[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Reactions of the *p*-Nitrobenzenediazonium and Diazotate Ions with Acid and Base

BY EDWARD S. LEWIS AND HARALD SUHR

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The perceptibly slow conversion of *p*-nitrobenzenediazonium ion to the *anti*-diazotate with aqueous base and the reverse process in acid have been studied quantitatively. The *syn*-diazotate and the conjugate acid of the *anti*-diazotate have been detected as intermediates of significant life. The kinetics of the reactions and some equilibria have been investigated, all by spectrophotometric methods.

Introduction

The conversion of diazonium salts to diazotates, the isomerism of the diazotates, and the structure and even existence of the conjugate acids of the diazotates have been subjects of investigation and controversy for over eighty years. The extensive work of Hantzsch on diazotates and their conjugate acids did not convincingly dispose of all structural or chemical problems, but his work did put the structures of many of the substances produced on a plausible basis. The published research in this field then slowed to an extent that Saunders[1] remarked that since that time "no other investigator has examined the *iso*diazohydroxides, nor does it appear an inviting field at the present time."

The original aim of the work here reported was to use spectrophotometric methods to measure equilibria of the type 1

$$ArN_2^+ + X^- \rightleftharpoons Ar—N=N—X \qquad (1)$$

and the use of basic X^- required a knowledge of the reaction with hydroxide ion. The *p*-nitro compound was selected as a favorable case for N–X bond formation, and the diazonium salt solutions are conveniently stable.

Experimental

All measurements of spectra were made by diluting a small volume of a solution of the diazonium salt or the diazotate with a much larger volume of solution of appropriate *p*H. The *p*-nitrobenzenediazonium fluoroborate and the sodium *p*-nitrobenzenediazoate were made by standard methods from recrystallized *p*-nitroaniline. By measuring the solution of diazo compound in a micropipet and putting this into a previously measured amount of buffer solution in the spectrophotometer cell, it was possible to get absorbance readings in as little as six seconds after mixing. All measurements of absorbance were made on a Cary model 14 recording spectrophotometer. The buffer solutions with a total borate or phosphate concentration of about 0.1 *M* were made according to the directions of Britton.[2] The spectrophotometric method of measuring the effect of *p*H on ionization was checked with these buffers using *m*-nitrophenol as an indicator. The results calculated in the form of the *p*H of the solution agreed with the recipe *p*H within ±0.03 *p*H unit for the phosphate buffers when a pK_a for the indicator of 8.25 was assumed, without any refinements for activity coefficients[3]; the *p*H calculated in the same way for the borate buffers (of different ionic strength) differed by as much as 0.07 unit. The *p*H reported is in every case that given in the recipe. A small error, undetected at the time of the experiments, was introduced when diazotate solution, containing free alkali, was added to buffer. In these cases the use of a *p*H meter could have been preferable.

All measurements, except in a few at low concentration of absorbing species, were made in 1-cm. cells, and the temperature was about 20° except where otherwise stated. The temperature effect on the diazotate isomerization was determined using thermostated 10-cm. cells. Temperatures given in Table I for this process are the average of the incoming and outgoing temperatures in the circulating system.

The spectra of unstable intermediates were obtained by mixing diazonium salt with 0.1 *N* sodium hydroxide (for the *syn*-diazotate) or *anti*-diazotate with 0.1 *N* hydrochloric acid (for the *anti*-diazohydroxide) and measuring the absorbance as soon as possible after mixing. For the former it was necessary to mix up a new solution for each wave length and extrapolate to zero time; for the latter, a reasonable part of the curve could be traced by the instrument before significant reaction had occurred. The spectrum of the *syn*-diazotate may be complicated by the presence of some *anti*-diazotate formed directly from the diazonium salt. Figure 1 shows, however, from the extinction coefficient at 380 mμ, that no more than 20% of the *anti*-diazotate can be present at zero time.

