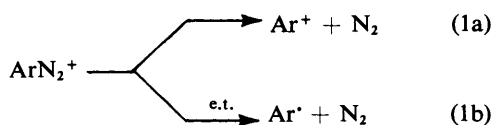# Substituent Effects on the Sandmeyer Reaction. Quantitative Evidence for Rate-determining Electron Transfer

Carlo Galli

Centro di Studio sui Meccanismi di Reazione del Consiglio Nazionale delle Ricerche, c/o Dipartimento di Chimica, Università di Roma ' La Sapienza ', 00185 Roma, Italy
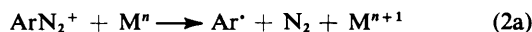
The substituent effect in the Sandmeyer reaction of aromatic diazonium salts induced by several reducing cations (Sn^{2+}, Cu^+, Fe^{2+}) has been determined in H_2O–dioxane (2 : 1). Electron-withdrawing substituents increase the reactivity of the substrate in the radical chlorodediazoniation process, while the reverse holds for electron donor ones. For the change of the reduction potential of the reductant from 0.15 to 0.77 V the Hammett ρ value varies from 0.6 to 1.0. Conventional spectrophotometry has been employed to measure the rate of the reaction of two diazonium ions with Fe^{2+}: reasonable agreement is found with the rate constants for the corresponding electron transfer step as calculated according to Marcus theory. The conclusion is drawn that the electron transfer step is rate determining in the Sandmeyer reaction under these conditions.

A wealth of information is available in the literature indicating that the reactions of diazonium salts in which the diazo-group is lost can occur either by a heterolytic (1a) or a homolytic path (1b).[1] Depending on the reaction conditions the former path can dominate over the latter or *vice versa*.

$$ArN_2^+ \left\{ \begin{array}{l} \longrightarrow Ar^+ + N_2 \qquad (1a) \\ \xrightarrow{\text{e.t.}} Ar^\cdot + N_2 \qquad (1b) \end{array} \right.$$

Unfortunately, due to the comparable energetics of the two processes, this is not always an unambiguous situation.[1a]

The Sandmeyer reaction is an halogenodediazoniation process for which clear evidence of the radical nature has been given. Recently the original reaction scheme proposed by Kochi[2] has been substantiated and also widened as to the scope.[3] The reaction can be represented as a two-step mechanism. The first step (2a) is a reductive electron transfer (e.t.) to the substrate. Besides the Cu^+ cation in the original approach by Sandmeyer,[4] it is now clear that other reducing agents (generally but not necessarily metal cations) can perform this step, the only requisite being a redox potential E_0 equal or less than 1 V.[3a] Qualitative evidence for this statement stems from a trend towards higher efficiency in the

$$ArN_2^+ + M^n \longrightarrow Ar^\cdot + N_2 + M^{n+1} \qquad (2a)$$

$$Ar^\cdot + CuX_2 (H_2O)_n \longrightarrow ArX + CuX(H_2O)_{n+1} \qquad (2b)$$

$$\text{Scheme. X = Br}^- \text{ or Cl}^-$$

halogenodediazoniation process as the reducing ability of the reductant M^n increases.[3a] The second step (2b) of the Sandmeyer reaction is a ligand transfer step from a ligand transfer agent to the intermediate aryl radical. Although a few ligand transfer agents do exist, the most efficient appears to be the Cu^{2+} ion.[3b]

As such, the Sandmeyer reaction is a single electron transfer (s.e.t.) process, which has been investigated in recent times with particular attention.[5] It is well known that quantitative structure–reactivity relationships are of fundamental help in elucidating reaction mechanisms.[6] However, apart from some scattered data, a quantitative and systematic investigation of substituent effects on reactivity in the Sandmeyer reaction does not appear to have been carried out so far. It would be

desirable both for a better comprehension of the mechanism of s.e.t. processes and for a comparison with known substituent effects in the field of the heterolytic reactions.[7] Qualitative data on substituent effects for the Sandmeyer reaction is available only from preparative work,[1a,8] suggesting an accelerating or anyhow favourable effect on reactivity by electron-withdrawing substituents.

Some attempts to correlate the polarographic half-wave reduction potentials of aromatic diazonium salts with substituent (σ) parameters are reported in the literature.[9] The most successful of these correlations[10] shows clearly that electron-withdrawing substituents increase the potential of the substituted diazonium salt, making easier the reduction at the cathode. This fits well with the Scheme concerning the e.t. step. Similarly, Packer *et al.*[11] have described the radical reduction of arenediazonium ions induced by e^-_{aq} produced by γ-radiolysis. Although some complexities arise from the fact that chain reactions are involved in the water–alcohol medium, whereby a variety of reducing agents are generated, a clear trend in the substituent effect reveals again that the reactivity of the dediazoniation process increases with the electron-withdrawing ability of the substituent. Pointing to the limits of their approach, these authors concluded[11a] that ' details of diazo-compound homolysis are probably best studied by methods avoiding the occurrence of chain reactions.'

