt of an electron by a diazonium ion which is very sensitive to the nature of substituents. X-Ray crystallographic studies have shown diazonium ions to be linear in their CNN moiety[64,65] whereas EPR coupling constants demonstrate aryldiazenyl radicals to be bent.[66,67] Theoretical work by Glaser's group[68–70] has indicated that a diazonium ion is more accurately represented by **3** than by the traditional Lewis structure **4**. (In **3** an aryl cation is coordinated datively at C(1) by a dinitrogen molecule which, though strongly polarised, carries little nett charge, the overall cationic charge being dispersed inductively to hydrogen atoms). The electron-deficient orbital of the phenyldiazenyl radical is a σ-orbital largely confined to the diazo moiety, **5**.[66,67] Clearly, when a diazonium ion receives an electron, there are substantial changes in both geometry and electronic structure. Recent work which reports calculation of the barriers to self exchange in $ArN_2{}^+/ArN_2{}^•$ couples by a variety of theoretical methods supports a strong substituent dependence.[71]



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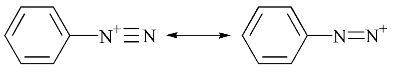

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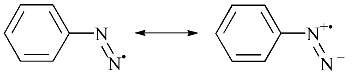


5

The unsubstituted couple $PhN_2{}^+/PhN_2{}^•$ is therefore expected to exhibit a self-exchange rate much reduced in comparison with that *ca.* 10^8 dm^3 mol^{-1} s^{-1} shown by the couple PhCN/PhCN$^-$ which, though isoelectronic, does not undergo substantial structural or orbital reorganisation[72] and, given a reaction constant > 5 for self-exchange in $ArN_2{}^+/ArN_2{}^•$ couples, it follows that the self-exchange rates of those with electron donating substituents must be comparatively slow.

Entries 17 to 21 represent other outer-sphere electron transfers to diazonium. Entry 22 refers to our previous work examining electron transfer between various phenothiazines and diazonium ions.[61] The main kinetic study used 4-methoxybenzenediazonium ion and we suggested a bonded mechanism because, in the cases of slower reacting phenothiazines, initial absorbance due to intermediates was observed. This interpretation has been questioned on the grounds that the rates of reaction of phenothiazine and its 10-methyl derivative could be calculated fairly closely by using the Marcus cross relation with assumed[73] or suspect[56] self-exchange rates; the initial absorbance was suggested to be due to a charge transfer complex formation.[56] Such cannot be the case: organic charge transfer complexes are formed rapidly at essentially the diffusion-controlled rate[74] whereas the observed absorbance developed over intervals of up to 100 s, dependent on the substrate. Furthermore, we also reported that diazonium ions which are more electrophilic than $3\text{-MeOC}_6H_4N_2{}^+$ behaved differently, producing a high concentration of phenothiazine radicals immediately on mixing. Referring to eqn. (20) and (21), it seems to us that if diazonium ions have self-exchange rates which span five orders of magnitude and standard reduction potentials which show an equivalent strong substituent dependence, the possibility arises for a given reductant, that the mechanism might change from outer-sphere for electron-deficient diazonium ions having relatively rapid self-exchange rates and high reduction potentials to inner-sphere for electron-rich diazonium ions having slow self-exchange rates and low reduction potentials. Kochi and co-workers[75] have described a gradation of mechanism in electron transfers from tetraalkyltins to tetracyanoethene or to hexachloroiridate(IV) which is dependent on the steric hindrance offered by the alkyl groups. Although simple 3- and 4-substituted diazonium ions will not present significantly different steric aspects to a given reductant, it seems reasonable to suggest for them a continuum of activated complexes for electron transfer arising from the interplay of driving force and intrinsic barrier.

It thus seems possible that phenothiazine (entry 22), a relatively poor reductant (E = 0.696 V *vs.* NHE)[76] should undergo inner-sphere reaction with electron-rich diazonium ions, its fast self-exchange rate[72] not compensating sufficiently for the combination of slow self-exchange rate and weak driving force in the cases of diazonium ions with electron donating substituents. The electron transfer mechanism may then change to outer-sphere for diazonium ions more electrophilic than 3-$MeOC_6H_4N_2^+$.