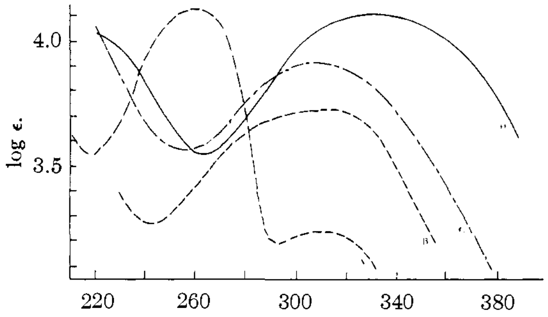

Fig. 1.—Absorption spectrum of *p*-nitrobenzenediazonium ion and its derivatives: A, ArN_2^+; B, *anti*-ArN_2OH; C, *syn*-ArN_2O^-; D, *anti*-ArN_2O^-.

Results

Preliminary observations on the spectra of solutions at *p*H 5 to 10 of the diazonium salt showed a *p*H dependence of spectrum with the change occurring largely between *p*H 7 and 9. The entire family of curves showed two isosbestic points at 280 and 238 mμ. This suggested that in the conversion of the diazonium salt to the only known diazotate there were no other substances present in significant concentration. This conclusion was drawn by Zollinger[4] from potentiometric titration of some other diazonium salts. However, the failure of an attempt to calculate an equilibrium constant from this family of curves showed that the situation was more complicated. The spectra of the two ions in question are shown in Fig. 1. The difficulty arose from two sources: a slow approach to equilibrium and an irreversible reaction leading to a drop in absorbance at the wave lengths used for analysis. While these difficulties were not en-

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(1) K. H. Saunders, "The Aromatic Diazo Compounds," 2nd edition, E. Arnold and Co., London, 1949, p. 135.

(2) H. T. S. Britton, "Hydrogen Ions," 3rd edition, Vol. 1, D. Van Nostrand Co., New York, N. Y., 1943, pp. 301–311.

(3) I. M. Kolthoff and H. A. Laitinen, "*p*H and Electro Titrations," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, give pK_a 8.25 at 25° and ionic strength 0.1 *M*.

(4) H. Zollinger, *Helv. Chim. Acta*, **37**, 1954 (1954).

tirely overcome, the error was reduced by starting with near equilibrium mixtures of diazonium ion and diazotate ions, so that less time was required to get reasonably close to the equilibrium. Figure 2 presents the data in the form of a plot of *p*H *vs.* the logarithm of the ratio of diazotate ion to diazonium ion. The length of the lines is an estimate of error from the analysis and the slow approach to equilibrium. The theoretical line of slope 0.5 with an equilibrium constant for reaction 2 of 8×10^{12} is also shown. The rather poor fit is understandable in view of the serious error from the irreversible reaction. No other reasonable form of equilibrium constant fits the data as well.

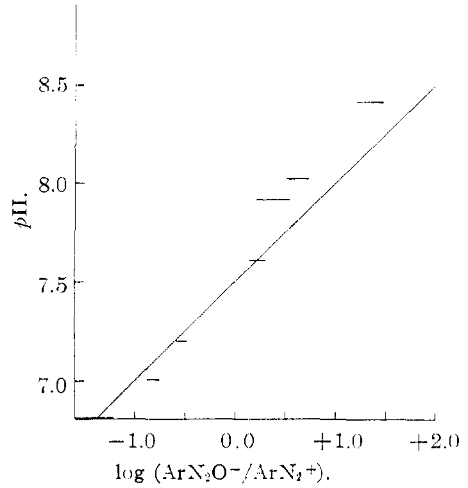

Fig. 2.—The variation of the ratio of *anti*-diazotate to diazonium ion with *p*H. The slope of the line is 0.5.