In a previous study,[3a] evidence was collected that the Sandmeyer reaction induced by some reducing cations is not a chain process. Hence, it was decided to exploit these reductants to evaluate not only the effects of substituents on the Sandmeyer reaction, but also how this effect can vary depending on the efficiency of the reductant used. The determination of absolute rate constant of the reaction was also attempted.

Results

To overcome the inherent and well known experimental complexity of a kinetic study of a halogenodediazoniation process,[12] relative rates of reaction were determined using a competitive technique. A substituted aromatic diazonium chloride was pitted together with benzenediazonium chloride taken as the reference compound. The chlorodediazoniation reaction was carried out in water–dioxane (2 : 1) at 10 °C in the presence of the reductant, $CuCl_2$ and an excess of Cl^-. The competitive processes are represented by equations (3)

Table 1. Competition experiments of chlorodediazoniation of substituted arenediazonium chlorides $(p\text{-}XC_6H_4N_2{}^+Cl^-)$ with several reductants in water–dioxane 2 : 1 [a]

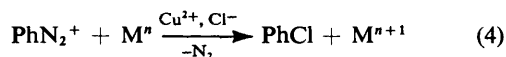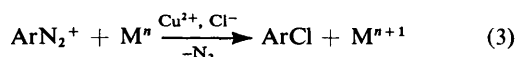| Substrate A X	Substrate B X	Reductant	Time (min)	Product A [b] $XC_6H_4Cl(\%)$	Product B [b] $XC_6H_4Cl(\%)$	k_A/k_B [c]
NO2	H	SnCl2	5	42	12	3.5
COCH3	H	SnCl2	5	49	17	2.8
Cl	H	SnCl2	5	45	35	1.3
CH3	H	SnCl2	10	40	43	0.92
OCH3	H	SnCl2	10	15	40	0.38
NO2	Cl	SnCl2	5	31	12	2.6
Cl	CH3	SnCl2	5	44	33	1.4
NO2	H	CuCl	5	47	13	3.7
COCH3	H	CuCl	5	45	17	2.6
Cl	H	CuCl	5	45	27	1.6
CH3	H	CuCl	10	33	43	0.79
OCH3	H	CuCl	10	17	52	0.33
NO2	Cl	CuCl	5	25	11	2.3
NO2	H	FeCl2	5	41	10	4.3
COCH3	H	FeCl2	5	33	10	3.4
Cl	H	FeCl2	10	36	22	1.7
CH3	H	FeCl2	10	23	38	0.59
OCH3	H	FeCl2	10	8	52	0.12
NO2	Cl	FeCl2	5	45	19	2.4
NO2	H	Na2S2O4	5	13	22	0.59 [d]
NO2	H	Ascorbic acid	10	12	21	0.59
Cl	H	Ascorbic acid	10	35	13	2.8
CH3	H	Ascorbic acid	10	31	14	2.2
OCH3	H	Ascorbic acid	10	36	29	1.3
NO2	Cl	Ascorbic acid	10	10	37	0.24
CH3	OCH3	Ascorbic acid	10	40	24	1.6

[a] In the presence of $CuCl_2$; the average temperature was *ca.* 10 °C. [b] Yields from g.l.c. experiments, evaluated with respect to the parent substrate. [c] From duplicate experiments; the error never exceeded 6%. [d] See text.

Table 2. Correlation of k_{rel} values for the chlorodediazoniation reaction with Hammett σ parameters and with the half-wave reduction potentials of the $p\text{-}XC_6H_4\overset{+}{N}_2$ substrates

X	k_{rel} [a] Sn^{2+} (E_0 0.15)	Cu$^+$ (E_0 0.16)	Fe^{2+} (E_0 0.77)	$\Delta G^{\ddagger}_{rel}$/kcal mol^{-1} [b] Sn^{2+}	Cu$^+$	Fe^{2+}	σ_p [c]	$E_{\frac{1}{2}}$/V [d] vs. s.c.c.
NO2	3.5	3.7	4.3	-0.70	-0.74	-0.82	0.78	0.43
COCH3	2.8	2.6	3.4	-0.58 [e]	-0.54 [e]	-0.69 [e]	0.52	
Cl	1.3	1.6	1.7	-0.15	-0.26	-0.30	0.11 [f]	0.35
H	1.0	1.0	1.0	0	0	0	0	0.30
CH3	0.92	0.79	0.59	0.047	0.13	0.30	-0.31 [f]	0.25
OCH3	0.38	0.33	0.12	0.54	0.62	1.19	-0.78 [f]	0.12
	p 0.62 [g] (r 0.987)	p 0.67 [g] (r 0.992)	p 1.0 [g] (r 0.981)	α 0.16 [h] (r 0.972)	α 0.18 [h] (r 0.990)	α 0.29 [h] (r 0.999)		

