mercuri-4-methoxy-2-methyl-2-pentene (**11**), formed in a 4:1 ratio. No nmr lines which might be assignable to the *cis* isomer of **10** could be observed.

Tetramethylallene (3.3 mmoles) on reaction with 2.6 mmoles of mercuric acetate produced a single compound, readily identifiable by nmr as 3-acetoxymercuri-4-methoxy-2,4-dimethyl-2-pentene (**12a**, 90% yield). Microanalysis of the bromomercuri derivative, mp 94–95°, confirmed the monoadduct structure.

Anal. Calcd for $C_8H_{15}OBrHg$: C, 22.57; H, 3.71. Found: C, 23.55, 23.68; H, 3.58, 3.72.

The Reaction of Diazonium Salts with Nucleophiles. XII. Equilibria, Rates, and Mechanisms in the Acidification of *anti*-Diazotates[1]

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Abstract: The existence and basicity of *anti*-diazotates is confirmed by concordant pH and kinetic measurements. The ionization of the conjugate acids (the position of protonation is unknown) fits the Hammett equation, $pK_a = 7.3\text{–}1.45\sigma$, in adequate agreement with much earlier work, but in sharp diagreement with one recent paper. These conjugate acids (*anti*-$ArN_2O^-\cdot H^+$) are intermediates in the quantitative conversion of *anti*-diazotates to the diazonium salts. The rate is given by the expression $d(ArN_2^+)/dt = k_1(ArN_2O^-\cdot H^+) + k_2(ArN_2O^-\cdot H^+)(H^+)$. The rate constant k_2 fits the Hammett equation roughly with a large negative ρ, but k_1 shows a distinct minimum in the Hammett plot; this observation suggests a mechanistic complexity, and two mechanisms for the unimolecular term are proposed. Ultraviolet maxima and extinction coefficients of diazonium salts and diazotates are reported, which are useful in estimating purities.

One of the oldest continuing controversies of organic chemistry is concerned with the structures of the substances present when diazonium salt solutions are made alkaline. The existence of stereoisomeric diazotates and their conjugate acids has been a subject of dispute since this isomerism was first proposed by Hantzsch in 1894.[2] More recent publications (in chronological order) have confirmed the Hantzsch scheme,[3] and have questioned the existence of the ionized *anti*-diazotate in water solution,[4] and have questioned the existence of the *syn*-diazotate.[5] Furthermore the rate of reaction of diazonium ion with hydroxide ion has been reported to be fast and reversible[3,6–8] and also to be slow.[5] The further structural problems in the nature of intermediate stages of protonation or hydroxide ion addition leading to the terms "diazohydroxides,"[9] "diazoanhydrides,"[10] and "nitrosamines,"[11] have not been yet entirely resolved, largely because of the mobility of the proton in the first and last, as explained by Zollinger.[12]

It is our opinion that the questions regarding the existence of the two diazotates are not well founded, but there does seem a need to resolve the problems posed by the apparently conflicting experimental results. This paper represents a study of several *anti*-diazotates and the equilibria and rates involved in their acidification. We shall not touch upon the question of the existence of the *syn*-diazotates raised by Porai-Koshits[5] except to note the ultraviolet absorption characterization of *syn*-diazotates reported by Lewis and Suhr[7] and their report of rapid equilibration (in good agreement with that of Wittwer and Zollinger[6]) seems unequivocal evidence of the presence of this isomer in solution, even though the characterization of the solids is unconvincing. The recent low-temperature preparation of solid *syn*-diazotates by Müller and co-workers[13] remove some of the remaining elements of doubt.

