Kinetics and Intermediates in the Several Forward and Reverse Reactions of Nitro-substituted Arenediazonium Ions with Hydroxide Ion

By **Paul D. Goodman** and **Terence J. Kemp,*** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL
Peter Pinot de Moira, Ozalid (UK) Ltd., Langston Road, Loughton, Essex IG10 3TH

Stopped- and quenched-flow kinetics and rapid-scanning u.v. spectrophotometry have been applied to the kinetics of the forward and reverse reactions of ArN_2^+ with OH^-, where Ar bears one or more strongly electronegative substituents (Cl, NO_2), in which case the *syn*-diazotate (formed rapidly from the initially produced diazohydroxide) functions as a reactive intermediate leading to the thermodynamically favoured *anti*-diazotate. Measurements of forward and reverse rates in some cases have enabled the determination of equilibrium constants for both acid–base and isomerisation reactions. It has thus been possible to extend the number of compounds for which these data are available, and hence derive more complete linear free energy relationships for both kinetic and equilibrium constants. (These include determinations of σ and σ^+ parameters for the 2-nitro- and 2-chloro-groups.) A complete description of the quenched-flow apparatus is provided. Time-resolved u.v.–visible spectra of the transient *syn*-diazotate have been obtained for the 4-nitro-, 2-chloro-4-nitro-, 2-chloro-4-nitro-, and 2,4-dinitro-substituted materials.

THE complex equilibria prevailing in alkaline solutions of arenediazonium salts, *viz.* reactions (1)—(6), have been

$$ArN_2^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} syn\text{-}ArN_2OH \qquad K_1 = k_1/k_{-1} \qquad (1)$$

$$syn\text{-}ArN_2OH + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} syn\text{-}ArN_2O^- + H_2O \qquad K_2 = k_2/k_{-2} \qquad (2)$$

$$syn\text{-}ArN_2O^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} anti\text{-}ArN_2O^- \qquad K_3 = k_1/k_{-3} \qquad (3)$$

$$ArN_2^+ + OH^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} anti\text{-}ArN_2OH \qquad K_4 = k_4/k_{-4} \qquad (4)$$

$$anti\text{-}ArN_2OH + OH^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} anti\text{-}ArN_2O^- + H_2O \qquad K_5 = k_5/k_{-5} \qquad (5)$$

$$syn\text{-}ArN_2OH \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} anti\text{-}ArN_2OH \qquad K_6 = k_6/k_{-6} \qquad (6)$$

investigated over a long period by a number of groups, and the current situation has been reviewed recently.[1,2] Since $K_2 \gg K_1$, an overall equilibrium constant is often used for steps (1) and (2) and equations (1) and (2) can

$$K = K_1K_2 = [syn\text{-}ArN_2O^-]/[ArN_2^+][OH^-]^2 \qquad (7)$$

be re-formulated as (8) and (9) where equation (10) applies. Also, (10) can be expanded to (11); thus

$$ArN_2^+ + H_2O \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} syn\text{-}ArN_2OH + H^+ \qquad K_{A1} \qquad (8)$$

$$syn\text{-}ArN_2OH \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} syn\text{-}ArN_2O^- + H^+ \qquad K_{A2} \qquad (9)$$

$$K_{A1}K_{A2} = K_1K_2K_W^2 = [syn\text{-}ArN_2O^-][H^+]^2/[ArN_2^+] \qquad (10)$$

$$\tfrac{1}{2}(pK_{A1} + pK_{A2}) + \tfrac{1}{2}\log([syn\text{-}ArN_2O^-]/[ArN_2^+]) = pH \qquad (11)$$

$(pK_{A1} + pK_{A2})/2$, sometimes denoted pK_{syn}, equals the pH of the medium (denoted pH_m) at which $[syn\text{-}ArN_2O^-] = [ArN_2^+]$, *i.e.* at half-conversion. Since $K_2 \gg K_1$, the diazohydroxide exists only at minimal concentrations even at the most favourable acidity, *i.e.* pH_m.

One can similarly re-formulate equations (4) and (5) as (12) and (13) since $pK_4 \gg pK_5$, the *anti*-diazohydroxide

$$ArN_2^+ + H_2O \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} anti\text{-}ArN_2OH + H^+ \qquad K_{A4} \qquad (12)$$

$$anti\text{-}ArN_2OH \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} anti\text{-}ArN_2O^- + H^+ \qquad K_{A5} \qquad (13)$$

$$pK_{anti} = \tfrac{1}{2}(pK_{A4} + pK_{A5}) \qquad (14)$$

$$K_3 = K_1K_2/K_4K_5 \qquad (15)$$

is always at minute concentrations to produce a two-equivalent buffer region.

The equilibria (1) and (2) are established rapidly whereas (3) is normally reached very slowly unless nitro-substituents are present, when the process is rapid; again, (4) is established slowly whilst (5) is mobile. Consequently, attempts to factorise K_1—K_5 into individual rate constants have centred on compounds giving reasonable spectral differentiation between contributing components and have incorporated rapid reactions methods, usually stopped-flow spectrophotometry or potentiometry.[1,2] k_1 has been determined for a variety of ArN_2^+, *e.g.* from 4.5×10^3 dm^3 mol^{-1} s^{-1} for [3] $C_6H_5N_2^+$ to 5.4×10^5 dm^3 mol^{-1} s^{-1} for p-$O_2NC_6H_4N_2^+$ (at 296 K) [4] and 4.5×10^5 dm^3 mol^{-1} s^{-1} for m-$O_2NC_6H_4N_2^+$ at 293 K.[5] k_{-1} is determined from the reaction of *syn*-diazotate with acidic buffer, when *syn*-diazohydroxide is generated rapidly in a pre-equilibrium; a typical value is 5.34×10^2 s^{-1} for m-$O_2NC_6H_4N_2OH$ at 293 K,[6] which yields (with k_1) a value of 8.4×10^2 dm^3 mol^{-1} for K_1.

As regards the isomerization steps, k_3 has been determined for several examples,[7-9] *e.g.* for p-$O_2NC_6H_4N_2O^-$, $k_3 = 5.4 \times 10^{-2}$ s^{-1} at 298 K.[9] k_{-3} has also been measured, together with k_3, for certain cases,[8] to yield K_3. Other steps examined are the *anti*–*syn*-isomerisation of some diazohydroxides [7,10] and the equilibrium constant K_{A5}.[7,10] The very strong substituent-dependence of the individual rate constants means that acidification of *anti*-diazotate solutions can lead to ArN_2^+ *via* several possible pathways.[1,2]

Attempts to examine the *syn*-diazohydroxide spectroscopically have been frustrated by its low concentration, and in the case of the nitro-substituted materials, even the *syn*-diazotate becomes a transient intermediate, the characterization of which has been disputed.[11,12]

We have employed conventional stopped-flow and rapid-scanning spectrometry and also a quenched-flow system to define more clearly the fast spectral and kinetic changes which occur when nitro-substituted benzenediazonium cations are reacted with OH^- ions and when solutions of *syn*- and *anti*-diazotates are acidified, and have extended the range of kinetic and equilibrium constants for reactions (1)—(16).