Aquacopper(I) (entry 23), despite being thermodynamically a relatively good reducing agent (E = 0.159 V *vs.* NHE),[44] also undergoes inner-sphere electron transfer with diazonium ions: when the latter have electron donating substituents, both reactants have low self-exchange rates and hence there is a high intrinsic barrier to electron transfer. When the diazonium ions have electron withdrawing substituents, their self-exchange rates and reduction potentials are higher but still insufficient to compensate the very low self-exchange rate of Cu^+aq[43] and electron transfer remains of inner-sphere character though no longer the rate determining step (association becomes rate determining).

Given a continuum of transition states between inner- and outer-sphere extrema, sharply distinguished correlation analyses are perhaps not to be expected for entries 13 to 24. However, a gradation in the values of λ is evident. Entries 12 to 19 inclusive have $\lambda \le 1$ and entries 22 to 25 which we believe to relate to inner sphere processes have $\lambda > 1$. It is interesting that entry 21 has a value λ which exceeds 1 although it is believed to refer to an outer-sphere transfer for the full range of diazonium ions. It is perhaps significant that rates calculated by the Marcus cross relation for reaction of hydroquinone with diazonium ions (albeit using the questionable self-exchange rates of entry 16) agree better with experiment for electron-deficient diazonium ions than for ions bearing electron-donating substituents which are wrong by more than two orders of magnitude.[60] Conceivably, for reductions of diazonium ions by hydroquinone the transition states for both mechanisms have configurations which are similar.

(vi) Outer-sphere reduction of electron-deficient diazonium ions by citratocopper(I)

Fig. 7 represents schematically the relative positioning of the free energy curves corresponding to the encounter (**E**), precursor (**P**) and successor (**S**) complexes in electron transfer reactions. In Fig. 7a and b, **E** and **S** are well separated in the reaction coordinate with the consequence that the right- and left-hand limbs, respectively, of their curves intersect (x) at a high value of G. There is, accordingly, a high activation free energy barrier to the outer-sphere electron transfer which would convert **E** directly into **S**. If a precursor complex **P** is interposed between **E** and **S**, relatively early in the reaction coordinate, such that the crossing point (z) of the curves of **E** and **P** occurs for a lower value of G than that (y) of the curves of **P** and **S** (Fig. 7a), the conversion of **P** into **S** (*i.e.* electron transfer) is rate determining and the situation corresponds to that observed for the reduction of 4-substituted diazonium ions by chlorocuprate(I) complexes or the reduction of diazonium ions having 3- or 4-substituents of +M character by aquacopper(I). Here, as the substituent sequence is traversed from electron donating towards electron accepting, the values of G at intersection (y) of the curves of **P** and **S** fall but each remains higher than that of the corresponding intersection (z) of **E** and **P**. In Fig. 7b the position of **P** occurs later in the reaction coordinate than in Fig. 7a and the crossing points (z) and (y) are such that the former occurs at the higher value of G, the conversion of **E** into **P** (*i.e.* the process we have called association) is then rate determining and the situation corresponds to that observed for the reduction of diazonium ions with −M substituents by aquacopper(I). Here, as the substituent sequence is traversed towards stronger electron acceptance, the values of G at intersection of the curves for **E** and **P** (z) fall but remain higher than those (y) of the corresponding intersections of the curves for **P** and **S**.