Results and Discussion

Several years ago, we presented evidence based upon ultraviolet absorption for the existence of four separate species in solutions of diazonium salts at various pH's.[3] These were: I, the diazonium ion, the only stable species at low pH; II, the *syn*-diazotate, present transiently on adding diazonium salts to high pH solution; III, the *anti*-diazotate, the rearrangement product of the *syn*-diazotate, and the stable species at high pH; and IV, the conjugate acid of III, formed transiently by acidifying III and slowly (and in poor yield) by adding diazonium salt to solutions of intermediate pH. The position of the equilibrium III + $H^+ \rightleftarrows$ IV was sharply questioned by LeFevre, Roper, and Reece,[4] who suggested that IV (or an isomer) was not extensively ionized even in fairly concentrated alkali solutions. While the isolation of clearly metal-containing salts from aqueous solutions

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[1] From the Ph.D. Thesis of Milton P. Hanson, Rice University, 1964.

[2] A. Hantzsch, *Ber.*, **27**, 1702 (1894).

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

[4] R. J. W. LeFevre, R. Roper, and I. H. Reece, *J. Chem. Soc.*, 4104 (1959); R. J. W. LeFevre and R. Roper, *ibid.*, 1875 (1963).

[5] B. A. Porai-Koshits, *Tetrahedron*, **11**, 30 (1960); B. A. Porai-Koshits and K. T. Ching, *Tr. Leningr. Tekhnol. Inst. im. Lensoveta*, **60**, 92, 103, 111 (1960).

[6] C. Wittwer and H. Zollinger, *Helv. Chim. Acta*, **37**, 1954 (1954).

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

[8] J. S. Littler, *Trans. Faraday Soc.*, **59**, 2296 (1963).

[9] A. Hantzsch, *Ber.*, **31**, 340 (1898), and many others.

[10] E. Bamberger, *ibid.*, **29**, 446 (1896); **53**, 2314 (1920).

[11] E. Bamberger, *ibid.*, **27**, 679 (1894), and many others since.

[12] H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 58.

[13] E. Müller, W. Rundel, H. Haiss, and H. Hagenmaier, *Z. Naturforsch.*, **15b**, 751 (1960).

argues against this, unusual crystal forces might make the solid stable at a pH at which the solution contained very little of the anion, so we have searched for alternative demonstrations of a more convincing nature.

Pure *anti*-diazotates are not readily prepared from strongly alkaline aqueous solutions, but the identity of these substances with those prepared by the method of Thiele[14] and Stolle[15] from arylhydrazines is clear, and this preparation gave us materials of purity in excess of 80% in all cases, as measured by the yield of diazonium salt produced on acidification measured by ultraviolet spectrum.

If potassium *anti*-*p*-nitrobenzenediazotate is extensively protonated in solutions in dilute aqueous alkali, then the ultraviolet spectrum of this solution should differ from that of the solid. In a potassium bromide disk (in which absolute absorbance is uncertain because of scattering, and concentration and thickness are not precisely determined) we find $\lambda_{\max}$ 337 mμ (log ϵ 4) and in aqueous alkali $\lambda_{\max}$ 330 mμ (log ϵ 4.18). The difference does not seem important.

If potassium *anti*-*p*-nitrobenzenediazotate is a very strong base, then the hydroxide ion concentration of a solution in water should be the same as the potassium ion. We find, to the contrary, that a solution of this diazotate in deionized water containing 2.2×10^{-3} *M* potassium diazotate has a pH of about 8.9. This crude measurement leads to the conclusion that the pK_a of the conjugate acid is about 6.2.

The dissociation constant can be determined by potentiometric titration of the diazotate with acid using a glass electrode. Our results are roughly in agreement with those of Grachev[16] and Littler,[8] and indirectly in agreement with those of Porai-Koshits and Passet,[17] as deduced by Lewis[18] by introducing some further equilibria. The method suffers from the thermal instability of the diazotate conjugate acid and reproducible time-stable titration curves are only even well approximated in two cases. The titration curves are not shown, but the results are to be found in Table I.

Table I. pK_a's of *anti*-$ArN_2O^- \cdot H^+$ in Water at 25.1°

Aryl group	Titration	Salt solution pH	Kinetic[a]	Spectral[b]
p-$CH_3C_6H_4$	...	...	7.40	...
C_6H_5	7.25 ± 0.06	7.8 ± 0.4	7.29	...
p-ClC_6H_4	7.1 ± 0.1	...	6.95	...
m-ClC_6H_4	...	...	6.75	...
p-$NO_2C_6H_4$	6.25 ± 0.05	6.4 ± 0.2	6.13	6.36 ± 0.03 (6.4)[c]
p-$N_2^+C_6H_4$	...	...	4.96[d]	...
2-Pyridyl	...	...	6.4	...