EXPERIMENTAL

Rapid Scanning Spectrometer.—This, together with its stopped-flow system, has been described fully before.[13]

Quenched-flow Apparatus.—This is illustrated in Figures 1(a) and (b) and is based on the general principle of mixing two solutions 1 and 2 at mixer (M1) to generate the reactive intermediate (RI) which persists until it encounters solution 3 at mixer (M2) when optical changes (loss of the absorption or RI or build-up of absorption of a product) can be time-resolved at a single monitoring wavelength.[14] In our experiments, solution 1 was the arenediazonium salt, and solution 2 was aqueous NaOH, which mixed at (M1) to give [at least by the time the mixed solution reached (M2)] the *syn*-diazotate. Solution 3 was a buffer solution designed to yield on reaction with the diazotate solution, arenediazohydroxide which rapidly yields the arenediazonium cation; the appearance of the latter was monitored at its wavelength maximum with a conventional spectrophotometric system. This consisted of the quartz windows (Q), monochromated light, an EMI type 9781R photomultiplier tube (PM) with all dynodes connected with 75 kΩ resistors. The amplified signal was displayed on a Tektronix type 564 storage oscilloscope (CRO) and simultaneously recorded with a Datalab transient recorder (TR). The transmittance–time curves were then plotted with a Servoscribe chart recorder (CR).

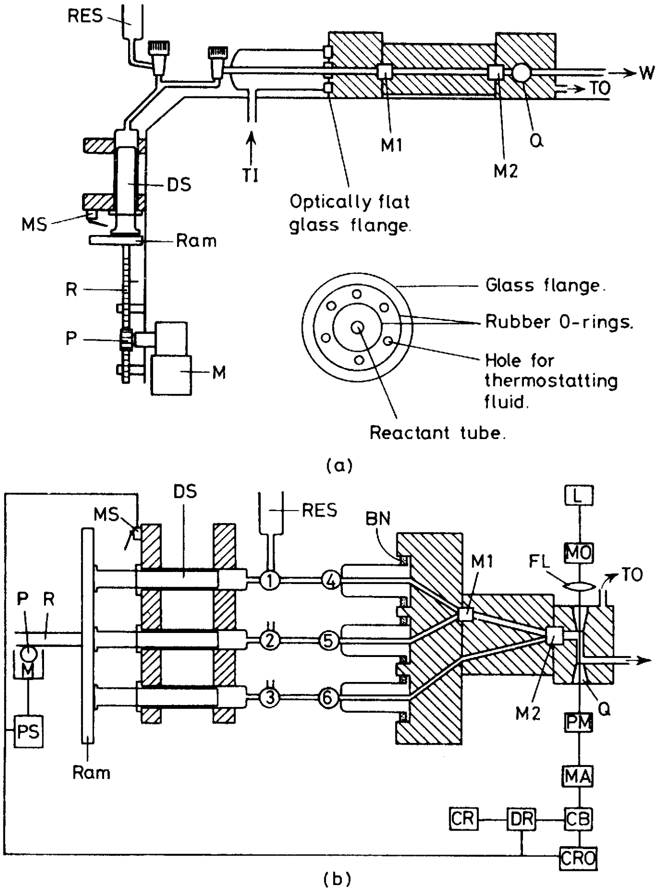


FIGURE 1 (a) Side and (b) plan views of the quenched-flow apparatus. Inset-glass flange connecting PTFE housing to mixing block. Key: RES, resevoirs (three); DS, drive syringes (three); MS, microswitch; R, rack; P, pinion; M, motor; Tl, thermostatting fluid inlet; TO, outlet; M1, first mixer; M2, second mixer; Q, quartz windows (two); W, waste outlet; BN, brass nut (three); PS, motor power supply; L, lamp; MO, monochromator; FL, focusing lens; PM, photomultiplier tube; MA, milliameter; CB, control box; CRO, cathode ray oscilloscope; DR, data recorder; CR, chart recorder; 1—6 taps; shaded area, PTFE blocks

The three drive syringes (DS1—3) were filled from three reservoirs (RES) with taps (1)—(3) open and (4)—(6) closed, and then with (1)—(3) closed and (4)—(6) open; they were driven by a variable-speed DC motor (powered by a stabilised power supply) connected *via* a rack-and-pinion drive to the ram (R). Once the system had been flushed through, the ram was stopped and simultaneously the motor switched off, and the oscilloscope and transient recorder triggered to record the reaction profile at the pre-set wavelength. The power supply to the electric motor incorporated a reverse-polarity switch so that the ram could be reversed conveniently prior to refilling the drive syringes.

The apparatus was thermostatted by circulating water from a Churchill pump, first through the jackets surrounding the three reactant tubes and then through the PTFE blocks along tubes which lay within 1 cm of the reactant tubes. The glass sections of this apparatus are similar to those employed in the stopped-flow apparatus used in conjunction with the rapid-scanning spectrometer, except that the drive syringes (DS) were at right angles to the direction of flow through the rest of the apparatus.

The drive syringes were driven at a speed such that, during the time taken to pass between the two mixers (t), a maximum yield of the *syn*-arenediazotate was obtained, but with as little of the *anti*-form as possible. The times required to achieve such conditions were found from data obtained with the rapid-scanning spectrometer. The speed control was calibrated as follows. The coupling reaction of *m*-chlorobenzenediazonium cations with sodium 2,3-dihydroxynaphthalene-6-sulphonate at *ca.* pH 6.5 was monitored[15] firstly using drive syringes (2) and (3) so as to commence the reaction at the exit from mixer (M2), and, secondly, using syringes (1) and (2) to begin coupling at the exit from mixer (M1). In the latter case, the reacting solution has to travel between the two mixing blocks before observation of the azo-dye formation commences, and so by comparison of the transmittance at the beginning of the two traces so obtained, one can evaluate the transit time (t). By recording the transmittance–time curves obtained with different motor speed control settings, their corresponding times (t) can be measured similarly. A range of times (t) between 0.3 and 2 s were found to be feasible. The reaction between Fe^{II} and SCN^- was used to ascertain the accuracy of the rate constants obtained with the apparatus and the results were found to be within 10% of the literature values.[16]

The main inaccuracy is probably due to the relatively long mixing time of nearly 0.2 s. (This problem could probably be diminished in the future by the incorporation of a ' stop-syringe ' as in the conventional stopped-flow apparatus.)

For the determination of the rate constants of N–O bond splitting of substituted *syn*-arenediazohydroxides (k_{-1}) the solutions used in the three syringes were typically as follows: solution (1), 0.005M-HCl + 10^{-4}M-ArN_2^+ made up to an ionic strength (I) of 0.25 mol dm^{-3} with KCl; solution (2), 0.05—0.1M-NaOH made up to I 0.25 mol dm^{-3} with KCl (NaOH concentration varied to give a range of pH); solution (3), 0.2M-NaH_2PO_4 + 0.05M-KCl.

Materials.—All arenediazonium salts, except for 4-phenylenebisdiazonium tetrafluoroborate, were prepared in solution by the standard methods described by Saunders [17] and then precipitated with fluoroboric acid to obtain solid tetrafluoroborate salts. 4-Phenylenebisdiazonium tetrafluoroborate was prepared after Lewis *et al.*[18] except that N_2O_3 [19] was produced from nitric acid and arsenic(III) oxide.