[a] Relative to X = H. [b] Evaluated at 10 °C. [c] From ref. 15. [d] From ref. 10. [e] Data not employed in the correlation of Figure 2 due to the lack of the corresponding $E_{\frac{1}{2}}$ value for the substrate. [f] A $\sigma_p{}^+$ value was used. [g] See Figure 1. [h] From Figure 2, see text.

and (4). Unambiguous internal competition was ensured by

$$ArN_2{}^+ + M^n \xrightarrow[-N_2]{Cu^{2+}, Cl^-} ArCl + M^{n+1} \qquad (3)$$

$$PhN_2{}^+ + M^n \xrightarrow[-N_2]{Cu^{2+}, Cl^-} PhCl + M^{n+1} \qquad (4)$$

employing both the reductant and the Cu^{2+} salt in deficit with respect to each substrate; short reaction times were also adopted. The amounts of ArCl and PhCl present in the crude product were then determined by g.l.c. analysis and used to calculate the relative reactivity of the two substrates. Table 1 collects all the relative reactivities resulting from these competitive experiments which were run with different reductants, namely, $SnCl_2$, CuCl, $FeCl_2$, $Na_2S_2O_4$, and

ascorbic acid. Five substituents, besides hydrogen, were examined, all in the *para*-position for the sake of homogeneity. It is important to observe that each reductant gave rise to a different set of relative reactivities (Table 2).

Other products were also detected in the crude products apart from the aryl halides. They may derive from reactions (5)—(8) where SH is the solvent (most likely dioxane). These

$$Ar^{\cdot} + SH \longrightarrow ArH + S^{\cdot} \qquad (5)$$

$$Ar^{\cdot} + Ar^{\cdot} \longrightarrow Ar\text{-}Ar \qquad (6)$$

$$Ar^{\cdot} + ArX \longrightarrow \longrightarrow Ar\text{-}ArX \qquad (7)$$

$$Ar^{\cdot} + ArN_2{}^+ \longrightarrow \longrightarrow Ar\text{-}N{=}N\text{-}Ar \qquad (8)$$
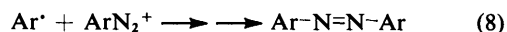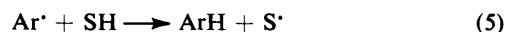
compounds however were formed generally in <2% yield and consequently did not interfere much with the evaluation of the relative reactivities, at least in the case of $SnCl_2$, CuCl, and $FeCl_2$. With these three reductants the 'expected'[10,11] reactivity trend in the substituent effect is obtained, i.e. the more electron withdrawing the substituent the more reactive the substrate, while the reverse is true for electron donor substituents. Although the relative reactivities fall within a narrow range, they can be unmistakably detected by the technique employed. Besides, on varying the reductant, there is an apparent increase of substrate selectivity on decreasing the reductant efficiency.[13]

The case of ascorbic acid, the worst reductant tested, is confusing. Yields of products are slightly lower and no significant trend in the substituent effect is observed. An experiment was also run with a stronger reductant, namely $Na_2S_2O_4$ (E_0 −1.12), for the pair p-nitroaniline–aniline. In this case the result of the competition experiment was affected by the occurrence of higher yields (ca. 15—20%) of products deriving from reactions (5)—(8) and by side-reactions such as further reduction of the nitro-substituent to the amino-group or reduction of the diazo-group to a hydrazine derivative. In the light of this complex behaviour and for the sake of clarity no other experiments were attempted with $Na_2S_2O_4$.

Discussion

Substituent Effects.—The results of the competitive experiments are summarized in Table 2. Separate columns give the relative reactivities obtained with each reductant whose redox potential (E_0) is also indicated.[14]

The effect of substituents can be quantitatively represented by a Hammett-type plot of the logarithm of relative rates *versus* the substituent constant σ. When the data for the $SnCl_2$ reductant were plotted against $σ_p$, a correlation coefficient r of 0.951 was obtained, while a better value (r 0.987; Figure 1) resulted[11] when employing the $σ_p^+$ values.[15] The data for the other two reductants were also plotted in this way (Figure 1). The fit varies from satisfactory to excellent.[16]