[a] Estimated error ±0.1. [b] Determined by the variation of ultraviolet spectrum with pH described as in ref 2. [c] From ref 3. [d] From ref 19.

The rate expression found in the earlier work[3,19] on *anti*-*p*-nitrobenzenediazotate and the diazotate from tetrazotized *p*-phenylenediamine proves to be general; it will be presented in more detail later. The rate could thus be used as a measure of the concentration of the conjugate acid of the diazotate. The pH dependence of this rate in the neutral to high pH region then gives the pH dependence of the conjugate acid concentration, and hence the pK_a. This proved to be the most general method of measurement of pK_a, except possibly for the fast mixing and titration technique of Littler.[8]

We conclude that the reaction *anti*-$ArN_2O^- \cdot H^+ \rightleftarrows ArN_2O^- + H^+$ does exist. We call the conjugate acid *anti*-$ArN_2O^- \cdot H^+$ because we make no effort to resolve the structural problem of the position of protonation except to note that the distinction between *syn* and *anti* remains in the conjugate acid. The pK_a values fit the Hammett equation with $\rho = +1.45$. Littler[8] reported $\rho = +1.17$, but his pK_a's do not show any serious discrepancies from ours, and the small number of points in both studies is probably sufficient to account for the difference. Our ρ gives no weight to the point for the *p*-N_2^+ substituent since the σ cannot be considered to be precisely determined,[20] although in fact it fits the line reasonably well, nor does it of course use the result for the *anti*-2-pyridinediazotate, for which no σ is applicable. Because ρ is substantially smaller than that for phenol or anilinium ion ionization, we conclude without any surprise that the negative charge in the diazotate is neither entirely located on nitrogen (Va), nor entirely on oxygen (Vb).

Va Vb

The problem of reconciling these results with the quite opposite conclusions of LeFevre and his co-workers[4] is disturbing. The equilibrium ultraviolet spectra from the two sources are not very different; we believe that LeFevre neglected the early, time-dependent behavior of the spectrum and thus overlooked the unstable intermediate.

The substituent effects on the rate behavior constitute the most interesting and novel feature of the current work. The rate law found for the *p*-nitro compound earlier[3] and considered as an entirely satisfactory (although not uniquely good) rate law for the *p*-N_2^+ case, which shows numerous further complexities,[19] now appears to be general. It is given in eq 1. The consequence of this rate law and the observed values of k_1 and k_2 are that at high pH, the second term is negligible and the rate decreases with increasing pH, representing the increasing ionization of *anti*-$ArN_2O^- \cdot H^+$ to the inert *anti*-diazotate. At an intermediate pH, the second term is still negligible, but virtually all the diazotate is converted to its conjugate acid, and the rate is independent of pH. At still lower pH, the second term becomes important and again the rate increases with decreasing pH. Figure 1 shows a typical log k_{obsd} *vs.* pH plot for the unsubstituted *anti*-benzenediazotate ion. The k_2 term could not be evaluated for the *anti*-2-pyridinediazotate, since the reaction was too fast to study well

$$d(ArN_2^+)/dt = k_1(anti\text{-}ArN_2O^- \cdot H^+) + k_2(anti\text{-}ArN_2O^- \cdot H^+)(H^+) \quad (1)$$

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(14) J. Thiele, *Ber.*, **41**, 2808 (1908).

(15) R. Stolle, *ibid.*, **41**, 2811 (1908).

(16) I. F. Grachev, *J. Gen. Chem. USSR*, **17**, 1834 (1947).

(17) B. A. Porai-Koshits and B. V. Passet, *Zh. Obsch. Khim.*, **29**, 1373 (1959).