In the reactions of arenediazonium salts with OH$^-$, the former were dissolved in HCl (0.02 mol dm^{-3}) made up to an ionic strength (I) of 0.25 mol dm^{-3} with KCl. These solutions were added to the appropriate buffer,[20] *i.e.* phosphate, borax, or hydrogencarbonate, also made up to I 0.25 mol dm^{-3}. The pH values of all reacted solutions were measured with a Pye model PW 9410 pH meter equipped with a glass electrode.

Solutions of aromatic diazotates were prepared by mixing slightly acidic solutions of the corresponding arenediazonium salts and sodium hydroxide solution (0.05 mol dm^{-3}). These were reacted with the appropriate buffer solution and the final pH measured as in the forward reaction. (I for both reactant solutions was made up to 0.25 mol dm^{-3} with KCl.)

RESULTS AND DISCUSSION

Kinetic Results.—The techniques of stopped- and quenched-flow spectrophotometry and rapid-scanning spectrometry were directed towards four aspects of the equilibria (1)—(5), *i.e.* (i) the reaction of *syn*-arenediazotate with acid; (ii) the reaction of *anti*-arenediazotate with acid; (iii) the reaction of arenediazonium cations with OH$^-$ ion; (iv) the *syn-* to *anti*-diazotate isomerization.

(i) *Reaction of* syn-*arenediazotates with acid. syn*-Arenediazotates having no strongly electron-withdrawing groups in the 2- and 4-ring positions are relatively stable, and their reactions may be followed by conventional spectrophotometric kinetic techniques, whereas compounds having such groups isomerise rapidly to their *anti*-forms, which necessitates use of the quenched-flow system.

p-Chlorobenzenediazonium tetrafluoroborate was selected as an example of a precursor giving a stable *syn*-diazotate, which was conveniently prepared by addition of a few cm^3 of a slightly acidic solution of the diazonium cation to aqueous NaOH (0.25 mol dm^{-3}). Its reactions at *ca.* pH 13 were followed after addition of one of five different couplers in buffered solution, to give the corresponding azo-dye; with each coupler, the dependence of the rate constant for appearance of dye upon the coupler concentration was measured and, with 2-naphthol, the pH-dependence as well. The two most reactive couplers, *i.e.* 2,3-dihydroxynaphthalene and its 6-sulphonic acid derivative, exist largely in their highly reactive doubly ionized forms at pH 13,[15] and the rate constant for dye formation from the corresponding *syn*-diazotates at pH 12.8 is the same for both couplers, and is independent of coupler concentration with a value of 0.260 ± 0.013 s^{-1} at 298 K. We consider this rate to correspond to conversion of the *syn*-diazohydroxide into the arenediazonium cation, *i.e.* the reverse step of equation (1). Štěrba *et al.*[6] measured the rate constants of reaction of six nitro- and polyhalogeno-substituted *syn*-diazotates with acid at pH < 7.5, where the slow step is the splitting of the N–O bond of the diazohydroxide, the concentration of which is pH-dependent. The rate constant k_{-1} is related to the apparent rate constant k_a by equation (16). Values of

$$k_a = k_{-1}[H_3O^+]/([H_3O^+] + K_2) \qquad (16)$$

K_2 were obtained by Štěrba *et al.*[6] from plots of log k_a *versus* pH and gave a good Hammett plot [equation (17)].

$$pK_2 = -1.3\Sigma\sigma + 8.1 \qquad (17)$$

We used equation (17) with a σ value for *p*-Cl of 0.23 [21] to obtain pK_2 7.70 which on substitution into equation (16) with k_a 0.26 s^{-1} yielded k_{-1} 3.20 × 10^4 s^{-1}. This value is further discussed below.

The other rather less reactive couplers gave less straightforward behaviour. With 2-naphthol, k_a was dependent both on coupler concentration and pH; thus plots of k_a *versus* [2-naphthol] were linear but with small intercepts both at pH 12.23 and 13.04, *e.g.* Figure 2 at pH 12.23, while a plot of log k_a *versus* pH over the range 12.2—13.3 (Figure 3) was linear with a slope of −1.62.

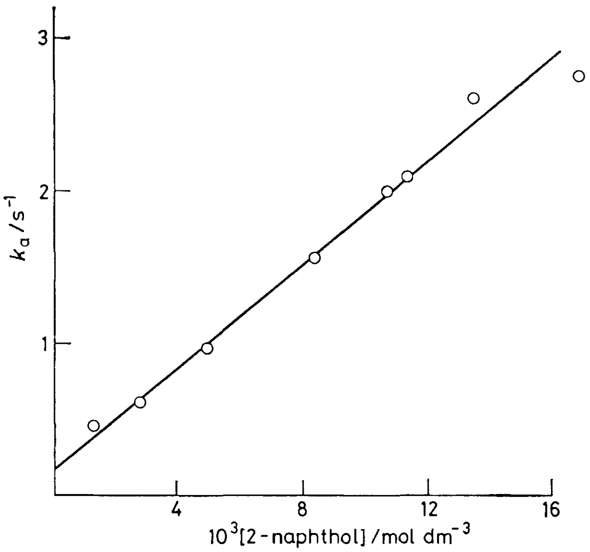


FIGURE 2 Dependence of apparent rate constant k_a upon coupler concentration for the reaction between 2-naphtholate ion and *syn-p*-chlorobenzenediazotate at pH 12.23

A scheme, [reaction (18)] yields the kinetic equation

(19). $[ClC_6H_4N_2^+]$ ·is related to $[syn\text{-}ClC_6H_4N_2O^-]$

$$syn\text{-}ClC_6H_4N_2O^- \xrightarrow[\text{fast}]{H_3O^+} syn\text{-}ClC_6H_4N_2OH \xrightarrow[\text{fast}]{-OH^-}$$
$$ClC_6H_4N_2^+ \xrightarrow[\text{2-naphtholate}]{\text{slow, } k_c} \text{azo dye} \qquad (18)$$

$$d[\text{azo dye}]/dt = k_c[ClC_6H_4N_2^+][\text{2-naphtholate}] \qquad (19)$$

$$K_1K_{A2} = \frac{[syn\text{-}ClC_6H_4N_2O^-][H_3O^-]}{[ClC_6H_4N_2^+][OH^-]} \qquad (20)$$

through the equilibria (1) and (9) [equation (20)] and hence equation (21) applies, which corresponds approxi-

$$d[\text{azo dye}]/dt = \frac{k_cK_w[syn\text{-}ClC_6H_4N_2O^-][\text{2-naphtholate}]}{K_1K_{A2}[OH^-]^2} \qquad (21)$$

mately to the kinetics described above. The discrepancies found (the intercepts, the deviation of the slope to a value less negative than —2.0) suggest a parallel competing reaction, possibly a radical-chain decomposition of the arenediazonium cation, which becomes prominent at low coupler concentration.