What is the meaning of obtaining linear relationships with Hammett $σ^+$ constants, which were developed from heterolytic reactions, in the case of an e.t. process? It gives informtion on the transition state of an s.e.t. process, indicating that the substituent is able to affect the transition state of the e.t. process leading to the diazenyl radical [reaction (9)], in a way that results in the enhancing or lowering of the electron

$$ArN_2^+ + M^n \longrightarrow M^{n+1} + ArN_2 \cdot \xrightarrow{\text{fast}} Ar \cdot + N_2 \qquad (9)$$
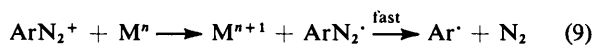
affinity of the substrate. In particular, the transferred electron can be allocated not only in the π* orbital of the NN bond but also in the π* of the aromatic moiety where the effect of the substituent can be felt. Electron withdrawing substituents can stabilize by resonance the diazenyl radical in the transition
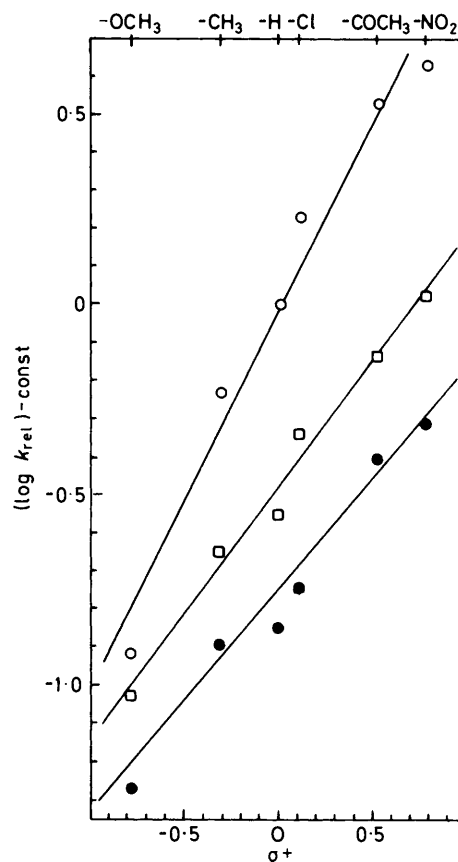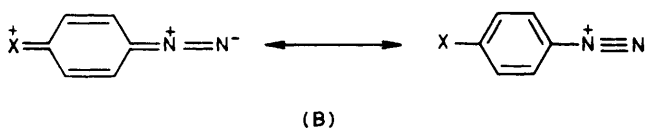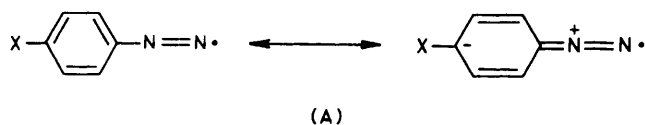

(A)

(B)

Figure 1. Correlations of log k_{rel} with $σ^+$ for reduction of diazonium salts

state (A), while electron releasing substituents are particularly efficient in the stabilization of the starting diazonium salt (B)[17] with a net depressing effect on reactivity. Hence the linear correlations of Figure 1, taken as indices of substituent–ring electronic interactions, suggest that the substituent effect can be handled in an analogous way both for e.t. processes and for heterolytic ones, although the nature of these processes is different.

The sign of ρ is positive for the three reported cases (Table 2), as is expected since the positive charge of the starting diazonium ion tends to vanish in the transition state and the ρ values are also rather small, which may suggest that the substituent influence is not generally strong[18] for these reactions, a reason probably being the distance between substituent and diazo-group. These findings resemble those obtained by Packer et al.[11a] in the previously quoted reduction of substituted arenediazonium ions by solvated electrons and support the mechanistic scheme given in the introduction of an electron transfer step to the diazonium ion.

What comes out from the set of ρ values collected in Table 2 is that on decreasing the redox ability of the reductant, the selectivity towards substrate increases. Such behaviour is in accord to the reactivity selectivity principle[19] and other examples are available in the literature about s.e.t. processes obeying this principle.[20]