$$ArN_2^+ + 2OH^- \rightleftarrows ArN_2O^- + H_2O \qquad (2)$$

It was possible to follow the change with time in absorbance on adding the diazonium salt to various buffers. At *p*H 10–14, the change followed a first-order course, with an exponential approach to the final absorbance and the rate was independent of *p*H, as shown in Table I. The table also shows the apparent first-order rate constants k_{app}, for the exponential approach to the final equilibrium from *p*H 7 to 8.75, now increasing with *p*H. Since the reaction is not complete in much of this region, lower accuracy is to be expected from the smaller change in absorbance. The table also shows a second-order "constant" k_2, derived by dividing k_{app} by the concentration of hydroxide ion. Between *p*H 8.75 and 10, a first-order course was not followed, although the reaction became faster as the *p*H was increased.

TABLE I

REACTION OF *p*-NITROBENZENEDIAZONIUM ION WITH BASE AT 20°

*p*H	$k_{app} \times 10^2$, sec.$^{-1}$ (±10%)	*p*H	$k_{app} \times 10^2$, sec.$^{-1}$ (±10%)	$k_2 \times 10^{-3}$, l. mole^{-1} sec.$^{-1}$
10^d	0.36^a	8.75^d	1.0	1.8
10^d	1.87^b	8.44^d	0.68	2.6
10^d	5.4^c	8.25^d	.35	2.0
10^d	2.76	8.02^g	.10	0.95
11^g	2.97	7.91^g	.079	0.97
12^g	3.03	7.66^g	.053	1.1
14^e	3.13	7.21^g	.024	1.5
$14+^f$	2.95	7.01^g	.026	2.5

[a] At 5°. [b] At 15°. [c] At 25°. [d] Borate buffers. [e] 1 *N* NaOH. [f] Concd. NaOH. [g] Phosphate buffers.

The reverse reaction of the diazotate with acid also could be followed, but only at *p*H < 8, and with precision only at *p*H < 5. On acidification, an apparently instantaneous drop in absorbance at 360 mμ was followed by a slower further drop. The extent of this immediate drop increased with acidity. It was assumed that the initial, rapid change in absorbance corresponded to the establishment of the equilibrium 3. On this basis an equilibrium constant for this reaction of 7.2×10^{-7} was calculated.[5] Figure 3 shows a plot of the logarithm of the ratio of the diazotate to its conjugate acid *vs.* *p*H showing reasonable agreement between the data and the theoretical line of unit slope derived from this constant. The perceptible scatter actually represents a small concentration dependence of the constants, such that the more concentrated solutions show greater dissociation. This is doubtless an experimental artifact since the diazotate solution contained free sodium hydroxide at a much higher concentration than the diazotate. Then the larger samples produced a small increase in *p*H, whereas the smaller samples of the stock diazotate solution shifted the *p*H of a negligible amount. Unfortunately it is not possible to calculate the magnitude of this error, but it is almost certainly less than ±20% of the constant calculated, which is based largely on the more dilute solutions.

$$anti\text{-}ArN_2OH \rightleftarrows anti\text{-}ArN_2O^- + H^+ \qquad (3)$$

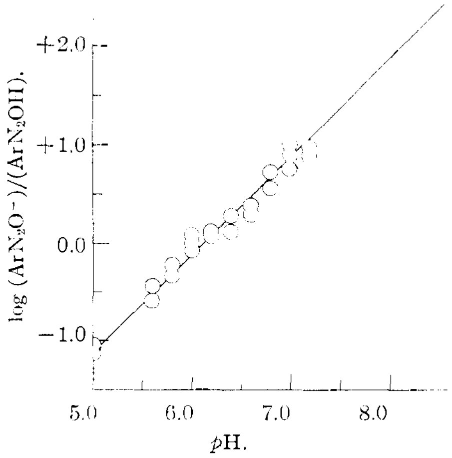

Fig. 3.—The influence of *p*H on the ionization of *anti*-ArN_2OH.