(18) E. S. Lewis, *Texas J. Sci.*, **11**, 275 (1959).

(19) E. S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, **82**, 5399 (1960).

(20) E. S. Lewis and M. D. Johnson, *ibid.*, **81**, 2070 (1959).

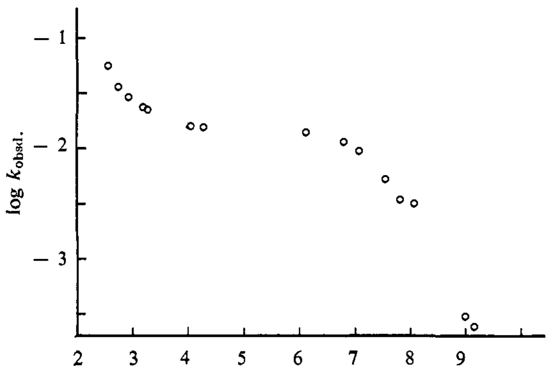

Figure 1. Dependence of rate of conversion of *anti*-benzenediazotate ion to diazonium ion on pH.

even by the time the flat portion of the curve had been reached. The values of k_1, k_2, and pK_a are readily obtained from these plots. Thus pK_a is the pH at which k_{obsd} is one-half plateau level, and at the (H^+), which we may call $(H^+)_{2x}$, at which k_{obsd} is twice the plateau level, the two terms of eq 1 are equal, so $k_2 = k_{plateau}/(H^+)_{2x}$.

The reaction rates were followed by loss of the diazotate peak, or by the formation of a coupling product with the sodium salt of 2-naphthol-3,6-disulfonic acid or with *m*-phenylenediamine. The reaction rate was shown to be independent of the concentration of the coupling reagent in the latter two cases, which were used when the diazonium salt was not stable. In several cases different methods were used on the same compound without effect on k_1, k_2, or pK_a. The value of k_1 for the *p*-nitro compound was independent of the buffer concentration and there was no evidence that k_2 ever contains any general acid catalysis component, although searching experiments more extensive than those of the earlier work[3] were not done. An attempt to determine the solvent isotope effect on k_2 for the *p*-nitro compound gave $k_{2D_2O}/k_{2H_2O} = \sim 1.3$, and $k_{1D_2O}/k_{1H_2O} = \sim 1.07$, but the precision on both k_1 and k_2 was too poor to allow any interpretation of the shape of the plot of *k vs.* mole % D_2O, to see if it fit the Gross–Butler equation as discussed by Purlee.[21] The values of k_1 and k_2 are shown in Table II and listed in order of the Hammett substituent constant σ.

Table II. Rate Constants for the First-Order and Acid-Catalyzed Conversion of the Conjugate Acids of *anti*-Diazotates to Diazonium Ions at 25.1°

Diazotate	σ	$k_1 \times 10^2$, sec^{-1}	k_2, l./mole sec
p-$CH_3C_6H_4$[a]	−0.069	5.0 ± 0.1	27 ± 4
C_6H_5[b]	0.0	1.5 ± 0.1	13 ± 1
p-ClC_6H_4[c]	+0.227	0.33 ± 0.01	7 ± 0.5
m-ClC_6H_4[c]	+0.373	0.23 ± 0.01	1.3 ± 0.2
p-$NO_2C_6H_4$[d]	+0.778	0.48 ± .01	0.053 ± 0.001
p-$N_2^+C_6H_4$[e]	+1.91	35 ± 1[a]	0.00195[a]
2-C_5H_4N[d]	...	5.8 ± 0.1	...

[a] Followed by rate of formation of diazonium salt. [b] Followed by formation of coupling product with *m*-phenylenediamine in the more acidic region and sodium 2-naphthol-2,6-disulfonic acid at higher pH. [c] Followed by coupling with *m*-phenylenediamine. [d] Followed by loss of diazotate absorption. [e] From ref 19 using the rate law of eq 1 rather than the one preferred in that paper. The measurements were made at 28.1°.

