823. *Diazonium Salt–Diazoate Equilibria.*

By R. J. W. Le Fèvre, R. Roper, and I. H. Reece.

Equilibria reached in alkaline aqueous media by the normal diazoates from aniline, *p*-chloroaniline, and sulphanilic acid, and by the isodiazoates from the three nitroanilines and sulphanilic acid, have been studied photometrically in relation to pH. A consistent scheme for the transformations involved is proposed (p. 4109).

This paper deals with diazonium salt–diazoate equilibria, a subject which has received little attention since the time of Hantzsch.[1-3] The experiments recorded form part of a programme initiated to provide quantitative data on the interconversions of n- and iso-diazoates and their common precursors, diazonium cations. In addition to questions of structure, details of the pH-dependent appearances of these and related species were obviously important. A few years ago relevant data were sparse (cf. ref. 4, p. 102, and pp. 378—399). Since then, the kinetics of a n- to iso-diazoate transformation in aqueous sodium hydroxide have been examined,[5] and ultraviolet spectral changes associated with pH and structure noted.[5,6] The present work utilises the absorption differences between the individuals involved to obtain equilibrium results for the n-diazoates from aniline, *p*-chloroaniline, and sulphanilic acid, and for the isodiazoates from the three nitroanilines and sulphanilic acid. More recently, Lewis and Suhr[7] have published observations, also spectrophotometric, of the *p*-nitrobenzene isodiazoate–diazonium salt system, and Wittwer and Zollinger[8] have described a potentiometric study of the equilibria $RR'C_6H_3{\cdot}N_2^+ + 2OH^- \rightleftharpoons RR'C_6H_3{\cdot}N{:}N{-}O^- + H_2O$ (where R and R′ were H, 3-SO_3^-; H, 4-Cl; or 4-Cl, 2-SO_3^- respectively). Comments on these contributions are made below.

Experimental

Preparation of Materials.—Diazonium salts and diazoates were prepared by standard methods given in refs. 4—6.

Buffer Solutions.—Phosphate, borate, and potassium hydrogen phthalate buffers, covering the pH range 4—12, were made up as prescribed by Manov *et al.*,[9,10] Vogel,[11] and Clark.[12] The Marconi TF 717A pH meter, used with glass electrodes, was standardised at pH 4·01 and 9·18 by 0·05M-potassium hydrogen phthalate and 0·01M-borax, respectively.[13] Measurements, all at 25°, were taken in triplicate, and their means accepted. Check calibrations were made between each set; reproducibility was ±0·02 unit (or ±0·03 with the special electrode for highly alkaline solutions).

Spectra.—Solutions of either a diazonium salt in 0·1N-hydrochloric acid or a diazoate in 0·1N-aqueous sodium hydroxide were diluted extensively with the appropriate buffer solution, and spectra of equilibrium mixtures recorded (Cary or Spectracord instruments). The ionic strengths of the solutions were calculated, and simple Debye corrections[14] applied to the derived equilibrium constants. The wavelengths and extinction coefficients of the three major types of solute are given in Table 1.

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[1] Hantzsch, " Die Diazoverbindungen," Ahren's Sammlung, 1903, **8**, 1.

[2] Hantzsch and Reddelien, " Die Diazoverbindungen," Springer, Berlin, 1921.

[3] Moore, Hantzsch Memorial Lecture, *J.*, 1936, 1051.

[4] Saunders, " The Aromatic Diazo-compounds and their Technical Applications," Arnold, London, 2nd Edn., 1949.

[5] Le Fèvre and Sousa, *J.*, 1955, 3154.

[6] *Idem, J.*, 1957, 745.

[7] Lewis and Suhr, *J. Amer. Chem. Soc.*, 1958, **80**, 1367.

[8] Wittwer and Zollinger, *Helv. Chim. Acta*, 1954, **37**.

[9] Manov, De Lollis, and Acree, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 115.

[10] Manov, De Lollis, Lindvall, and Acree, *ibid.*, 1946, **36**, 543.

[11] Vogel, " Text-book of Quantitative Inorganic Analysis," Longmans, Green and Co., 2nd Edn., 1951, 870.

[12] Clark, " The Determination of Hydrogen Ions," Baillière, Tindall and Co., London, 1928, 209.