The slow drop in absorbance of acidified solutions of the diazotate corresponded to ultimate con-

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[5] I. F. Grachev (*J. Gen. Chem.* (*U.S.S.R.*), **17**, 1834 (1947), *C. A.*, **42**, 5866 (1948)) reports the acid dissociation constant of "*p*-nitrobenzenenitrosamine" as 2.45×10^{-6} at 13°. While the order of magnitude agreement is reasonable, there appears no obvious reason for the discrepancy of a factor of more than three. It is not possible to correlate any of the remaining equilibria reported in Grachev's paper with anything in our work. The calculation of 79% R-NNOH (presumably our *syn*-diazohydroxide) at *p*H 8.6 is hard to reconcile with the isosbestic points. Some of the difficulty may arise from the attempt to interpret the abstract, rather than the original paper.

version to the diazonium ion. The disappearance of absorption at about 340 mμ fitted a first-order course over the whole range studied, from *p*H 8 to strongly acid solutions; the apparent first-order constants k_{obs} are given in Table II. In the range *p*H 8 to 5 the reaction was not followed very far, since it was too slow, and therefore almost any simple rate law would fit as well. The rate expression 4 fits the data reasonably well, when

$$-\mathrm{d}(\mathrm{ArN_2OH})/\mathrm{d}t = 2.3 \times 10^{-3}\,(\mathrm{ArN_2OH}) + 4.0 \times 10^{-2}\,(\mathrm{H^+})(\mathrm{ArN_2OH}) \quad (4)$$

coupled with the ionization equilibrium 3 for the high-*p*H regions. In the column headed k_{calc} are the constants calculated from this expression. In the right part of the table k_{calc} is the unimolecular constant (in this case 2.8×10^{-3}) multiplied by an expression showing the fraction in the protonated form as shown in eq. 5. In this calculation as in all others, we have used *p*H and $-\log(\mathrm{H^+})$ interchangeably. The precision is not sufficient to call for a more refined treatment.[6]

$$k_{\text{calc}} = 2.8 \times 10^{-3}(\mathrm{H^+})/[7.2 \times 10^{-7} + (\mathrm{H^+})] \quad (5)$$

TABLE II

REACTION OF *p*-NITROBENZENEDIAZOTATE WITH ACIDIC SOLUTIONS AT 20°

*p*H	$k_{\text{obs}} \times 10^3$, sec.$^{-1}$	$k_{\text{calc}} \times 10^3$, sec.$^{-1}$	*p*H	$k_{\text{obs}} \times 10^3$, sec.$^{-1}$	$k_{\text{calc}} \times 10^3$, sec.$^{-1}$
−0.54[a]	136[b]	136	5.6	2.3[b]	2.2
+0.24[c]	30[b]	25	5.8	1.9[b]	1.9
1.0	5.7[b]	6.3	6.0	1.7	1.6
2.0	3.1[b]	2.7	6.2	1.2[b]	1.3
3.0[d]	2.5[b]	2.3	6.4	1.1	1.0
4.0[d]	2.3[b]	2.3	7.0	0.48	0.34
5.0	2.5[b]	2.6[e]	8.0	0.07	0.039

[a] H_0 of 15% H_2SO_4, ref. 13, p. 268. [b] Average of at least two runs with a deviation from the mean of 10–20%. [c] H_0 of 5% H_2SO_4. [d] Citrate phosphate buffers, ref. 2, p. 345. [e] k_{calc} from here on is based on a first-order constant 2.8×10^{-3} sec.$^{-1}$, and was determined in phosphate buffers at 22.5°.