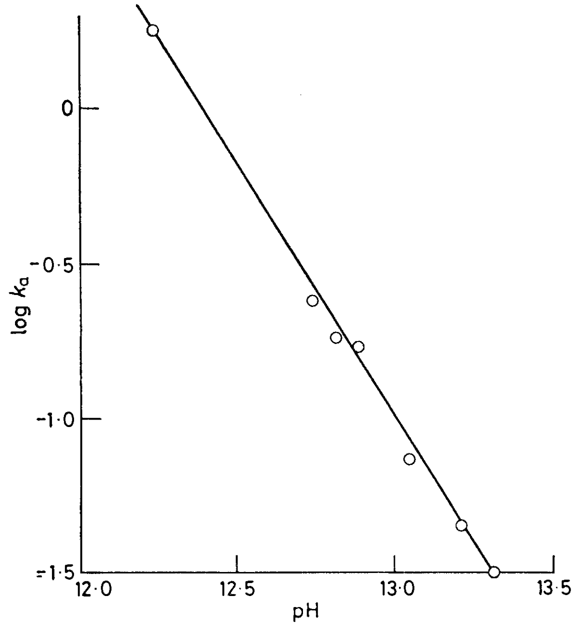


FIGURE 3 pH Dependence of apparent rate constant k_a for the reaction of *syn-p*-chlorobenzenediazotate with 2-naphtholate ion (0.01 mol dm^{-3})

The coupling of *syn-p*-chlorobenzenediazotate ion with 2-hydroxynaphthalene-6-sulphonate and 2-hydroxynaphthalene-6,8-disulphonate ions gave (i) only approximately first-order plots for dye formation, (ii) Michaelis–Menten kinetics for the dependence of k_a upon coupler concentration, (iii) considerable experimental scatter in the points, (iv) for a fixed diazotate concentration, an increase in the optical density of the dye at the end of reaction, implying the presence of an important competing side-reaction.

The quenched-flow studies of *syn*-arenediazotates bearing strongly electronegative groups were commenced with the *o*- and *p*-nitro-compounds which were produced at mixer (M1) and reacted with a stream of acidified sodium 2,3-dihydroxynaphthalene-6-sulphonate at (M2). The apparent rate constants were as follows:

(i) Reaction of *p*-nitrobenzenediazotate with H_3O^+ + coupler

pH	6.22	6.72	7.04
k_a/s^{-1}	11.6	12.2	10.5

(ii) Reaction of *o*-nitrobenzenediazotate with H_3O^+ + coupler at pH 6.74

10^3 [coupler]/mol dm^{-3}	1.5	3.5	7.0
k_a/s^{-1}	6.5	8.3	11.8

(a plot of k_a *versus* [coupler] gives k_a 5.0 s^{-1} at zero [coupler]).

Now calculation of the pseudo-first-order rate constant for the pH and coupler concentration employed from the known absolute coupling rate constant [15] yields k_c *ca.* 6 s^{-1}, and we conclude the values of k_a do *not* refer to the rate constants of the N–O bond splitting process. Unfortunately, the rate constants for the *o*- and *p*-compounds could not be determined in the absence of coupler (a) because at pH < 6 the reaction is too fast for detection by the apparatus in its present form and (b) at high pH the thermal decomposition of the diazonium cation becomes too significant. It was decided therefore to work with two arenediazotates (2-chloro-4-nitro- and 4-chloro-2-nitro-) which give sufficient spectral differentiation between the diazotate and diazonium forms to enable the appearance of the latter to be monitored (Table 1): working outside the pH ranges specified gave problems either of excessive rate or thermal decomposition of the diazonium cation. Plots of log k_a *versus* pH give plateau values for k_a at highest pH of 10 s^{-1} (for the 2-chloro-4-nitro-compound) and 16 s^{-1} (estimated) for the 4-chloro-2-nitro-compound. [These curves are very similar to that given by Štěrba for the 3-nitro-4-chloro-compound in Figure 1(b) of ref. 1.] In the plateau region, all *syn*-diazotate is converted to *syn*-diazo-

TABLE 1

Rate constants for the reaction of *syn*-arenediazotates with H_3O^+

(T 298 K, I 0.25 mol dm^{-3})

syn-Arenediazotate	pH	k_a/s^{-1}
2-Chloro-4-nitro	4.62	9.0
	5.17	12.5
	5.93	2.45
	6.21	1.55
	6.35	1.15
	6.71	1.03
4-Chloro-2-nitro	4.62	11.1
	5.17	8.9
	6.16	4.61
	6.35	2.60
	6.70	1.82
	7.16	0.59

hydroxide and k_a equals k_{-1}. We could also use equation (16) in conjunction with the data of Table 1 to obtain pK_2 values for these two diazotates (Table 2). The data for k_{-1} are combined later with those obtained for k_1 (see below) to obtain equilibrium constants and also in determining free-energy relationships in this series.

TABLE 2

Calculated value for pK_2 from the reaction of *syn*-arenediazotates with H_3O^+

(T 298 K, I 0.25 mol dm^{-3})

syn-Arenediazotate	k_{-1}/s^{-1}	pH	k_a/s^{-1}	pK_2
2-Chloro-4-nitro	10	5.93	2.45	5.44
	10	6.21	1.55	5.44
	10	6.35	1.15	5.46
	10	6.71	1.03	5.71
			Average	5.51
4-Chloro-2-nitro	16	6.16	4.61	5.73
	16	6.35	2.60	5.63
	16	6.70	1.82	5.81
	16	7.16	0.59	5.93
			Average	5.78

(ii) *Reaction of* anti-*arenediazotates with acid.* The reactions of *anti*-diazotates at pH < pH$_m$[1] have been studied extensively, but much less is known of their behaviour at high pH and our efforts have been concentrated here. The *p*-nitro-derivative was chosen as a model compound as its behaviour at lower pH is well established.[4,11,22] The formation of the diazonium cation from the *anti*-diazotate was monitored *via* appearance of the coupled product at pH 8—10. k_a was found to be independent of (i) the nature of the coupler, (ii) coupler concentration, and (iii) (in this pH range) acidity. Clearly the *anti*- to *syn*-isomerization is rate-determining and $k_a = k_{-3}$, *i.e.* 5.03 × 10^{-4} s^{-1}. To check that the coupler was acting only to scavenge p-$O_2NC_6H_4N_2^+$ ions, the reaction was repeated under similar conditions without coupler and the rate was determined from the loss of *anti*-diazotate absorption at 305 nm. Both sets of data are shown in Figure 4 from which it is evident that the rates converge at pH < 9 but that in the absence of coupler, the rate at pH > pH$_m$ (9.44) falls off abruptly, reaching ultimately a new plateau region.