Table III shows the temperature dependence of k_1 and k_2 for the *anti*-*p*-nitrobenzenediazotate. These yield activation energies of roughly 20 and 24 kcal/mole, respectively. A pH 4.2 buffer was used to establish k_1, and k_2 was then determined by subtracting this rate from that in 0.1 *N* H_2SO_4. Rates were measured by disappearance of the diazotate peak.

Table III. Temperature Dependence of the Rate Constants in the Acidification of *anti*-*p*-Nitrobenzenediazotate

Temp, °C	$k_1 \times 10^3$, sec^{-1}	$k_2 \times 10^2$, l./mole sec
11.9	1.1	0.7
15.3	1.6	0.8
20.0	2.8	2.1
24.9	4.9	3.4
25.3	5.2	4.8

The rate constant for acid catalysis, k_2, falls regularly with increasing Hammett σ, and the correlation with $\rho = -2.4$ is rather rough but perhaps satisfactory, since the k_2's are all determined by difference between the observed rate constant and k_1, and the observed rate constant was usually less than $2k_1$, so the errors are increased.

The first-order rate constant k_1 clearly does not fit the Hammett equation, although the rate can be fitted by the expression $k_1 = k_a + k_b$, in which $\log k_a = 1.3 \times 10^{-2} - 2.6\sigma$ and $\log k_b = 3 \times 10^{-3} + 1.1\sigma^-$. The use of σ^- for k_b is quite arbitrary since there are only two points on this branch, and represents only our conviction that there is a strong resonance interaction with the substituent. Clearly one is on somewhat uncertain ground when fitting six points to a four-parameter equation, but the existance of the rate minimum is clear, so we can at least suggest a mechanistic reason for the deviations from the Hammett equation. Indeed, a duality of mechanisms is often called upon to explain such deviations, and we shall do so now, recognizing the possible weakness of the argument. The negative ρ mechanism k_a can readily be fitted by a simple ionization (eq 2) and the reverse of this reaction has been

$$anti\text{-}ArNNO^- \cdot H^+ \longrightarrow ArN_2^+ + OH^- \qquad (2)$$

recognized, especially by Littler.[8] An estimate of the expected ρ can be reached using the method of Sager and Ritchie[22] as applied to diazonium salt reactions by Ritchie.[23] This leads one to an expectation of $-4.2 < \rho < 0$ for the direct ionizations (assuming the diazohydroxide structure), and the value of ρ is dependent on the position of the transition state along the reaction coordinate. The observed value of −2.6 for ρ is well within this range and the mechanism is quite reasonable.

The arylnitrosamines are cross-conjugated systems as illustrated in contributiong structures VIa–d for the *p*-nitro case. There is substantial hindrance to rotation about the N–N bond, demonstrated clearly by nmr measurements on N-nitrosodimethylamine,[24] related to structures such as VIb. The competition for the

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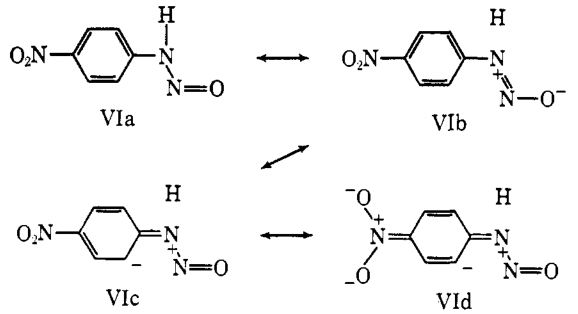
[21] E. L. Purlee, *J. Am. Chem. Soc.*, **81**, 263 (1959).

[22] W. F. Sager and C. D. Ritchie, *J. Am. Chem. Soc.*, **83**, 3498 (1961).

[23] C. D. Ritchie, J. Saltiel, and E. S. Lewis, *ibid.*, **83**, 4601 (1961).

[24] C. E. Looney, W. D. Phillips, and E. L. Reilley, *ibid.*, **79**, 6136 (1957).