From the data collected in Table 2 and from the linear correlations obtained (Figure 1) it is apparent that the three reductants (Sn^{2+}, Cu^+, Fe^{2+}) share the same kind of mechanism and consequently give the same trend for the substituent effect. No such clear behaviour appears in the case of ascorbic acid, although one would have expected an even
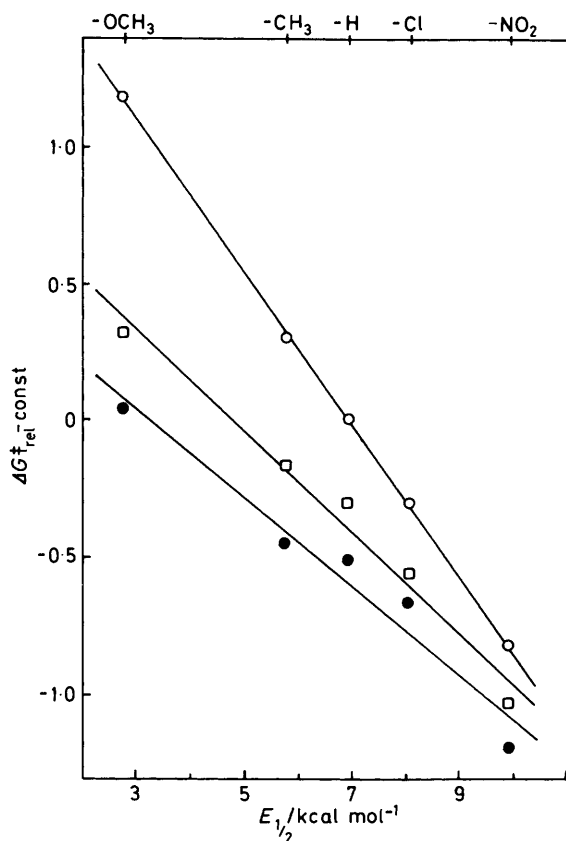
Figure 2. Correlation of $\Delta G^{\ddagger}_{rel}$ with $E_{\frac{1}{2}}$ for reduction of diazonium salts

higher selectivity on the basis of its E_0 value (*i.e.* 0.86).[3a] This is strange in that ascorbic acid is known to give electron transfer reactions in other instances.[21] A tentative explanation for this inconsistency is that ascorbic acid is the worst reductant within the reported set, its redox potential being close to that value of 1 V which appears to be the threshold for an s.e.t. process in a halogenodediazoniation reaction[3] [step (2a)]. In this case, depending on the substituent, incursion of a heterolytic process could emerge along with the homolytic e.t. process. If a positive ion is then formed [step (1a)], the opposite effect of the substituent on this intermediate would be likely.[1a,22] This could affect the outcome of the competition experiments in an unpredictable way and afford experimental behaviour without a meaningful trend.

Correlation of Relative Reactivities with Polarographic Data.—The suggestion made before that the substituents exert their effect by enhancing or lowering the electron affinity of the diazonium salts was tested by a correlation of the relative rates collected in Table 2 with the polarographic reduction potentials of substituted diazonium salts reported in the literature.[10] The plots (Figure 2) are drawn as $\Delta G^{\ddagger}_{rel}$ ($= -RT \ln k_{rel}$) *versus* the substrate reduction potentials expressed in kcal mol^{-1}. Good correlations are obtained and the slope values α are reported in Table 2.

The finding of these linear relationships gives support to the aforementioned suggestion about the importance of the electron affinity upon reactivity in the Sandmeyer reaction and indicates strict correspondence between the e.t. process occurring at the electrode and that occurring *via* a reducing agent in homogeneous solution. An interpretation of the meaning of the α values may be given by resorting to Marcus

theory for the rate of e.t. reactions. It is not the purpose of this paper to enter the details of the theory, since more authoritative reviews have already appeared on the subject and particularly a very recent one by Eberson.[23] The aim of this author is to exploit the Marcus theory to discover quantitative information about the system at hand. Several examples can now be found in the literature regarding reduction or oxidation reactions of organic substrates occurring by outer-sphere e.t. where the use of the Marcus equation allows the calculation of rate constants. This equation links the free energy change of a cross electron transfer step (ΔG^{*}_{12}) as in equation (10). ΔG°_{12} is the standard free energy change
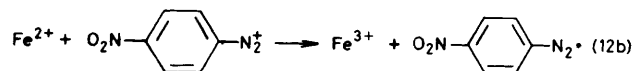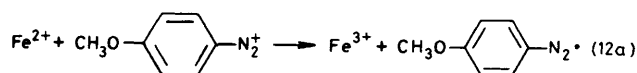
$$\Delta G^{*}_{12} = \frac{1}{2}(\Delta G^{*}_{11} + \Delta G^{*}_{22}) + \alpha \Delta G^{\circ}_{12} + \frac{(\Delta G^{\circ}_{12})^2}{8(\Delta G^{*}_{11} + \Delta G^{*}_{22} - w)} \quad (10)$$

for the cross reaction. ΔG^{*}_{11} and ΔG^{*}_{22} refer to the related self-exchange reactions; the w term is the electrostatic energy contribution necessary to bring the two reactants together at reaction distance. The transfer coefficient α represents the fraction of the electrochemical driving force which affects the reaction in the transition state. When all the parameters $(\Delta G^{*}_{11}, \Delta G^{*}_{22},$ and $\Delta G^{\circ}_{12})$ are available, equation (10) affords the ΔG^{*}_{12} value wherefrom the rate constant of the e.t. process can be calculated according to equation (11). Although

$$k = Z e^{-\Delta G^{*}_{12}/RT} \quad (11)$$

originally developed for reversible systems, the Marcus equation can be safely applied also to irreversible systems, as Eberson has recently pointed out,[24] and consequently it is becoming increasingly popular among organic chemists.[25]