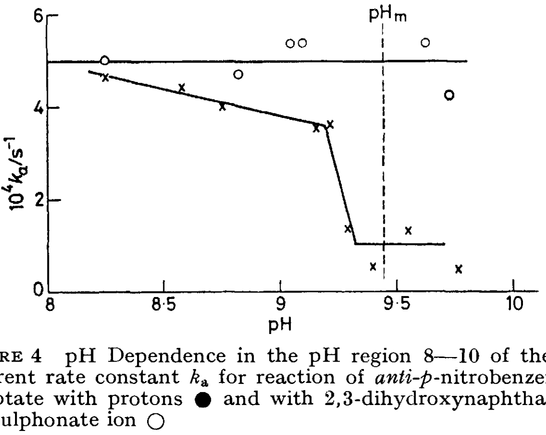


FIGURE 4 pH Dependence in the pH region 8—10 of the apparent rate constant k_a for reaction of *anti-p*-nitrobenzenediazotate with protons ● and with 2,3-dihydroxynaphthalene-6-sulphonate ion ○

Analysis of the spectral profile of the reaction in the presence of coupler using the SP 800 spectrometer revealed a clear isosbestic point, but at pH > 9 in the absence of coupler, no isosbestic point was apparent, suggesting competing or consecutive reactions. Again, while the disappearance of diazotate at pH 7.55 (in the absence of coupler) followed good first-order kinetics, at pH > 9, the kinetics became good zero-order, indicating a complete change of mechanism. The zero-order reaction at pH > 9 was influenced by O_2: thus deoxygenation increased the tendency towards first-order kinetics at a higher pH than an aerated sample while oxygenation increased the tendency to zero-order kinetics. (No further attempt to clarify the nature of this high pH process was made.)

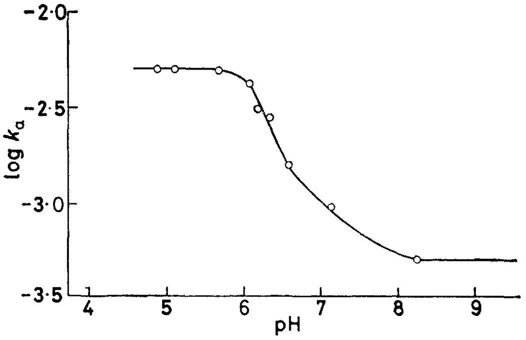


FIGURE 5 pH Dependence in the pH region 5—9 of the apparent rate constant k_a for reaction of *anti-p*-nitrobenzenediazotate with 2,3-dihydroxynaphthalene-6-sulphonate ion

The dependence of k_a upon pH at lower pH (in the presence of coupler), presented in Figure 5, indicates two additional features, *i.e.* (i) a sharp increase in rate below pH 7 with $\Delta \log k_a / \Delta$ pH $= -0.9$ and (ii) a new plateau region below pH 6 with $k_a = 5.03 \times 10^{-3}$ s^{-1} (295 K), which corresponds to a change of the rate-determining step to the isomerization of the *anti*- to *syn*-diazohydroxide, *i.e.* $k_a = k_{-6}$; this result compares with that of Lewis and Hanson [10] of 4.8 × 10^{-3} s^{-1}.

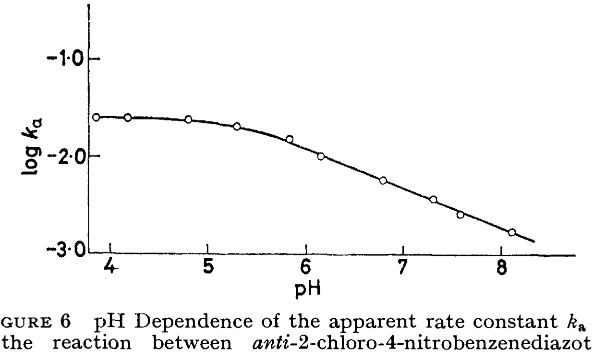


FIGURE 6 pH Dependence of the apparent rate constant k_a for the reaction between *anti*-2-chloro-4-nitrobenzenediazotate and protons

The pH-dependence of k_a for the corresponding reaction of 2-chloro-4-nitrobenzenediazotate with acid is markedly different from those found with the *p*-nitro- and 2-nitro-4-chloro-compounds [7] (Figure 6). The gradient is only −0.4, although the low-pH plateau is clearly defined, corresponding to k_{-6} 4.0 × 10^{-2} s^{-1} (*cf.* the figure [7] for the 4-chloro-2-nitro-compound of 2.7 × 10^{-2} s^{-1}). The low value of the gradient may refer to a merging of the two pH regions corresponding to the equilibria K_5 and K_3.

(iii) *Reaction of arenediazonium cations with* OH^- *ions to give* syn-*diazotates.* This is the step most easily measured and considerable data are available.[1-5,11] Our measurements were confined therefore to (*a*) compounds discussed in sections (i) and (ii), and (*b*) to some other diazonium salts not previously examined in order to obtain more comprehensive free energy relationships. (Two literature values were re-measured [3,22,23] as a check of our own apparatus.) Measurements were normally performed at several pH values, and k_1 estimated from the apparent rate constant k_a from $k_1 = k_a/[OH^-]$. Table 3(a) includes detailed measurements for four compounds while Table 3(b) summarises results for all eight examined. These are discussed below.

TABLE 3

Measurements of the rate constant, k_1 at 298 K (I 0.25 mol dm^{-3})

(a) pH Dependence of the apparent rate constant, k_a

Benzenediazonium cation	pH	k_a/s^{-1}	$10^{-5}k_1/dm^3\ mol^{-1}\ s^{-1}$	Gradient of log k_a/pH plot
4-Nitro	9.36	8.8	3.84	1.06
	9.42	9.0	3.42	
	9.80	23.4	3.71	
	9.95	34.0	3.82	
2-Nitro-4-chloro	9.14	8.50	6.16	0.905
	9.37	18.0	7.69	
	9.64	27.1	6.20	
	10.10	68.0	5.40	
2-Chloro-4-nitro	8.50	5.3	17.0	1.10
	8.85	11.4	16.0	
	9.08	23.5	20.0	
2,4-Dinitro	6.33	0.27	94	
	6.36	0.32	110	
	6.72	0.45	73	
	7.40	1.80	69	

(b) Summary of averaged values for $k_1/dm^3\ mol^{-1}\ s^{-1}$

Substituent	$10^{-5}k_1$	Literature value for $10^{-5}k_1$	Reference
4-Nitro	3.7	3.0 (I 1 mol dm^{-3})	22
		5.4 (I 0.005 mol dm^{-3})	3
2-Nitro	3.37		
2-Nitro-4-chloro	6.31		
2-Chloro-4-nitro	16.7		
2,4-Dinitro	86.4	75 (I 0.5 mol dm^{-3})	23
4-Diazonium	225		
2-Chloro	5.04		
4-Cyano	1.91		

TABLE 4

Rate constants k_3 for the isomerisation of *syn*-diazotates to their *anti*-forms (T 298 K, I 0.25 mol dm^{-3})

Substituent(s)	k_3/s^{-1}	Literature values for k_3/s^{-1}	Reference
4-Chloro		5.0 × 10^{-6} [a]	9
4-Cyano	1.98 × 10^{-4}		
2-Chloro	6.0 × 10^{-5}		
3-Nitro	4.53 × 10^{-4}		
3-Chloro	1.57 × 10^{-4}		
2-Nitro	3.3 × 10^{-3}	1.5 × 10^{-3}	7
4-Nitro	7.9 × 10^{-2}	6.2 × 10^{-2}	4
H		2.0 × 10^{-6} [a]	9
2,4-Dinitro	24	20.9	7
2-Chloro-4-nitro	1.3 × 10^{-1}	3.2 × 10^{-2}	7
4-Chloro-2-nitro	1.0 × 10^{-2}	4.3 × 10^{-3}	7
2,6-Dichloro-4-nitro		5.5 × 10^{-3}	7
2-Nitro-4-methyl		7.8 × 10^{-4}	7
2-Nitro-5-chloro		1.0 × 10^{-2}	7

[a] Values extrapolated from data at 353—373 K.