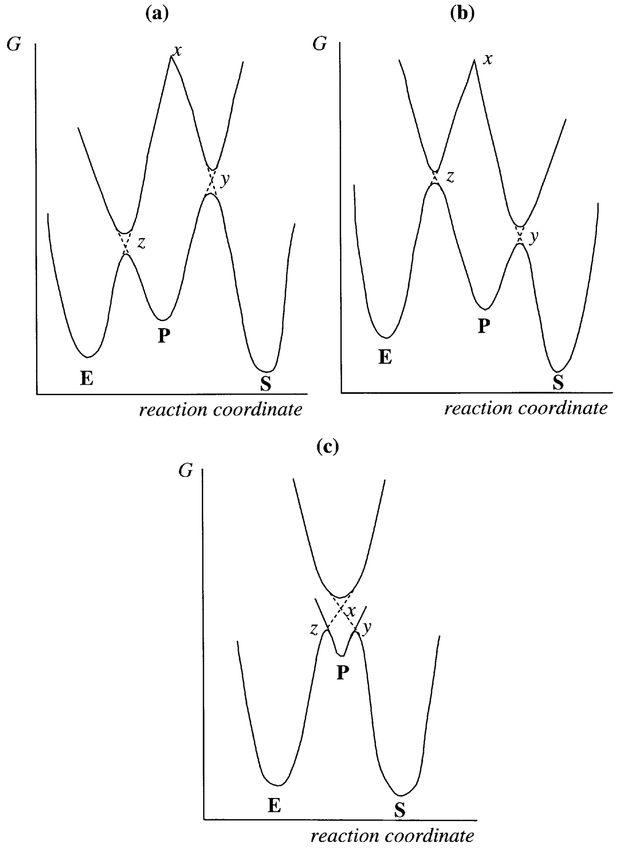


Fig. 7 Schematic representation of reaction profiles for electron transfer reactions.

In (iii) above we identified the intercepts of eqn. (14) and (18) as $\log_{10}$ (k^{-A}_H/k^{ET}_H) for the simple and citrate-promoted hydroxylations, respectively, and it was also noted that the intercept for eqn. (18) is small and, within the experimental uncertainty, could be zero (*cf.* Table 4 entry 15). A zero intercept could occur in two circumstances. The first is that, fortuitously, $k^{ET}_H = k^{-A}_H$, *i.e.* the precursor complex in an inner-sphere reduction of the unsubstituted diazonium ion could react in the forward and reverse directions with equal probability; in terms of Fig. 7a or b the intersections (z) and (y) now occur at the same value of G. The second circumstance is that the intersections (x), (y) and (z) lie close together (Fig. 7c) so that the energy minimum corresponding to **P** is shallow and close to the maximum produced by the intersection of the curves of **E** and **S**. In this situation, the difference in magnitudes of k^{-A} and k^{ET} for all substituents decreases, $\log_{10}$ (k^{-A}/k^{ET}) tends to 0 and, as x, y and z converge, inner-sphere association resembles ever more closely the activation for outer-sphere electron transfer. Such convergence can thus explain the gradation from inner- to outer-sphere mechanisms suggested above. For sufficiently shallow energy minima for **P**, the distinction between inner- and outer-sphere processes would be difficult to discern in terms of reaction rate or correlation analysis. The reductions of diazonium ions by some phenothiazines and by hydroquinone may represent this condition.

We suggest that the reduction of diazonium ions bearing 4-substituents of −M character by the citratocopper(I) reductant may also be represented by Fig. 7c; thus eqn. (17) and (18) do not denote a change of rate determining step within an inner-sphere electron transfer mechanism [as in the case of reduction by aquacopper(I)] but rather, a change of mechanism from inner-sphere reduction of diazonium ions with +M substituents to evident outer-sphere reduction of diazonium ions with −I/−M substituents. The multidentate citrate ligand provides the metal centre with a more rigid inner coordination sphere than occurs in the aqua-complex (the separation of **E** and **S** in the reaction coordinate is relatively reduced) with the consequence that the cost in inner-sphere reorganisation energy on electron transfer is reduced. As a result, the rate of self-exchange in the citratocopper redox couple will be increased relative to that in the aquacopper couple. This, together with higher self-exchange rates for diazonium ions with electron withdrawing substituents, will result in a significant lessening of the intrinsic barrier to outer-sphere electron transfer [the value of G at intersection (x) of the **E** and **S** curves is significantly reduced]. It seems therefore that the promotional effect of citrate on the reduction step of Sandmeyer hydroxylation arises not only from an enhanced driving force of the reaction (lower $E^\ominus$ for the reducing couple) but also from a reduction of the intrinsic barrier to electron transfer enabling a change from inner- to outer-sphere mechanism. The finding of such a change according to the type of substitution in the diazonium ion lends further credence to the idea of a continuum of electron transfer transition states between formal inner- and outer-sphere extremes.