[13] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955, 357.

[14] Eastman and Rollefson, " Physical Chemistry," McGraw-Hill, 1st Edn., 1947, 373.

TABLE 1. *Wavelengths and extinction coefficients used in equilibria measurements.*

Substituent in parent aniline	Diazonium salt (0·1N-HCl)	n-Diazo-component (0·1N-NaOH)	Isodiazo-component (0·1N-NaOH)
H	262(12,390)	262(2350)	—
p-Chloro-	282(16,750)	282(2860)	—
o-Nitro-	220(19,400)	—	—
	277(5890)	—	242(12,500)
m-Nitro-	229(23,300)	—	271(17,100)
	290—300(1480)	—	—
p-Nitro-	260(16,560)	—	330(13,430)
p-Sulphonoxy-	268(15,550)	268(3710)	279(11,510)

RESULTS

General.—Alteration of the alkalinity or acidity of the medium produced modifications in the spectra consistently with the following scheme:

$$\begin{tikzcd}
& & \text{n-Diazoate (0·1N-NaOH)} \arrow[dll, shift left, "\text{H}^+\text{ (fast)}"] \\
\text{Diazonium salt (0·1N-HCl)} \arrow[urr, shift left, "\text{OH}^-\text{ (fast)}"] & & \\
& & \text{Isodiazoate (0·1N-NaOH)} \arrow[ull, "\text{H}^+\text{ (slow)}"]
\end{tikzcd}$$

For the nitro-derivatives, where solid normal diazoates cannot be isolated, observations suggested:

$$\text{Diazonium salt (0·1N-HCl)} \underset{\text{H}^+\text{ (slow)}}{\overset{\text{OH}^-\text{ (slow)}}{\rightleftharpoons}} \text{Isodiazoate (0·1N-NaOH)}$$

Early experiments showed that the spectral changes were quantitative and that the Beer–Lambert laws were obeyed.

Equilibria involving Isodiazoates.—It being assumed that the absorption spectrum obtained from a solution of diazonium salt in 0·1N-hydrochloric acid is that of pure " diazonium " component, and that obtained from a solution of potassium isodiazoate in 0·1N-sodium hydroxide is that of pure " diazo " component, and the ultraviolet absorptions of equilibrium mixtures being measured at two wavelengths (Table 1), the ratio log [diazo-component]/[diazonium component] was calculated and plotted against pOH for solutions of various pH. Since attainment of equilibrium is slow, and since the equilibrium may be disturbed by the irreversible decomposition * $ArN_2^+ + OH^- \longrightarrow ArOH + N_2$, the equilibrium curves were treated by the method of Dewar and Urch.[15] Those curves which did not yield a linear plot for optical density/$E^{\text{m}}_{\text{diazo-component}}$ *vs* $E^{\text{m}}_{\text{diazonium component}}/E^{\text{m}}_{\text{diazo-component}}$ for various wavelengths, thereby indicating the presence of a third absorbing component, were rejected.

TABLE 2. *Results for the equilibrium* $o\text{-}NO_2\cdot C_6H_4\cdot N_2^+ + OH^- \rightleftharpoons$ iso-$o\text{-}NO_2\cdot C_6H_4\cdot N{=}N\cdot OH$.*

pH	$\log \frac{[\text{diazo}]}{[\text{diazonium}]}$	$\log K_0$	$\log K_0'$	pH	$\log \frac{[\text{diazo}]}{[\text{diazonium}]}$	$\log K_0$	$\log K_0$
9·02	1·42	6·66	11·64	7·89	0·19	6·53	12·64
8·80	1·15	6·61	11·81	7·78	0·23	6·56	12·78
8·80	1·13	6·59	11·79	7·74	0·27	6·66	12·92
8·60	0·89	6·54	11·94	7·17	−0·47	6·46	13·29
8·42	0·72	6·55	12·13	7·12	−0.36	6·62	13·50
8·16	0·62	6·70	12·53	7·12	−0·45	6·53	13·41
7·89	0·29	6·63	12·74				

* $\log K_0'$ is the constant calculated for the equilibrium $o\text{-}NO_2\cdot C_6H_4\cdot N_2^+ + 2OH \rightleftharpoons$ iso-$o\text{-}NO_2\cdot C_6H_4\cdot N{=}N{-}O^- + H_2O$.