(iv) *Isomerization rates of* syn-*diazotates to their* anti-*form* (k_3). k_3 was measured for nine examples, of which five had been obtained previously under various reaction conditions. The small discrepancies apparent in Table 4 may be attributed to ionic strength effects and the slightly different temperatures utilised. A discussion of the Hammett plot of these data is given in the next section. k_3 for the *p*-nitro-compound can be combined with k_{-3} (see above) of 5.03 × 10^{-4} s^{-1} to give K_3 1.57 × 10^2, *i.e.* somewhat lower than the figure of 6.0 × 10^2 calculated indirectly by Littler.[22] Assuming equilibrium (13) is rapid, equation (22) may be derived [7] from which a

$$k_a = k_{-6}[H^+]/(K_5 + [H^+]) \qquad (22)$$

value for K_5 of 6.75 × 10^{-7} mol dm^{-3} was calculated, *cf.* a literature figure [11] of 7.2 × 10^{-7} mol dm^{-3} (all at 298 K).

Linear Free Energy Relationships.—These have been utilised widely, especially by Štěrba,[1] in discussions of the rates and equilibria of equations (1)—(6), and our new data provide both a test and an amplification of existing correlations. As our compounds often contained two or more substituents, with one of these in the 2-position, it was first necessary to derive Hammett σ-constants for the 2-chloro- and 2-nitro-groups. (There are no universally accepted σ values for 2-substituents because of their steric effect, and there often are different values for a given substituent for different reactions.[24-26]) These were obtained by plotting log k_1 [*i.e.* for equation (1)] *versus* Σσ for ten benzenediazonium cations bearing only 3- and/or 4-substituents, and extracting the σ values for the 2-chloro- and 2-nitro-groups from the positions corresponding to our corresponding measured values of k_1 on the plot. These were:

Substituent	2-Chloro	2-Nitro
σ-Value	0.39	0.72

These values compare with those of 0.47 and 0.71, given by Štěrba [27,28] for a coupling reaction. These values were then used to calculate Σσ for six compounds bearing 2-substituents, and a Hammett plot was obtained for k_1 for sixteen diazonium cations with ρ 2.26 ± 0.12 [*cf.* a literature value of 2.06 [5] (Figure 7)]. Taft [25] obtained a better correlation between Štěrba's values [5] for k_1 and the σ_R^+ parameter. We obtained σ^+ parameters for the 2-chloro- and 2-nitro-substituents as before of 0.34 and 0.70 respectively, but no improvement in the correlation of log k_1 *versus* σ^+ was apparent (ρ 2.18 ± 0.12). Probably this is because the substituents we are dealing with are all electron-withdrawing, and there is little possibility of transfer of charge to the reaction centre. The positive ρ value indicates that there is an increase in electron density on the atom adjacent to the ring during reaction, *i.e.* the positive charge on the diazonium group becomes neutral in the diazohydroxide. The exceptionally low value of k_1 for the 2,6-dichloro-4-nitrobenzenediazonium ion is presumably due to the two-fold steric effect: certainly the presence of a single 2-substituent is only marginally influential, thus the σ values for the 2-chloro- and 2-nitro-groups (0.39 and 0.72) are fairly similar to those of the 4-chloro- and 4-nitro-groups (0.23 and 0.78),[21] and to Taft's polar *ortho*-σ constants [26] (0.20 and 0.80).

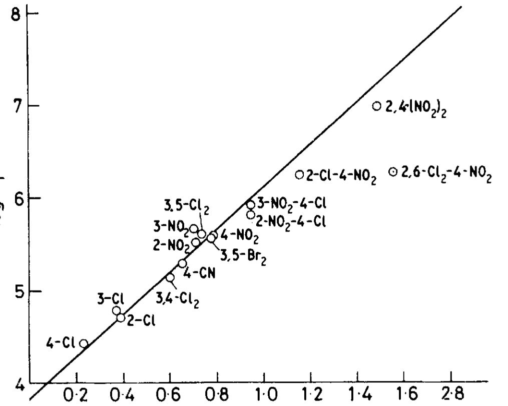
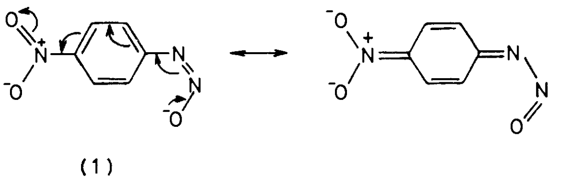


FIGURE 7 Hammett plot for k_1 (the reaction between substituted benzenediazonium cations and hydroxide ion)

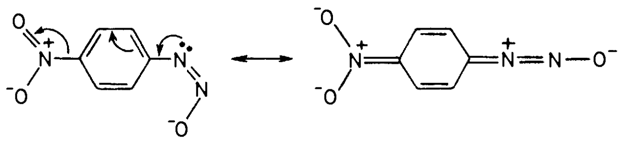
As before, a Hammett plot of k_3 (the *syn*- to *anti*-diazotate isomerisation) necessitated derivation of *ortho*-σ (and also σ^-) constants for this process; these were evaluated in the same way as for k_1 (see above) with the results:

Substituent	2-Chloro	2-Nitro
σ-Value	0.27	0.74
σ^--Value	0.31	0.98

The correlation with σ^- [25] was much the superior with a correlation coefficient of 0.979 and with ρ 3.07. (The conventional Hammett plot yielded ρ 4.46 ± 0.46.) We note that our values of k_3 for the 2-chloro-4-nitro- and 4-chloro-2-nitro-diazotates correlate much better with the other data than the literature values.[7] Once again, the data point for the strongly hindered 2,6-dichloro-4-nitro-compound deviates strongly from the line. The good correlation with σ^- implies electron transfer to the substituent from the reaction centre. Species (2) has been proposed as the most probable intermediate or transition state in the isomerization of arenediazotates substituted with strongly electron-withdrawing groups, while those without such groups isomerise *via* species (1).[22] Littler [22] has suggested (from fewer data) that the σ (rather than σ^-) constants yield a better correlation but Štěrba [7] has successfully used the σ^- constants with the Yukawa–Tsuno equation [29] to obtain ρ 2.1, which is considerably less than our figure of 3.07 calculated from many more data.