(vii) Association as the rate determining step

The term 'association' requires clarification. The implication of Scheme 4 is that it constitutes that reorganisation of the encounter complex to the precursor complex which enables inner-sphere electron transfer to occur and, if 'inner-sphere' is to have its usual inorganic connotation[48] in respect of the copper(I) complex, either the diazonium ion should enter into coordination of the copper or a ligand coordinated to copper should act as a nucleophile towards the diazonium ion and serve as the bridge for relay of the electron. Whatever is the nature of the association process, its dependence on only the inductive effects of substituents [*cf.* eqn. (14), (16) and (18)] requires explanation and the product of the association process should be such as to facilitate electron transfer in a process which is strongly sensitive to the mesomeric effects of the substituents in the diazonium moiety.

Many transition metal complexes are known in which the metal centre is ligated formally by a diazonium ion *via* one or both of its nitrogen atoms but none has been reported to involve copper.[9] Comparing PhN_2^+ with known ligands of Cu^I such as CO, MeCN and PhNC, the diazonium ion is expected to be a poorer σ-donor. Also, on account of the d^{10} configuration of Cu^I, the *d*-orbitals are contracted and back-donation from metal to ligand is also expected to be weak. These expectations are particularly true for the Glaser structure,[68–70] **3**, in which N_β constitutes the positive end of the N–N dipole and the diazo moiety experiences back-donation of π-electron density from the aromatic ring. Until evidence is found to the contrary, we presume these factors preclude the ligation of Cu^I by diazonium ions in any of the ways found for other transition metals and discount 'association' involving such ligation.

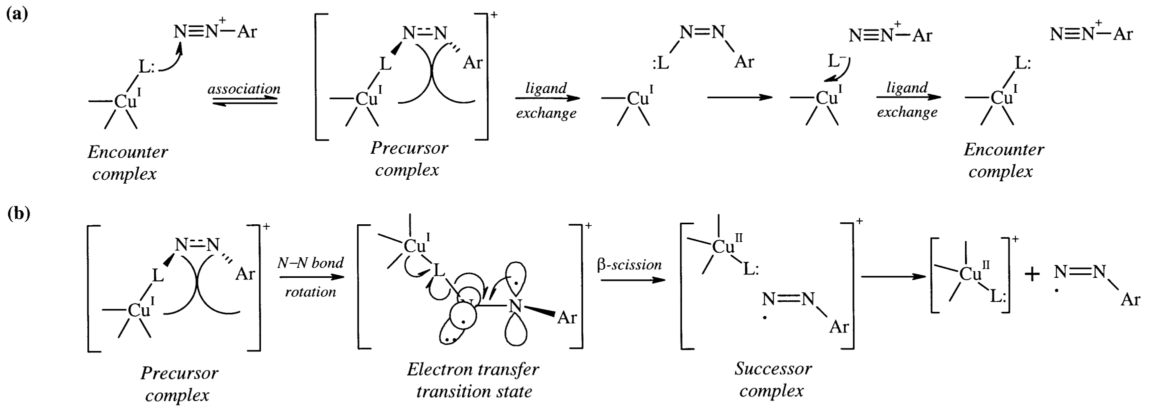
Simple nucleophiles such as OH^- or CN^- add to diazonium ions at N_β to give *Z*-adducts as kinetically controlled products which may undergo subsequent isomerisation to the thermodynamically stabler *E*-isomers. Zollinger[77,78] has explained the stereoselectivity of addition in terms of early transition states in which the separation of the incoming nucleophile and N_β is relatively large and the nucleophile–aryl ring interactions of the *syn*-approach are consequently small in comparison with the N_β lone-pair–aryl ring interactions of the *anti*-approach. By contrast, if the transition state for addition is late, the forming bond is well developed and hence shorter and nucleophile–aryl ring interactions are corresponding larger in the configuration leading to the *Z*-adduct and the *E*-stereoisomer then becomes the preferred primary addition product (*e.g.* azo-coupling). The difference in magnitude of the reaction constants between entries 1 and 2 of Table 5, on the one hand, and entries 6–11 on the other, is also a consequence of the relative earliness of the transition states for addition of OH^- and CN^-.[77,78]