In all cases studied, the graph of log [diazo-component]/[diazonium component] against pOH formed a straight line having slope unity. A sample plot is shown in Fig. 1, together with typical equilibrium data in Table 2.

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* Cf. Lewis and Suhr.[7] The absorption spectra of decomposed solutions resemble fairly closely those of the corresponding phenols, and the evolution of nitrogen can be observed.

[15] Dewar and Urch, *J.*, 1957, 345.

Such data show the equilibrium measured to be concerned with one hydroxyl group—possibly the following:

$$X\cdot C_6H_4\cdot N^+{\equiv}N + OH^- \rightleftharpoons \text{iso-}X\cdot C_6H_4\cdot N{=}N{-}OH \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

Lewis and Suhr [7] ascribe the observed initial rapid decrease caused in the ultraviolet absorption at 340 mμ by the acidification of potassium *p*-nitrobenzeneisodiazoate to the equilibrium

$$\text{iso-}p\text{-}NO_2\cdot C_6H_4\cdot N{=}N{-}O^- + H^+ \rightleftharpoons \text{iso-}p\text{-}NO_2\cdot C_6H_4\cdot N{=}N{-}OH$$

and the subsequent slower decrease in absorption to the equilibrium (1) above. On examining this point we find that the first-order loss of diazo-component at 330 mμ, calculated on the assumption that the curve obtained for *p*-nitrobenzeneisodiazoate in 0·1N-sodium hydroxide represents pure diazo-component, can be extrapolated to intersect at zero time at a point corresponding to the initial concentration of diazo-component calculated on the same assumption. If the absorbing species after the initial rapid change were different, in fact one having a much lower absorbance at this wavelength, such a linear extrapolation could not be realised. The initial rapid change in absorbance is simply a result of the exponential nature of the concentration change.

FIG. 1. p-*Nitroaniline derivatives.*

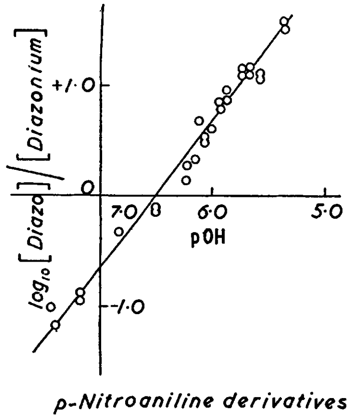
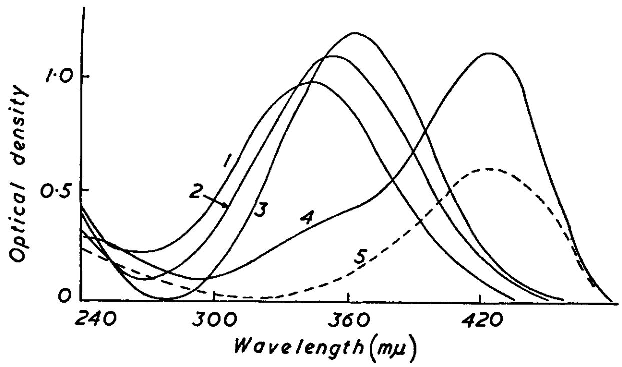


FIG. 2. *Potassium* p-*nitrobenzeneisodiazoate spectra in concentrated potassium hydroxide.*



1, *ca.* 6N-KOH. 2, 12N-KOH. 3, ⩾12N-KOH. 4, *As curve* 3, *but after* 60 *hr.* 5. p-*Nitrophenol in* ⩾12N-KOH.

To test whether or not the principal absorbing species in solutions of isodiazoates in dilute alkali is the isodiazohydroxide, spectra for these materials were determined in increasingly concentrated alkali solutions. For the potassium *p*-nitrobenzeneisodiazoate the curves obtained are shown in Fig. 2. Similar, but much smaller, changes were observed for other diazoates. The absorption spectrum of potassium benzeneisodiazoate in >10N-alkaline lithium iodide showed no change in either maximum wavelength or intensity, indicating that the changes observed in concentrated alkali are not due to simple salt effects.