Application of the Marcus Equation to the Sandmeyer Reaction.—This application is limited to the Fe^{2+} case, the only one among the reducing cations reported in Table 2 for which the ΔG^{*}_{11} value appears to be available with the needed accuracy in the literature.[26] Two representative substrates were chosen and equation (10) was applied to evaluate the rate of the e.t. steps (12a and b), the approximation being

$$Fe^{2+} + CH_3O-\!\!\!\langle\ \rangle\!\!\!-N_2^+ \longrightarrow Fe^{3+} + CH_3O-\!\!\!\langle\ \rangle\!\!\!-N_2 \cdot \quad (12a)$$

$$Fe^{2+} + O_2N-\!\!\!\langle\ \rangle\!\!\!-N_2^+ \longrightarrow Fe^{3+} + O_2N-\!\!\!\langle\ \rangle\!\!\!-N_2 \cdot \quad (12b)$$

made that the ΔG^{*}_{22} value reported in the literature[27] for 4-methoxybenzenediazonium salt applies also to the other diazonium salt.[23] Knowledge of the redox potentials[10,14,23] gave the ΔG° values of the two processes. The details of the calculation are reported in the Appendix. The resulting rate constants were calculated at 20 °C from equation (11) and are reported in Table 3.

It was then of interest to look for an experimental determination of the rate constants of the related Sandmeyer reactions to compare with the rates of the e.t. model steps as obtained from the Marcus equation. In the two reactions used for calculations (12a and b) it is expected that the Fe^{3+} cation is produced. It exhibits a maximum of absorbance at 385 nm, which is in a spectral region free from absorption bands of the other species involved in the Sandmeyer process. It was then

Table 3. Comparison of experimental rate constants of some dediazoniation processes with the rate constants calculated for the corresponding electron transfer steps involved

Reaction	$\Delta G^{*}_{12}/$ kcal mol^{-1} [a]	$k_{calc.}/$ l mol^{-1} s^{-1} [b]	$k_{exp.}/$ l mol^{-1} s^{-1}	t °C
(12a)	17.6	7.7×10^{-3}	7.9×10^{-2}	20
(12b)	12.7	31	3.3	20

[a] Calculated from equation (10). [b] Calculated from equation (11).

possible to follow spectrophotometrically the kinetics for the whole process (13). Preformed arenediazonium fluoroborates

$$ArN_2^+ \xrightarrow[CuCl_2]{Fe^{2+}} ArCl + Fe^{3+} \quad (13)$$
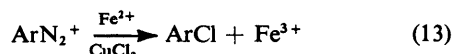
were used for better accuracy. Good pseudo-first-order plots were obtained in water at 20 °C and the rate constants are reported in Table 3.

If one considers the uncertainty which affects the parameters of equation (10), and in the light of the confidence limits which can be given to rate constants calculated from the Marcus equation (i.e., at least two orders of magnitude [23]), the agreement between experimental and calculated rates is rather good and indicates that the rate-limiting step in the two Sandmeyer processes examined is indeed the e.t. step (2a). As a matter of fact, literature evidence [28] gave much higher rate constants for the ligand transfer step (2b) of the order of 10^7—10^9 l mol^{-1} s^{-1} for chlorine. Incidentally, a ratio k_{p-NO_2}/k_{p-OMe} of 42 results from the experimental kinetic data of Table 3, in line with the value (36) obtained on the basis of the relative reactivities reported in Table 2 from competition experiments with Fe^{2+} cation.

Kinetic measurements were also attempted for the Sn^{2+} and Cu$^+$ reductants. The reactions were too fast to follow even by the stopped-flow technique ($k \geqslant 10^5$ l mol^{-1} s^{-1} at least). That the e.t. steps are faster with these better reductants is expected, but they may be comparable with the rate of the ligand transfer step (2b). Consequently, the e.t. step would no longer be rate-determining in such cases. This might explain the very small α values obtained (Table 2) for these two cations, in comparison with larger α values reported by Eberson [27] for well behaved, rate-determining e.t. processes.