Discussion

The nature of the irreversible reaction which interfered with the equilibrium measurements can be guessed. It is most serious at an intermediate *p*H, and must therefore be a reaction between species not both prevalent at extreme *p*H. The reaction of this type between the diazonium and hydroxide ions yielding the unsubstituted diazo oxide (eq. 6) is an attractive guess which can be indirectly supported by numerous examples. Nucleophilic displacements activated by the diazonium group of nitro by halide,[7] of halide by thiocyanate[8] and by the hydroxide ion[9] have been reported. The further observation that nitrous acid is produced from the action of acid on *p*-nitrobenzenediazotate[10,11] must be discounted as support of this view, since the isolation of the diazoamino compound[11] shows that nitrous acid results from a reversal of the diazotization process. The isolation of this product shows that a substantial part of the irreversible reaction cannot be accounted for by reaction 6. Nevertheless, the simultaneous presence of a powerfully activating group and a good nucleophile will certainly lead to analogous displacements when other reactions do not predominate.[12]

$$\mathrm{O_2NC_6H_4N_2^+ + OH^- \longrightarrow HOC_6H_4N_2^+ + NO_2^-} \\ \mathrm{\longrightarrow OC_6H_4N_2 + HNO_2} \quad (6)$$

The slow reactions occurring in the conversion of the diazonium ion to the stable *anti*-diazotate are unquestionably consecutive reactions, one rate determining at the higher *p*H, the other at the lower. The *p*H-independent process is almost certainly the isomerization 7.

$$syn\text{-}\mathrm{ArN_2O^-} \longrightarrow anti\text{-}\mathrm{ArN_2O^-} \quad (7)$$

The *p*H dependence of the other reaction is not entirely clear, the "constants" k_2 are the observed rate constants divided by the hydroxide ion concentration. If we eliminate the borate buffer results, we are left with a constantly rising value of k_2 as the *p*H falls. The elimination of borate buffer data can be justified on the basis of the substantially lower ionic strength of this buffer system at the low *p*H end, and need not be construed as a specific borate (or phosphate) ion effect, which, if present, would be expected to cause far bigger changes in the rate constants. Since the *p*H is constant, the reaction follows a pseudo-first-order approach to equilibrium from either side. Therefore, the apparent rate constant k_2 is actually a sum of the pseudo-first-order constants for the forward and reverse reactions.[13] If we assume a first-order dependence on hydroxide ion for the forward reaction [rate = $k_+(\mathrm{OH^-})(\mathrm{ArN_2^+})$], the stoichiometry of reaction 2 requires a reciprocal dependency of the reverse rate on hydroxide concentration [rate = $k_-(\mathrm{ArN_2O^-})/(\mathrm{OH^-})$]. We can then deduce the equation 8, which has been applied to the data in Fig. 4 by plotting k_2 *vs.* $(\mathrm{OH^-})^{-2}$. The reasonably linear plot yields the values $k_+ = 9.3 \times 10^2$ l./mole sec., and $k_- = 1.6 \times 10^{-11}$ mole/l. sec. The rate constant k_- can be transformed into the equivalent form of a unimolecular decomposition of the *anti*-diazohydroxide by using the dissociation constants of this substance and of water. In this form, the constant is 1.2×10^{-3} sec.$^{-1}$, in sufficiently good agreement with the observed value of 2.3×10^{-3} to support the explanation for the variation of k_2 with *p*H.

$$k_2 = k_+ + k_-/(\mathrm{OH^-})^2 \quad (8)$$

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(6) One can apply an equation of the same form to the data of Grachev (*Zhur. Obshchei Khim.*, **17**, 2268 (1947); *C. A.*, **43**, 169$^{\text{h}}$ (1949)) for the "nitrosamine"-diazonium ion conversion. From his results at 20° and *p*H 5.6 and 1.9, assuming that his time units are in minutes (not stated in the abstract), the equation (in time units of seconds) would be $k_{\text{obs}} = 4.7 \times 10^{-3} + 8.0 \times 10^{-2}\,(\mathrm{H^+})$. The similarity suggests that the process is probably the same in both cases, the factor of two discrepancy may not be serious.

(7) Reference 1, p. 118.

(8) A. Hantzsch and B. Hirsch, *Ber.*, **29**, 947 (1896).