(1)



(2)

Our three new values for k_{-1} of equation (1) (see above) can be combined (a) with literature values for k_{-1} to give a comprehensive Hammett plot (Figure 8) and (b) with our own values of k_1 (Table 3) to give values for K_1 (which equals k_1K_w/k_{-1}). These in turn can be combined with values of K_2 (Table 2) to give pH$_m$ which equals 0.5(pK_1 + pK_2). In Table 5 are compiled both new and literature data for these various rate and equilibrium constants. (Values of σ-constants for 2-chloro- and 2-nitro-groups were those we obtained for the reaction of ArN$_2^+$ with OH$^-$, described above). Štěrba [6] noted that the σ-constants of the substituents in the 3,4,5-trichloro-compound are somewhat less than additive, and recommends $\Sigma\sigma$ 0.87, a figure we have utilised.

TABLE 5

Compiled rate and equilibrium constants for the reactions (1) and (2); T 293 K, I 0.25 mol dm^{-3}

Substituent(s)	log k_{-1}	pK_2	pH$_m$	pK_1	σ[21]
4-Chloro	4.505	7.70	10.97[5]	14.24	0.23
3,4-Dichloro	3.477[6]	7.30[6]	9.83[5]	12.36	0.60
3-Nitro	2.728[6]	7.15[6]	9.10[6]	11.05	0.71
3,5-Dichloro	2.780[6]	7.05[6]	9.09[5]	11.13	0.74
3,5-Dibromo	2.695[6]	7.00[6]	9.10[5]	11.20	0.74
3,4,5-Trichloro	2.484[6]	6.90[6]	8.75[5]	10.60	0.97
3-Nitro-4-chloro	2.39[6]	6.90[6]	8.58[5]	10.26	0.94
2,6-Dichloro-4-nitro[8]	1.796	4.81	5.37	6.48	1.56
2,4-Dinitro[22]			5.58		1.49
2-Chloro-4-nitro	1.00	5.51	7.14	8.78	1.17
2-Nitro-4-chloro	1.204	5.78	7.59	9.40	0.95

The Hammett plot of log k_{-1} (Figure 8) has a correlation coefficient of 0.956 and a gradient of −3.86 when the data point for the hindered 2,6-dichloro-4-nitro-compound is omitted. This compares quite well with Štěrba's [6] figure of −3.4 for six compounds, indicating the validity of including *ortho*-substituted molecules. The Hammett plot of pK_1 (Figure 9) gives the large negative ρ value of −5.86 (correlation coefficient 0.992 from nine points), implying a strong charge dependence of equation (1): the figure corresponds quite well with the difference of the ρ values for k_1 and k_{-1}, *i.e.* 2.26 − (−3.86) = 6.12. Interestingly, the sources of the deviations of the points for 2,6-dichloro-4-nitro-compound from the Hammett plots for k_1 and k_{-1} cancel out in the plot for pK_1.

In Figure 10 is presented the Hammett plot for pK_2 based on the data of Table 5, which yields ρ —2.42 $\pm$ 0.34; *cf.* the literature figure of —1.3. Clearly K_2 is much less susceptible to charge effects, which conforms with the general picture for large rate or equilibrium constants. The Hammett plot for pH_m for 12 compounds gave, as expected, a gradient of —4.40, *i.e.* close to the average of those for pK_1 and pK_2 (—4.14).

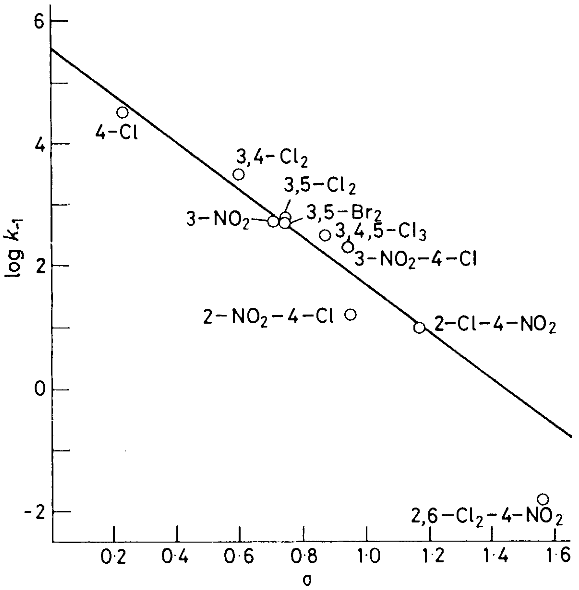


FIGURE 8 Hammett plot for k_{-1} (decomposition of *syn*-benzenediazohydroxide)

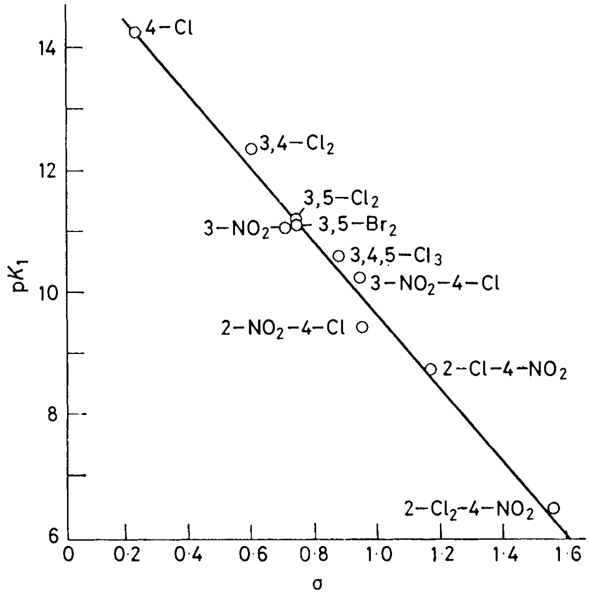


FIGURE 9 Hammett plot of pK_{A1}

Transient Spectra of syn- *and* anti-*Diazotates.*—*syn*-Diazotates with strongly electron-withdrawing groups in their 2- or 4-positions isomerise rapidly and cannot be