In all cases the absorption maximum was shifted to longer wavelength accompanied by increased intensity. By analogy with the observed behaviour for substituted phenols,[16] the effect can reasonably be correlated with the equilibrium

$$\text{iso-}Ar\cdot N{=}N\cdot OH \rightleftharpoons \text{iso-}Ar\cdot N{=}N{-}O^- + H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The results obtained for systems involving the equilibrium (1) are shown in Table 3.

TABLE 3. *Equilibrium constants for the equilibrium* $ArN_2^+ + OH^- \rightleftharpoons \text{iso-}Ar\cdot N{=}NOH$.

Substituent	*p*-NO₂	*o*-NO₂	*m*-NO₂	*p*-SO₂·O⁻ *
log K_0	6·83 ± 0·11 †	6·59 ± 0·05	6·88 ± 0·05	6·72 ± 0·05

* This should be considered more as a hydrolysis constant, since the normal diazoate interferes with the forward reaction.

† The errors presented are the mean deviation. The true experimental error is probably somewhat greater than this.

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[16] Doub and Vanderbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714, 2997; 1949, **71**, 2414.

Equilibria involving n-Diazoates.—Engler and Hantzsch,[17] and more recently, Wittwer and Zollinger,[8] have indicated that conversions of the type diazonium ion $\rightleftharpoons$ n-diazoate ion are rapid. Our own observations support this. The decomposition of diazonium compounds in alkaline solutions is also known to be faster than that of the corresponding iso-diazo-derivatives (Saunders, ref. 4, p. 99).

With the same assumption concerning the pure components as for the isodiazoates, the ultraviolet absorptions of equilibrium mixtures were measured at a single wavelength by extrapolation to zero time. Again, log {[diazo-component]/[diazonium component]} was calculated, and plotted against pOH.

For the two substituted derivatives, straight-line plots with slope 2 were obtained (Fig. 3) suggesting the equilibrium

$$p\text{-X}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{N}^+{\equiv}\text{N} + 2\text{OH}^- \rightleftharpoons \text{n-}p\text{-X}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{N}{=}\text{N}{-}\text{O}^- + \text{H}_2\text{O} \quad . \; . \; . \; . \; . \quad (2)$$

For the unsubstituted aniline compounds, the curve approached unit slope, indicating the n-benzenediazohydroxide to be a weaker acid than the corresponding substituted diazohydroxides. There are signs, in the region of high pH, of a change of slope, possibly due to some ionisation of a diazohydroxide, although this must necessarily be speculative, in view of the inaccuracies associated with pH determination in the range used.

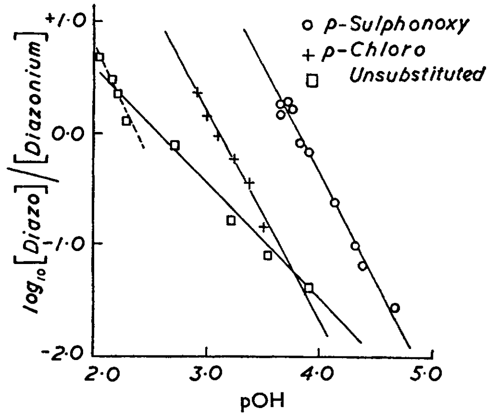

FIG. 3. *n-Diazoate–diazonium equilibria.*

○ p-*Sulphonyloxy-*. + p-*Chloro-*.
□ *Unsubstituted.*

The measured equilibrium constants are shown in Table 4.

TABLE 4. *Equilibrium constants* (log K_0) *involving n-diazoates at* ca. 25°.

$p\text{-X}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{N}_2^+ + 2\text{OH}^- \rightleftharpoons$	$\text{n-}p\text{-X}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{N}{=}\text{N}{-}\text{O}^- + \text{H}_2\text{O}$
X = p-Cl	6·59 ± 0·04
p-SO$_2$·O	8·02 ± 0·08
* p-Cl	6·78 ± 0·05
$p\text{-X}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{N}_2^+ + \text{OH}^- \rightleftharpoons$	$\text{n-}p\text{-X}{\cdot}\text{C}_6\text{H}_4{\cdot}\text{N}{=}\text{N}{\cdot}\text{OH}$
X = p-H	2·85 ± 0·07

* Wittwer and Zollinger's value at 0° and ionic strength 0·73.