(9) K. J. P. Orton, *J. Chem. Soc.*, **83**, 796 (1903); **87**, 99 (1905).

(10) A. Hantzsch, M. Schümann and A. Engler, *Ber.*, **32**, 1703 (1899).

(11) B. A. Porai-Koshits and I. V. Grachev, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 571 (1946); H. H. Hodgson and W. H. H. Norris, *J. Chem. Soc.*, 87 (1949).

(12) The formation of diazoresins of unknown structure has been reported to be particularly serious for *m*-nitrobenzenediazonium ion (ref. 14), a molecule where both the nitro group and the diazonium group are capable of promoting hydride displacement. Furthermore hydride loss is presumably aided by the presence of oxidizing agents such as the nitro group.

(13) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 102.

The fact that the forward process uses only one hydroxide ion leads to the conclusion that there is a fast step using the other hydroxide ion required by the stoichiometry. Equations 9 and 10 followed by the isomerization 7 can reasonably represent the case.

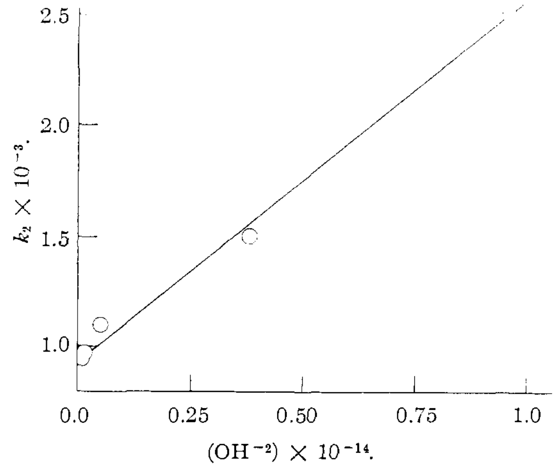

Fig. 4.—Effect of hydroxide ion concentration on the apparent second-order rate constants for the reaction of diazonium ion with hydroxide ion.

$$\mathrm{ArN_2^+ + OH^- \xrightarrow{k_+\ \text{slow}} \mathit{syn}\text{-}ArN_2OH} \qquad (9)$$

$$\mathrm{\mathit{syn}\text{-}ArN_2OH + OH^- \xrightarrow{\text{fast}} \mathit{syn}\text{-}ArN_2O^-} \qquad (10)$$

That reaction 9 is perceptibly slow is perhaps surprising, since the fast coupling rates of this particular diazonium ion are well known. Presumably the other diazonium salts will react more slowly, although the higher *p*H required to produce the *syn*-diazotates[4] may more than compensate for a smaller k_+.

The activation energy of the isomerization 7 can be calculated roughly from the data in Table I. An Arrhenius plot with an activation energy of 22.5 kcal. fits these data reasonably well and also fits nearly as well the potentiometric kinetics of Grachev[6] for the reactions of the diazotate to give the "nitrosaminate" and also the reaction of the "diazodiazotate" to give the "diazonitrosaminate." The rather high activation energy for such a fast reaction is strongly suggestive of a unimolecular isomerization process rather than some more complex mechanism yielding first-order kinetics.

The spectrum of the *syn*-diazotate, obtained by an extrapolation to zero time, is consistent with the structure assigned, since it shows a less intense maximum at shorter wave length than the *anti*-isomer. In contrast to the other *syn*-diazotates reported by Le Fèvre and Sousa[14] there is a clear maximum, although it is possible that there is a slight contamination with the *anti*-isomer as explained in the Experimental part. The spectrum of the *anti*-diazotate agrees with that reported by these authors.

The rapid attainment of equilibrium between the *anti*-diazotate and its conjugate acid prompts us to assign to the latter the *anti*-diazohydroxide structure, presumably identical with the *anti*-diazohydrate containing a hydroxyl group of Hantzsch and Pohl.[15] However, our evidence does not exclude either the nitrosamine structure or another conjugate acid involving the nitro group.