The reaction constants found for the association steps in the reaction of 4- and 3-substituted diazonium ions with aquacopper(I), respectively 1.91 and 1.37 [*cf.* eqn. (14) and (16)], are thus consistent with a very early transition state for nucleophilic attack by a bridging ligand at N_β. The requirement of σ_I as the only explanatory variable in eqn. (14) and (16) suggests that the direction of approach of the reductant lies in the molecular plane of the diazonium ion (and hence is orthogonal to the π-system through which the substituent's mesomeric effects are exerted); this, too, is consistent with a very early transition state for the addition of the reductant to N_β as any significant steric interaction of the reductant with the *syn*-aryl ring would be expected to deflect its line of approach out of the molecular plane. We therefore postulate that Sandmeyer precursor complexes are *Z*-adducts of the reductant at the β-nitrogen atom of the diazonium ion, the linkage between the two moieties being a bridging ligand. In the case of aquacopper(I) as the reductant, we suggest the bridge is likely to be a hydroxide ligand rather than a water ligand as the loss of a proton would both increase the nucleophilicity of the bridging oxygen atom and provide a neutral, rather than cationic, reaction partner for the diazonium ion.

(viii) The activation of electron transfer

In the vibrational ground state of the *Z*-adduct proposed for the precursor complex, it is expected that there will be a significant dihedral angle, $LN_\beta N_\alpha C(1)$, (where L is the bridging ligand) on account of the steric interactions of the bulky attachments in *Z*-configuration on the azo function. The principle of microscopic reversibility requires that the heterolytic dissociation of the adduct directly into the components from which it was formed must be associated with a vibration which stretches the $L–N_\beta$ bond and closes the dihedral angle (Scheme 5a). An alternative heterolysis of the precursor complex may also be envisaged which involves the breaking of the $L–Cu^I$ bond. Such a dissociative process would eliminate *Z*-ArN=NL as a composite 'ligand' from the inner coordination sphere of the metal ion. *Z*-ArN=NL would then itself be expected readily to lose L^- giving the diazonium ion. Thus the formation of the precursor complex, formulated as suggested, would be expected, one way or another, to be rapidly reversible to give the species which combined to produce it, as required by the kinetic analysis (*cf.* Scheme 4). Another vibration of the precursor complex during its limited lifetime must cause activation of the electron transfer; we suggest this to be rotation about the N–N bond (Scheme 5b).

As a result of the reduced N–N π-overlap in the precursor complex arising from the twist due to steric interactions, N–N bond rotation should be easier than that about a sterically unencumbered N–N π-bond. Opening of the $LN_\beta N_\alpha C(1)$ dihedral angle towards 90° would have the consequence of further uncoupling the π-bond and bringing of the $N_\beta L$ σ-bond into eclipse with the singly occupied p_z orbital on N_α. This would allow a β-scission producing an aryldiazenyl radical and a change of oxidation state of the copper (Scheme 5b). There are grounds for expecting N–N bond rotation, and hence homolysis, to be particularly sensitive to the nature of the ring substitution. The *Z* to *E* isomerisation of diazoate anions, $ArN{=}NO^-$