VIa VIb VIc VId

unshared pair on the amino nitrogen between structure VIb and by VIc and VId together will reduce the double-bond character of the N-N bond, and the presence of especially favorable electron-withdrawing groups such as *p*-nitrophenyl, *p*-diazonitroophenyl, or 2-pyridyl will further facilitate rotation about this bond. This argument will not be qualitatively altered if the diazotate is protonated on oxygen instead of nitrogen, although of course the amount of double-bond character will be much greater with O-protonation. In fact, if we assume a tautomeric equilibrium between the *anti*-diazohydroxide structure and the nitrosamine structure, there is a good chance that the predominant species might be dependent on the substituent. While a major shift in this equilibrium with substituent would show up as a deviation in the Hammett plot of K_a, a smaller shift would probably not be conspicuous.

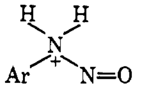
We therefore propose that the predominant mechanism for the k_1 term with electron-withdrawing groups is given in eq 3 and 4. The fast establishment of

$$anti\text{-}ArN_2O^-\cdot H^+ \xrightarrow{\text{slow}} syn\text{-}ArN_2O^-\cdot H^+ \qquad (3)$$

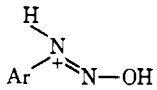
$$syn\text{-}ArN_2O^-\cdot H^+ \xrightarrow{\text{fast}} ArN_2^+ + OH^- \qquad (4)$$

equilibrium among all *syn* species has already been established. The facilitation of *syn–anti* isomerization by electron-withdrawing substituents has been observed before frequently. We can only guess about the reasonableness of the observed activation energy. The activation energy for N-nitrosodimethylamine is strongly solvent dependent, having a value of 23[24] or 20–23[25] kcal/mole as the neat liquid, of about 21 kcal in the gas phase,[26] and a value varying between 18 and 38 kcal in various concentrations in ethylene glycol,[27] which probably is most closely analogous to our aqueous solution value. The barrier in N-nitroso-N-methylaniline was not measurable, presumably because the equilibrium between the two isomers is unfavorable.[24] The suggestion that the activation energy for reaction 3 with Ar = p-$NO_2C_6H_4$ is 20 kcal/mole is defensible, since this includes about 5-kcal[18] difference in energy between the *syn* and *anti* isomers.

Two mechanisms can be proposed for the acid-catalyzed term, and we have little reason for making a choice. Assuming specific oxonium ion catalysis, the likely positions of protonation are either on nitrogen or on oxygen. Protonation on nitrogen can be expected to facilitate *anti* to *syn* conversion; if the protonated species has the structure VII, the barrier should be completely gone, and if it is VIII, the barrier should be reduced from that of the material with the proton only on oxygen. The value of ρ (*ca.* -2.4) is reasonable for



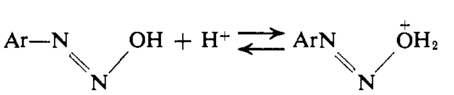
VII



VIII

this process, if we assume that the reaction after the protonation contributes very little to ρ, since it may well have very little activation energy.

Protonation on oxygen will make the rotation more difficult, but will convert the oxygen to a better leaving group. With analogy to the mechanism suggested for the k_a portion of k_1, one can postulate the mechanism represented by reactions 5 and 6; while protonation on oxygen would be expected to have $0 > \rho > -1$, the second step might add to this an amount less than that for reaction 2, since the more exothermic reaction of the conjugate acid would have a value of ρ more nearly zero following the Hammond postulate.[28] Either mechanism therefore can be reasonably expected to fit the observed substituent effects.