Conclusions.—This paper reports the following results. (1) The substituent effect on the Sandmeyer reaction has been studied and found to be dependent on the redox potential of the reductant used. (2) The relative reactivities of substituted arenediazonium salts correlate well with their half-wave reduction potentials, whereby the involvement of a radical pathway is confirmed. (3) Absolute rate constants have been measured for the first time for the Sandmeyer reaction induced by Fe^{2+} and found to be in reasonable agreement with the rate constants predicted by the Marcus equation for the e.t. step involved. This is evidence of rate-determining electron transfer.

Experimental

Reagent grade commercially available compounds were used in this study. The reaction conditions here described are typical of all the competition experiments. The two starting anilines (roughly 2 mmol each) were diazotized under standard conditions [3] with HCl (12 mmol) and NaNO$_2$ (4 mmol) in dioxane-water (1 : 2), the temperature not exceeding 5 °C. After removal of the ice-water bath and addition of CuCl$_2$ (1.8 mmol), the reaction was started by adding 1.8 mequiv. of

the reducing agent all at once. The resulting mixture was stirred for 5 or 10 min, its average temperature being *ca.* 10 °C within this time interval. The reaction was quenched by rapid dilution with water and extraction with ether, after addition of the internal standard. Products yields were determined by g.l.c. analysis performed on a Hewlett–Packard 5830A flame ionization instrument, fitted with a 100 cm × 4 mm column of 3% OV-17 on 80—100 mesh Chromosorb GAW-DMCS. Molar response factors relative to the internal standard were determined for all the compounds and used in the evaluation of the g.l.c. results. Relative reactivity values were calculated by use of equation (14) for the competitive reactions [29] where

$$\frac{k_A}{k_B} = \frac{\ln[sub\ A]_0/([sub\ A]_0 - [prod\ A]_t)}{\ln[sub\ B]_0/([sub\ B]_0 - [prod\ B]_t)} \quad (14)$$

[sub A]$_0$ and [sub B]$_0$ refer to the starting anilines, and [prod A]$_t$ and [prod B]$_t$ refer to the two chlorodediazoniation products at time *t*. Reproducibility of measurements was tested. Occasional checks pitting two substituted compounds together confirmed within experimental error their relative reactivity as evaluated from the competition experiments with the unsubstituted benzenediazonium salt reported in Table 1.

The spectrophotometric study was carried out on a Varian 634 instrument at 20.0 °C in degassed twice distilled water solution. The kinetics were followed at 385 nm by monitoring the appearance of the absorption of the Fe^{3+} cation. Initial concentrations were [Fe^{2+}] 0.021, [ArN$_2$$^+BF_4$$^-$] 1 × 10^{-3}, [Cu^{2+}] 2 × 10^{-3}, and [Cl$^-$]$_{tot}$ 4 × 10^{-3}M and the final solutions were pale orange but clear. A published procedure was followed to prepare the diazonium fluoroborate salts.[30] The experimental data were treated occording to the method of Guggenheim,[31] pseudo-first-order plots being linear up to 70—80% reaction.

Appendix

For one-electron reactions the Marcus theory predicts an α value equal to or greater than 0.5, depending on the electrochemical driving force.[32] Accordingly, the value of 0.5 was used here. Equation (10) was resolved for reaction (12a) employing the following parameters:

$$Fe^{2+} + Fe^{3+} \rightleftharpoons Fe^{3+} + Fe^{2+}$$

ΔG^{*}_{11} 14.2 kcal mol^{-1} (ref. 27); E_0^{11} 0.77 eV (ref. 14)

$$ArN_2^+ + ArN_2\cdot \rightleftharpoons ArN_2\cdot + ArN_2^+$$

ΔG^{*}_{22} 2.5 kcal mol^{-1} (ref. 28); E_0^{22} 0.12 eV (refs. 10 and 27)

wherefrom:

$\Delta G^0_{12} = (E_0^{11} - E_0^{22}) = 15.0$ kcal mol^{-1}, assuming 1 eV = 23.06 kcal mol^{-1}

taking:

$$w = 2\ kcal\ mol^{-1}\ (ref.\ 33)$$

then:

$$(\Delta G^{*}_{12})_{(12a)} = 17.6\ kcal\ mol^{-1}$$

From equation (11), where Z (collision frequency) = 10^{11} l mol^{-1} s^{-1} (ref. 23):

$$(k)_{(12a)} = 7.7 \times 10^{-3}\ l\ mol^{-1}\ s^{-1}\ (at\ 20.0\ °C)$$

For reaction (12b) the same procedure was followed, the only difference being E_0^{22} 0.43 eV (ref. 10) for the diazonium salt, while the same ΔG^{*}_{22} value was employed. Accordingly:

$$\Delta G^0_{12} - 7.8\ kcal\ mol^{-1}$$

then

$$(\Delta G^*_{12})_{(12b)} = 12.7 \text{ kcal mol}^{-1}$$

and

$$(k)_{(12b)} = 31 \text{ l mol}^{-1} \text{ s}^{-1} \text{ (at 20.0 °C)}$$

References

1 (a) H. Zollinger, 'Azo and Diazo Chemistry,' Interscience, New York, 1961; (b) Acc. Chem. Res., 1973, 6, 335; (c) H. B. Ambroz and T. J. Kemp, Chem. Soc. Rev., 1979, 8, 353; (d) A. F. Hegarty, ' The Chemistry of Diazonium and Diazo Groups,' Wiley-Interscience, New York, 1978, Part 2, Ch. 12.