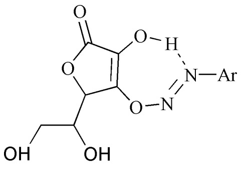


Scheme 5

is strongly substituent dependent, exhibiting a dichotomy between +M and −M substituents comparable with that found for the hydroxylation reactions reported here.[79] Aryl substituents with −M effects which conjugate with the N=N double bond reduce its bond order and so facilitate the rotation about the N–N axis which leads to isomerisation. Aryl substituents with +M effects such as 4-Cl do not so reduce the barrier to rotation and a different mechanism obtains, *i.e.* inversion of N_β in the diazohydroxide, ArN=NOH, which has a considerably higher activation energy.[80] Diazoate anions and diazohydroxides have no propensity for direct N–O bond homolysis but other O-linked compounds such as azo-ethers, ArN=NOAr′ and diazoanhydrides, ArN=NON=NAr do homolyse.[81] Such homolyses can be understood in terms analogous to those proposed for a Sandmeyer precursor complex, *i.e.* N–N bond rotation in a sterically congested *Z*-adduct, the only difference being that the β-scission now produces a second, stabilised radical (respectively, Ar–O$^\bullet$ and ArN=NO$^\bullet$) in addition to the diazenyl radical. In the Sandmeyer precursor complex, the capacity of the copper to change its oxidation state provides a particularly effective way of stabilising the 'radical' co-produced with the aryldiazenyl radical.

If the extent of N–N bond rotation required to give sufficient orbital overlap for β-scission to occur should be less when there is a relatively strong driving force than when the driving force is weak, the occurrence of precursor complexes manifesting low barriers to electron transfer can be understood (*cf.* Fig. 7b), *e.g.* the reductions of diazonium ions bearing −M substituents by aquacopper(I) where association rather than electron transfer is rate determining. Conversely, if β-scission of the Cu^I–L bond should be relatively difficult despite effective eclipsing of the p_z orbital on N_α, the occurrence of different electron transfer rates for reductants having similar reduction potentials can be understood. In the foregoing paper we reported that cyanocuprate(I) complexes reduce diazonium ions much more slowly than chlorocuprate(I) complexes of similar reduction potential. In the former reductants the bridging ligand is diatomic and the electron transfer, formally from the metal to nitrogen in order to maintain the octet of the latter on β-scission, must involve the intervening carbon atom. We suggest the additional atom in the path of the transferred electron inhibits β-scission and reduces the apparent 'conductivity' of the cyanide ligand relative to that of a chloride ligand.[1]

The bond-rotation mechanism of electron transfer also allows a rationalisation of the initially surprising observation that ascorbate does not readily reduce diazonium ions but instead may give stable diazo-ether adducts, *e.g.* **6**.[29] If the interactions which normally ensure the kinetically preferred formation of the *Z*-adduct on addition of a nucleophile to a diazonium ion should be attenuated in the case of ascorbate by the possibility of hydrogen bonding between N_α and the ascorbate 2-OH group, the *E*-adduct **6** could be formed directly in increased proportion. In **6** the N–N bond rotation necessary for radical formation is inhibited by the fact that the π-bond is stronger than those in *Z*-adducts, due to lack of steric effects, and also because the *E*-configuration is additionally stabilised against isomerisation by the H-bond. Evidently, the activation energy for access to the albeit stabilised ascorbyl radical from **6** is too high for the reaction to be feasible except perhaps for the 4-nitro derivative which has been reported to decompose on heating[29] and where the effect of the substituent would be to reduce the N–N bond order and facilitate rotation. The formation of an increased proportion of stable *E*-adduct also explains the low homolytic yields (< 50%) in instances where some reduction of diazonium ions by ascorbate does occur.[28]



6

Conclusions

Correlation analysis of relative reaction rates reveals two distinct types of behaviour in the reduction of diazonium ions by aquacopper(I). Kinetic analysis indicates these to correspond, within an inner-sphere process, to rate determining electron transfer for the unsubstituted diazonium ion and those bearing +M substituents and to rate-determining association of the reactants for those bearing −M substituents. In the presence of citrate two types of behaviour are again observed: rate determining electron transfer within an inner-sphere process for diazonium ions bearing +M substituents but for those bearing −M substituents the behaviour is now consistent with a change to an outer-sphere reduction mechanism. When mixed chlorocuprate(I) complexes reduce diazonium ions, inner-sphere rate determining electron transfer is observed across the whole substituent range.

A critical survey of reductions of diazonium ions reported in the literature leads to the conclusion that there exists a gradation of mechanism between formal inner- and outer-sphere extremes which arises because the reduction potentials and self-exchange rates of diazonium ion/diazenyl radical couples manifest a strong substituent dependence.