The conversion of the *anti*-diazohydroxide to diazonium salt clearly involves at least two mechanisms. The second term of eq. 4 is presumably the usual acid-catalyzed loss of a hydroxyl group, involving the loss of water from the conjugate acid of the diazohydroxide. The first-order term may represent either the ionization 11 or an isomerization 12 followed by ionization. We cannot at present distinguish between these processes. A rough activation energy of about 16 kcal. or more can be calculated if we assume that the reaction of Engler and Hantzsch[16] measured conductimetrically after the addition of the diazotate to a twofold excess of hydrochloric acid at 0° is the same reaction.

$$\mathrm{\mathit{anti}\text{-}ArN_2OH \longrightarrow ArN_2^+ + OH^-} \qquad (11)$$

$$\mathrm{\mathit{anti}\text{-}ArN_2OH \longrightarrow \mathit{syn}\text{-}ArN_2OH} \qquad (12)$$

The rates at higher *p*H are fitted reasonably well by equations 4 and 5; the higher value of the first-order constant (selected to best fit these data) is not unreasonable considering the temperature difference. The agreement of the data over this wide range of rates (nearly a factor of 2000) with the calculated values is gratifying and lends support to the assumption that in this *p*H range there are only the two kinetically distinguishable routes back from diazotate to diazonium ion represented by the two terms in the rate equation. The discrepancy at the highest *p*H, while possibly not experimentally significant, is in the direction demanded by the occurrence of a small amount of the reverse of reaction 7, which is called for by the principle of microscopic reversibility. This reverse reaction may also be the initial step in the coupling of *anti*-diazotate in basic solution observed by Hantzsch.[17]

We have found no evidence of a further isomer of the diazohydroxide, the nitrosamine of Hantzsch and Pohl,[15] but a possible structure of their compound is suggested by the method of preparation. If one calculates the rate of reaction 6 as a function of *p*H with the equilibrium 2 also considered, it can be seen that regardless of the value of the rate constant for (6), the rate must attain a maximum which is rather sharp at *p*H 7.5. Since this *p*H can be obtained readily from carbon dioxide and sodium bicarbonate, the possibility that the nitrosamine was really the unsubstituted diazo oxide cannot be ignored, especially since Orton[9] has shown that some of Hantzsch's other nitrosamines were indeed diazo oxides. The spectra given by Hantzsch and Lifschitz[18] for these compounds are unfortunately not reliable. The spectrum of the stable diazotate shows two maxima where ours (and Le Fèvre's[14]) shows only one.

Acknowledgment.—We wish to acknowledge

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[14] R. J. W. Le Fèvre and J. B. Sousa, *J. Chem. Soc.*, 745 (1957).

[15] A. Hantzsch and W. Pohl, *Ber.*, **35**, 2964 (1902).

[16] A. Engler and A. Hantzsch, *ibid.*, **33**, 2147 (1900).

[17] A. Hantzsch, *ibid.*, **27**, 2968 (1894).

[18] A. Hantzsch and J. Lifschitz, *ibid.*, **45**, 3011 (1912).

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HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE, AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF SOUTHAMPTON]

Reactivity of the Phenyl Cation in Solution

BY EDWARD S. LEWIS

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The relative rates of reaction of the phenyl cation (produced from the benzenediazonium ion) with water and with chloride ion have been measured by measurement of the yields of chlorobenzene as a function of chloride ion concentration. The corresponding competition between water and sulfate ion was studied with lower precision. The competition factor (k_{Cl}/k_w) of less than three is small and is consistent with the very high reactivity of this unstable carbonium ion.