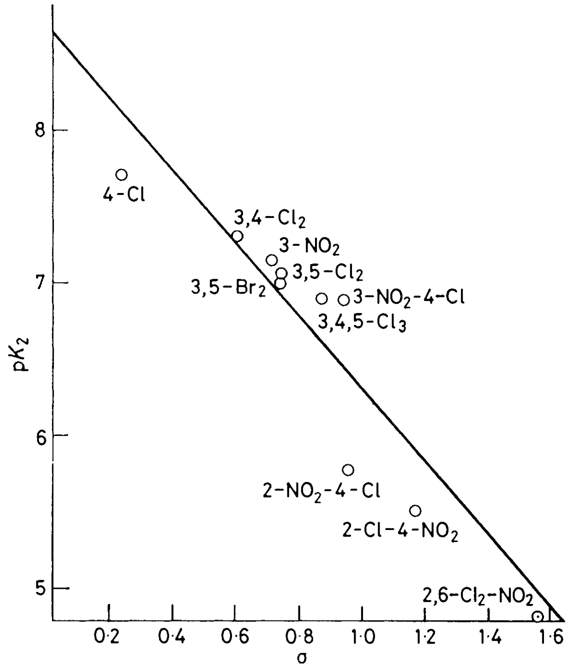


FIGURE 10 Hammett plot of pK_{A2}

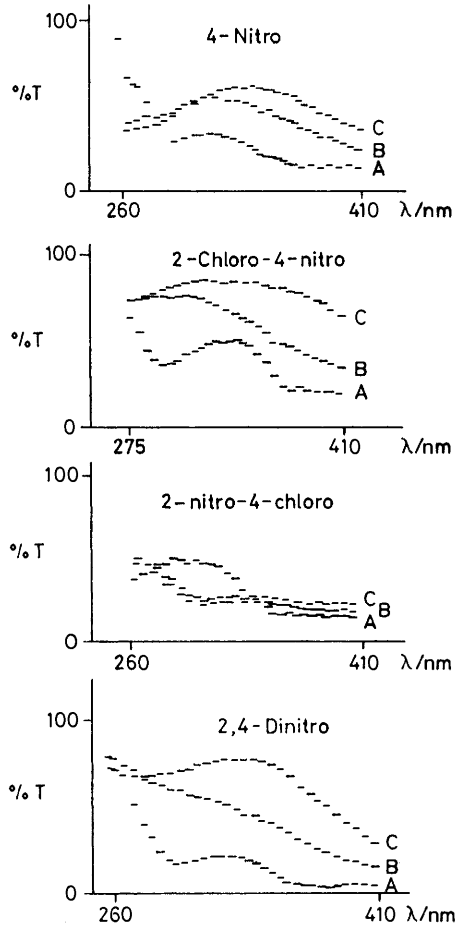


FIGURE 11 U.v. spectra of (A) four arenediazonium cations and their corresponding (B) *syn*- and (C) *anti*-diazotates

isolated, and consequently their u.v. spectra have not been obtained. Application of the rapid-scanning spectrometer in conjunction with the stopped-flow system enabled us to observe the spectra of four unstable *syn*-diazotates, which are detailed in Figure 11, together with spectra of the corresponding spectra of their *anti*-forms and the arenediazonium cations. Our experimental spectrum of *syn*-4-nitrobenzenediazotate is quite comparable to that calculated by Lewis *et al.*[11] This spectrum, and also those of the 2-chloro-4-nitro- and 2-nitro-4-chloro-compounds may be observed at $pH > 7.5$ where $k_1 < k_3$. However, the spectrum of *syn*-2,4-dinitrobenzenediazotate can be observed only at $pH > 9$, because at $pH < 9$, $k_1 < k_3$ and only the change from ArN_2^+ to the *anti*-diazotate is observable. At high pH, the pH-independent rate constant k_3 is the same as at $pH < 9$, while k_1 increases ten-fold per unit pH, so at $pH > 9.5$, $k_1 > k_3$ and so the spectral change due to the *syn*- to *anti*-isomerization is observed with a rate constant k_3. The spectrum of the *syn*-diazotate of 4-phenylenebisdiazonium cation could not be observed because the formation of monodiazotate occurs only at $pH < 5$ (otherwise *both* diazonium groups are converted into diazotate), and in this region $k_1 > k_3$. The spectra of the four *syn*-diazotates are comparable with those recorded for the more stable materials without electron-withdrawing groups.[1] In general, the *syn*-forms have smaller $\varepsilon_{max.}$ and lower $\lambda_{max.}$ than the corresponding *anti*-isomers.

We thank Ozalid (UK) for a CASE award to P. D. G., and the S.R.C. for this support and for a grant (with Dr. P. Moore) to purchase the rapid-scanning spectrometer. The quenched-flow apparatus was constructed in the Department Workshop by Mr. H. Wiles, to whom we express our thanks.

[1/243 *Received*, 16*th February*, 1981]

REFERENCES

[1] V. Štěrba in 'The Chemistry of Diazonium and Diazo Groups, Part 1', ed. S. Patai, Wiley, Chichester, 1978, ch. 2.

[2] A. F. Hegarty in 'The Chemistry of Diazonium and Diazo Groups, Part 2', ed. S. Patai, Wiley, Chichester, 1978, ch. 12.

[3] C. D. Ritchie and D. J. Wright, *J. Am. Chem. Soc.*, 1971, **93**, 6574.

[4] C. D. Ritchie and D. J. Wright, *J. Am. Chem. Soc.*, 1971, **93**, 2425.

[5] V. Beránek, V. Štěrba, and K. Valter, *Collect. Czech. Chem. Commun.*, 1973, **38**, 257.

[6] J. Jahelka, O. Macháčková, and V. Štěrba, *Collect. Czech. Chem. Commun.*, 1973, **38**, 706.

[7] J. Jahelka, O. Macháčková, V. Štěrba, and K. Valter, *Collect. Czech. Chem. Commun.*, 1973, **38**, 3290.

[8] O. Macháčková and V. Štěrba, *Collect. Czech. Chem. Commun.*, 1972, **37**, 3313.

[9] E. S. Lewis and H. Suhr, *Chem. Ber.*, 1958, **91**, 2350.

[10] E. S. Lewis and M. P. Hanson, *J. Am. Chem. Soc.*, 1967, **89**, 6268.

[11] E. S. Lewis and H. Suhr, *J. Am. Chem. Soc.*, 1958, **80**, 1367.

[12] R. J. W. Le Fèvre, R. Roper, and I. H. Reece, *J. Chem. Soc.*, 1959, 4104.

[13] T. J. Kemp, P. Moore, and G. R. Quick, *J. Chem. Soc., Dalton Trans.*, 1979, 1377.

[14] F. J. W. Roughton in 'Technique of Organic Chemistry', ed. A. Weissberger, Interscience, New York, 1963, vol. VIII, Part II, ch. XIV.

[15] A. Cox, P. D. Goodman, T. J. Kemp, and P. Pinot de Moira, *Int. J. Chem. Kinet.*, 1981, **13**, 97.

[16] J. F. Below, jun., R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, 1958, **80**, 2961.

[17] K. H. Saunders, 'The Aromatic Diazo Compounds and their Technical Applications', E. Arnold, London, 1949.

[18] E. S. Lewis and M. D. Johnson, *J. Chem. Soc.*, 1959, **81**, 2070.

[19] P. W. Schenk in 'Handbook of Preparative Inorganic Chemistry, Vol. 1', ed. G. Brauer, Academic Press, New York, 1963, 2nd. edn., p. 487.

[20] 'Handbook of Chemistry and Physics', The Chemical Rubber Company, Cleveland, 50th edn., section D.102.

[21] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[22] J. S. Littler, *Trans. Faraday Soc.*, 1963, **59**, 2296.

[23] O. Macháčková and V. Štěrba, *Collect. Czech. Chem. Commun.*, 1972, **37**, 3467.

[24] M. Charton, *Prog. Phys. Org. Chem.*, 1971, **8**, 235.

[25] S. Ehrenson, R. T. Brownlee, and R. W. Taft, jun., *Prog. Phys. Org. Chem.*, 1973, **10**, 1.

[26] R. W. Taft, jun., in 'Steric Effects in Organic Chemistry', ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

[27] V. Macháček, J. Panchartek, V. Štěrba, and M. Večera, *Collect. Czech. Chem. Commun.*, 1970, **35**, 844.

[28] M. Matrka, J. Panchartek, Z. Ságner, and V. Štěrba, *Chem. průmsyl*, 1969, **19**, 67.

[29] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1959, **32**, 971.