The precursor complex in inner-sphere reductions of diazonium ions is suggested to be the *Z*-adduct of the reductant at N_β of the ion; it is short lived on account of its ready heterolysis back to initial components. The activation for electron transfer is suggested to be a rotation and uncoupling of the N–N bond which allows a homolytic β-scission producing an aryldiazenyl radical and either a second stabilised radical or, in the case of a

Table 6 Yields and melting/decomposition points of diazonium tetrafluoroborates

Substituent	Yield (%)	Mp/°C	Lit. mp/°C	Ref.
4-OMe	95	141–142	142	83
4-OPh	32	177–178	159–160	84
4-Me	97	101–102	109–110	83
H	99	96–98	108–110	83
4-F	90	161–162	161–161.5	85
4-Cl	71	133–134	136–137	83
4-CF_3	69	105–106	116–117	86
4-COMe	68	85–87	94–95	87
4-CO_2Et	76	105–106	93–95	88
4-CN	97	140–141	150	89
4-NO_2	85	152–153	157–158	83
3-OMe	53	82–83	87–88	83
3-Me	51	96–97	97–101	83
3-Cl	53	142–143	146–148	83
3-CF_3	77	149–150	146–147	90
3-NO_2	50	179–180	168–170	90
3,5-$(CF_3)_2$	62	202–204	—	91
3,5-$(NO_2)_2$	83	203–205	203	83

Sandmeyer reduction step, a concomitant change of oxidation state of the copper. The mechanism of bond rotation and β-scission in an initial adduct also allows the low reactivity of ascorbate and cyanocuprate in the reduction of diazonium ions to be rationalised.

Experimental

(i) Diazonium tetrafluoroborates

Diazonium tetrafluoroborates were obtained from the corresponding anilines using the following general method (scaled down in some instances).[82] The appropriate aniline (0.1 moles) was dissolved in a mixture of 50% fluoroboric acid (34 cm^3) and distilled water (40 cm^3). After cooling to 0 °C, sodium nitrite (6.9 g) in 15 cm^3 of distilled water was added in 2 cm^3 portions. The mixture was stirred for 30 minutes and the thick precipitate was collected and re-dissolved in acetone. The diazonium tetrafluoroborate was then precipitated by the addition of diethyl ether. The yields and melting/decomposition points observed are given in Table 6.

(ii) Phenols and aryl halides

The phenols and aryl chlorides required for product authentication and calibration purposes were all commercial materials as were the 4-bromobenzonitrile used as internal standard for GC and other reagents.

(iii) Competitive hydroxylation and chlorination

The following procedures are typical of those used to measure the relative rates of reduction of various pairs of substituted diazonium ions. For simple hydroxylation, the appropriate two diazonium tetrafluoroborate salts (1 mmol of each) were dissolved in a solution of $Cu(NO_3)_2$ (100 cm^3, 0.3 mol dm^{-3}). For chlorinations, KCl (0.03 mol) was added to the mixture. For measurements of citrate-promoted hydroxylations, the method was altered to take account of the promotional effect. Thus for the competed pairs of diazonium ions with the following 4-substituents: MeO/Me, PhO/Me and Me/H, the reaction solution was $Cu(NO_3)_2$ (0.05 mol dm^{-3}) and trisodium citrate (0.1 mol dm^{-3}) whereas for all other pairs these concentrations were doubled. To initiate the reaction, whilst stirring vigorously, the appropriate amount of an aqueous solution of ascorbic acid was added to produce a concentration in the reaction mixture in the range 5×10^{-6}–5×10^{-3} mol dm^{-3}; in order to ensure rapid mixing, volumes in the range 0.1–2.0 cm^3 of appropriate molarity were added. Nitrogen evolution was immediate. After ten minutes of stirring, the reaction mixture was extracted with ethyl acetate (25 cm^3) containing internal standard (4-bromobenzonitrile, 0.02 mol dm^{-3}). The extract was analysed by GC, performed on an FFAP column (temperature program 60 °C for 5 min then 16 °C min^{-1} until 230 °C). The only detectable products in all cases were the expected phenols or aryl chlorides. Their yields were determined from the peak areas using response factors previously determined for each product by use of authentic materials.

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