Introduction

The evidence for the intermediacy of the phenyl cation in the decomposition of benzenediazonium salts is considerable. It includes the kinetics which show independence of rate on anions,[1] independence on acidity over a wide range[2] and a very low solvent sensitivity.[3] Furthermore the effect of substituents on the rate is inconsistent with a solvent attack mechanism, but fits well the unimolecular nitrogen loss mechanism.[4] Qualitative observations of the formation of chloro compounds from reactions in the presence of chlorides[5] also are to be expected from an intermediate aryl cation, and the isolation of an interesting series of compounds, including the diphenylchloronium ion, are most easily understood as reactions of the phenyl cation with chlorobenzene, etc.[6]

In this paper the formation of chlorobenzene from the decomposition of benzenediazonium ions in aqueous chloride solutions is studied quantitatively, both as a further confirmation of the mechanism and to study the reactivity of the very unstable phenyl cation. Reactions 1, 2 and 3 represent the assumed mechanism.

$$ArN_2^+ \xrightarrow[k_1]{\text{slow}} Ar^+ + N_2 \qquad (1)$$

$$Ar^+ + H_2O \xrightarrow{k_w} ArOH + H^+ \qquad (2)$$

$$Ar^+ + Cl^- \xrightarrow{k_{Cl}} ArCl \qquad (3)$$

The yields of phenol (Y_{ArOH}) and chlorobenzene (Y_{ArCl}) can be shown to be related by the equation 4.

$$\frac{Y_{ArCl}}{Y_{ArOH}} = \frac{k_{Cl}(Cl^-)}{k_w(H_2O)} \qquad (4)$$

The ratio k_{Cl}/k_w will be called the competition factor for the chloride ion. The constancy, except for salt effects, of this competition factor, which is equal to $Y_{ArCl}/Y_{ArOH}.(H_2O)/(Cl^-)$, is confirmation of the mechanism.

Equation 4 also would be derived from the mechanism represented by the bimolecular displacements 5 and 6, but a kinetic distinction exists.

$$ArN_2^+ + H_2O \xrightarrow{k'_w} ArOH + H^+ + N_2 \qquad (5)$$

$$ArN_2^+ + Cl^- \xrightarrow{k'_{Cl}} ArCl + N_2 \qquad (6)$$

For the first mechanism the observed rate law would be

$$d(N_2)/dt = -\ k_1(ArN_2^+)$$

while for the bimolecular mechanism the rate law would be

$$d(N_2)/dt = -\ [k'_w + k'_{Cl}(Cl^-)](ArN_2^+)$$

Unfortunately the seemingly clearcut distinction between the two kinetic laws is difficult when k'_{Cl} is small, because k'_w or k_1 is slightly depressed by salts so that the small rate decrease in the presence of sodium chloride must be compared with the decrease in the presence of some inert electrolytes. The decrease in rate observed by Blumberger[7] on addition of sodium chloride appears to be comparable to the decrease on addition of sodium sulfate or nitrate, but a precise correction for salt effect is impossible. In contrast, the increase in rate with hydrochloric acid reported by Blumberger almost certainly represents the contribution of a mechanism with a different rate-determining step. The retardation on adding electrolyte is entirely consistent with Pray's observation[3] that the rate of decomposition of benzenediazonium chloride in various solvents increases in the order water < ethanol < ether–ethanol.

We shall not consider extensively the uncatalyzed bimolecular displacement since the results reported here do not help to distinguish between the two mechanisms, and since the evidence in the first paragraph makes it improbable. It cannot be discarded completely, however, for the bimolecular displacement of nitrogen by bromide has been detected[8] in the case of the *p*-nitrobenzenediazonium ion. Furthermore, the rapid nitrogen loss

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[1] J. C. Cain, *Ber.*, **38**, 2511 (1905).

[2] H. Euler, *Ann.*, **325**, 292 (1902).

[3] H. A. H. Pray, *J. Phys. Chem.*, **30**, 1477 (1926).

[4] E. D. Hughes, quoted in J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 294 (1951); E. S. Lewis and E. B. Miller, THIS JOURNAL, **75**, 429 (1953).

[5] P. Griess, *Ann.*, **113**, 335 (1860), and many later reports.

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