2 J. K. Kochi, J. Am. Chem. Soc., 1957, 79, 2942.

3 (a) C. Galli, J. Chem. Soc., Perkin Trans. 2, 1981, 1459; (b) 1982, 1139.

4 T. Sandmeyer, Chem. Ber., 1884, 17, 1633.

5 H. K. Hall, J. Chem. Educ., 1980, 57, 49.

6 J. E. Leffler and E. Grunwald, ' Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963, Ch. 6.

7 A. Pross and L. Radom, Prog. Phys. Org. Chem., 1981, 13, 1.

8 Y. Nakatani, Tetrahedron Lett., 1970, 4455; L. Horner and H. Stöhr, Chem. Ber., 1952, 85, 993.

9 J. K. Kochi, J. Am. Chem. Soc., 1955, 77, 3208.

10 R. M. Elofson and F. F. Gadallah, J. Org. Chem., 1969, 34, 854.

11 (a) J. E. Packer, C. J. Heighway, H. M. Miller, and B. C. Dobson, Aust. J. Chem., 1980, 33, 965, and preceding papers in the series; (b) C. J. Heighway, J. E. Packer, and R. K. Richardson, Tetrahedron Lett., 1974, 4441.

12 J. F. Bunnett and C. Yiyima, J. Org. Chem., 1977, 42, 639.

13 G. H. Williams, ' Homolytic Aromatic Substitution,' Pergamon Press, London, 1960, pp. 81—92.

14 E_0 values were from ' Handbook of Chemistry and Physics,' C.R.C. Press, Cleveland, 1978, 59th edn.

15 P. Zuman, ' Substituent Effects in Organic Polarography,' Plenum Press, New York, 1967, p. 46.

16 According to the terminology suggested by H. H. Jaffé, Chem. Rev., 1953, 53, 191, for describing the degree of correlation as measured by the r value.

17 See C. Casewit, J. D. Roberts, and R. A. Bartsch, J. Org. Chem., 1982, 47, 2875.

18 H. Tagaya, T. Aruga, O. Ito, and M. Matsuda, J. Am. Chem. Soc., 1981, 103, 5484.

19 A. Pross, Adv. Phys. Org. Chem., 1977, 14, 69.

20 S. Bank and D. A. Juckett, J. Am. Chem. Soc., 1976, 98, 7742; T. T. Tsou and J. K. Kochi, ibid., 1979, 101, 6319.

21 D. Mansuy, M. Fontecave, and J. P. Battioni, J. Chem. Soc., Chem. Commun., 1982, 317; H. M. Swartz and N. J. F. Dodd, in ' Oxygen and Oxy–Radicals in Chemistry and Biology,' eds. M. A. J. Rodgers and E. L. Powers, Academic Press, New York, 1981, p. 161.

22 E. S. Lewis and E. B. Miller, J. Am. Chem. Soc., 1953, 75, 429.

23 L. Eberson, Adv. Phys. Org. Chem., 1982, 18, 79.

24 L. Eberson, Acta Chem. Scand., Ser. B, 1982, 36, 533.

25 J. Albery and M. M. Kreevoy, Adv. Phys. Org. Chem., 1978, 16, 97.

26 Ref. 23, Table 5, p. 108.

27 Ref. 23, Table 17, pp. 166 and 168.

28 V. D. Parker, Acta Chem. Scand., Ser. B, 1981, 35, 533; C. L. Jenkins and J. K. Kochi, J. Org. Chem., 1971, 36, 3103.

29 J. F . Bunnett, in ' Investigation of Rates and Mechanism of Reactions,' ed. E. S. Lewis, Wiley, New York, 1974, Part 1, p. 159.

30 A. Roe, Org. React., 1949, 5, 205.

31 A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd

32 R. A. Marcus, Ann. Rev. Phys. Chem., 1964, 15, 155; ' Special Topics in Electrochemistry,' ed. P. A. Rock, Elsevier, Amsterdam, 1977, p. 161; J. Chem. Phys., 1957, 26, 867. edn., Wiley, New York, 1961, p. 49.

33 Ref. 23, Table 3, p. 100.