DISCUSSION

For the isodiazoate systems examined, the equilibrium constants and spectral changes observed in strong alkali indicate that these isodiazoate ions are predominantly hydrolysed to the corresponding isodiazohydroxides even in dilute alkaline solutions. The n-diazoates studied (other than the unsubstituted potassium benzene-n-diazoate) are evidently not appreciably hydrolysed in their solutions. At least for diazo-derivatives of sulphanilic acid, the normal diazohydroxide is a considerably stronger acid than the isodiazohydroxide. Such observations bring the diazohydroxides, considered as *cis*- and *trans*-isomers, into

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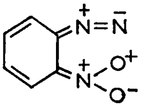
[17] Engler and Hantzsch, *Ber.*, 1900, **33**, 2174.

line with the recorded relative acid strengths of *cis*- and *trans*-oximes and cinnamic acids (cf. Saunders,[4] p. 389) where the *trans*-compounds are invariably the weaker acids.

Furthermore, Le Fèvre and Sousa and earlier workers have observed abnormally gross differences between the ultraviolet absorption spectra of n- and iso-diazoates, compared with the corresponding differences between *cis*- and *trans*-diazo-cyanides, -sulphonates, -azobenzenes, etc. These differences need no longer be considered anomalous, since the present work shows the main absorbing species in dilute alkaline solutions of n- and iso-diazoates to be the n-diazoate ion and the isodiazohydroxide respectively. The spectra attributed by Lewis and Suhr to the *p*-nitrobenzenediazohydroxide might equally well be interpreted as those of a mixture of diazonium salt and diazohydroxide.

Quantitatively, the measured equilibrium constants (eqn. 1) for the *m*- and *p*-nitro-iso-diazo-systems are the same within experimental error. This is as expected in view of the stronger conjugative $-T$ effect of the diazonium ion[18] than of the nitro-group. For the *o*-nitroisodiazo-equilibrium, steric interaction between the nitro- and the diazonium group would reduce the contribution of the form:



to the mesomeric state of the diazonium ion; this, together with the now more important inductive effect of the *o*-nitro-group, should enhance the positive nature of the diazonium nitrogen atom and thus facilitate nucleophilic attack by a hydroxyl group, resulting in a smaller equilibrium constant. The measured constant for the *p*-sulphonyloxy-compounds also is slightly less than for the *p*- and *m*-nitro-compounds, consistently with the weaker inductive effect from this group.[19]

Attempts to measure equilibrium constants with substituents of different polar type failed owing to the more rapid decomposition of these compounds. However a constant for the *p*-chlorobenzenediazonium ion–diazoate equilibrium was obtained by Wittwer and Zollinger, using a titration technique. Their value, when converted to our basis, is $\log K = 6{\cdot}78 \pm 0{\cdot}05$,* at 0° and for solutions of ionic strength 0·73. With use of values for the heat of reaction as listed by Saunders (ref. 4, p. 353) and an integrated form of the van't Hoff equation and with a Debye ionic-strength correction, Wittwer and Zollinger's equilibrium constant reduces to 6·80, agreeing satisfactorily with our value of 6·59.

That the substituted n-diazohydroxides should be stronger acids than the unsubstituted benzene-n-diazohydroxide is to be expected from the electron-withdrawing nature of the substituents. The isodiazoate results show that the strong mesomeric effect from the diazonium group swamps any electropolar effect from the substituent group. The chlorine atom, however, can exert a $+T$ effect which will be enhanced by the $-T$ effect of the diazonium group (Ingold,[19] p. 801). The tendency is towards attainment of neutrality of the $-N_2^+$ group, and consequently to a smaller equilibrium constant for the chloro-derivative than for the sulphanilic acid equilibrium.

The kinetic results of Lewis and Suhr[7] can be reconciled with present observations concerning the *p*-nitrobenzene–isodiazoate transformations and equilibria. Our experiments indicate that the overall reaction of the *p*-nitrobenzenediazonium ion with dilute alkali is

$$p\text{-}NO_2{\cdot}C_6H_4{\cdot}N^+{\equiv}N + OH^- \underset{k_+}{\overset{k_-}{\rightleftharpoons}} \text{iso-}p\text{-}NO_2{\cdot}C_6H_4{\cdot}N{=}N{\cdot}OH$$

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* In the cited paper the value quoted for $(pK_1 + pK_2)/2$ is 10·61 and in another section of the paper, 11·61. Our result agrees with the value 10·61.

[18] Bolto, Liveris, and Miller, *J.*, 1956, 750; cf. Miller, *Rev. Pure Appl. Chem.* (*Australia*), 1951, **1**, 171.

[19] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, 298, 801.

To explain the variation of the second-order rate constant k_2 with pH, Lewis and Suhr derived the equation $k_2 = k_+ + k_-/[\mathrm{OH}^-]^2$. If the reaction followed is the above, the corresponding equation will be $k_2 = k_+ + k_-/[\mathrm{OH}^-]$. Lewis and Suhr's rate data being used, a plot of k_2 against $1/[\mathrm{OH}^-]$ gives a good straight line for all but one point at pH 7·01. It may be noted that Saunders (ref. 4, p. 99) shows graphically that *p*-nitrobenzeneisodiazoate has minimum stability at pH 7. To quote Lewis and Suhr " Since the reaction is not complete in much of this region, lower accuracy is to be expected from the smaller change in absorbance "—that is, at low pH. Although the calculated value of k_- ($1{\cdot}14 \times 10^{-4}$) differs from their experimental figure for the unimolecular decomposition of diazohydroxide ($2{\cdot}3 \times 10^{-3}$), the ratio k_+/k_- deduced from this graph gives an equilibrium constant, $\log K = 6{\cdot}86$, in accord with that from our results, *viz.*, $\log K = 6{\cdot}83$.

For the reaction of the *p*-nitrobenzeneisodiazoate with acid, if this is

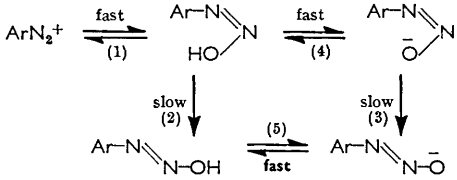
$$\text{iso-}p\text{-NO}_2{\cdot}\text{C}_6\text{H}_4{\cdot}\text{N=NOH} \longrightarrow p\text{-NO}_2{\cdot}\text{C}_6\text{H}_4{\cdot}\text{N}^+{\equiv}\text{N} + \text{OH}^-$$

the following equation can be derived:

$$\log k_{\text{obs.}} = \log (1 + k_+/k_- \,.\, [\mathrm{OH}^-]) + \log k_-$$

Using our experimental value of $6{\cdot}76 \times 10^6$ for k_+/k_- and the rate data of the American authors (excluding rate constants for citrate–phosphate buffers), we can plot $\log (1 + k_+/k_- \,.\, [\mathrm{OH}^-])$ against $\log k_{\text{obs.}}$. The curve deviates considerably from linearity in the region of low pH. The intercept at $\log (1 + k_+/k_-[\mathrm{OH}]) = 0$ gives a value $k_- = 2{\cdot}5 \times 10^{-3}$. Lewis and Suhr's experimental value is $2{\cdot}3 \times 10^{-3}$.

Conclusions.—A consistent scheme for the diazonium–isodiazoate transformations under study can be written as follows:



It is likely that reaction (1) is generally fast in view of the rapid coupling of normal diazoates together with the fact that coupling is known to proceed *via* the diazonium ion (cf. Ingold, ref. 19, p. 297). For unsubstituted derivatives our studies have shown its rapidity; substitution by a *p*-nitro-group should enhance the positive nature of the diazonium group [19] and result in an even faster reaction.

The ultraviolet spectra in strong alkali together with the equilibrium measurements show the isodiazohydroxide to be the predominant species in equilibrium with diazonium ion. The relative amounts of n-diazohydroxide and n-diazoate ion present should be a function of the pH. At low pH the n-diazohydroxide should occur mostly, and reaction (2) be rate controlling. The dependence of n-diazohydroxide concentration on pH by virtue of equilibrium (4) accounts for the variation of the apparent first-order rate constant observed by Lewis and Suhr. At higher pH, dissociation of the n-hydroxide to the n-diazoate ion would be virtually complete, and reaction (3) rate controlling. Since diazoate-ion concentration is no longer determined by pH, the apparent first-order rate constant should also be independent of pH, as is observed.

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