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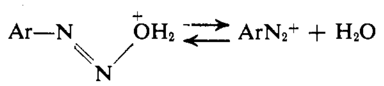

(6)

In connection with this work, a major problem has been that of the purity of the samples. We present in Table IV extinction coefficients of pure diazonium salts and diazotates determined as follows. Diazonium salts were prepared both as tetrafluoroborates and hexafluorophosphates, and some as bisulfates, and all were crystallized. The extinction coefficients given are those obtained from at least two and sometimes all three of these salts, and none were increased by further recrystallization. Only potassium *anti-p*-nitrobenzenediazotate was obtained in a highly pure state; the other *anti*-diazotates had substantial apparently transparent inorganic contaminants. There was no evidence that the conversion of the diazotates to diazonium salts was less than quantitative, so the diazotates were assayed by acidification and measurement of the ultraviolet absorption. The more rigorous purification and demonstration of purity have necessitated revision of some of the values of Lewis and Suhr.[3] In addition to the change in the spectrum of the *anti-p*-nitrobenzenediazotate implicit in Table IV, we have redetermined with more attention paid to instability the spectrum of its conjugate acid and starting material purity, and find λ_{max} 300 mμ (ϵ 1.05 × 10^4), compared to the earlier value λ_{max} 315 mμ (ϵ 5 × 10^3). Since the peak is quite broad, we do not find the discrepancy in λ_{max} serious.

When either *anti-p*-nitro- or *anti-p*-chlorobenzenediazotates are acidified in fairly concentrated cold solutions, an unstable crystalline substance precipitates. As far as we can tell, this is the same substance isolated by Porai-Koshits and Passet.[29] These detonate with a small shock, are soluble in isopropyl alcohol but not water, and have resisted attempts at further purification.

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(25) K. H. Abrahamson, P. T. Inglefield, E. Krakower, and L. W. Reeves, *Can. J. Chem.*, **44**, 1685 (1966).

(26) R. K. Harris and R. A. Spragg, *Chem. Commun.*, 362 (1967).

(27) D. J. Blears, *J. Chem. Soc.*, 6256 (1964).

(28) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(29) B. A. Porai-Koshits and B. V. Passet, *Zh. Obsch. Khim.*, 30, 286 (1960).

Table IV. Extinction Coefficients of Various ArN_2^+ and *anti*-ArN_2O^- Salts

Ar	Diazonium salts in 0.01 *M* H_2SO_4 λ_{max}, mμ	$\epsilon \times 10^{-4}$	Diazotates in 0.01 *M* NaOH λ_{max}, mμ	$\epsilon \times 10^{-4}$ [a]	Diazotate assay,[b] %
p-$CH_3C_6H_4$	277	1.63	278	1.4	83
C_6H_5	262	1.25[c]	274	1.2	81
p-ClC_6H_4	280	1.79	278	1.2	91
m-ClC_6H_4	265	0.983	274	1.1	85
p-$NO_2C_6H_4$	260	1.70	330	1.5	97
2-C_5H_4N	. . .	. . .[d]	286	1.1[d]	88[d]
p-$CH_3O_2CC_6H_4$	263	1.53			
m-$CF_3C_6H_4$	257	1.10			
m-$NO_2C_6H_4$	233	2.10			
p-$CH_3OC_6H_4$	313[e]	2.51[e]			

[a] Based on concentration of diazonium salt produced on acidification as determined by extinction coefficients in the previous column. [b] Based on mass of solid used to produce the solutions used for ultraviolet work. [c] Value determined by L. D. Hartung. [d] The 2-pyridinediazonium ion is very unstable, giving 2-pyridone rapidly. The diazotate extinction coefficient and assay is based upon the yield of 2-pyridone on acidification. [e] Determined by R. E. Holliday. The value in the thesis of M. P. Hanson is given as λ_{max} 305 mμ (ϵ 2.45 × 10^4). The λ_{max} is a transcription error from the original spectrum; the discrepancy in ϵ is probably rather larger than those we expect. Other attempts at reproducing these values have fallen within about 1% in ϵ.

Ultraviolet and infrared spectra did not clarify the structure, but the low solubility in water suggests that it is not the same as the substance detected in dilute solution. The slightly more stable *p*-nitro compound shows λ_{max} 286 mμ in isopropyl alcohol, with log ϵ 4.0 (calculated as if it were $ArN_2O^- \cdot H^+$). In a potassium bromide disk the complex infrared showed a maximum at 6.77 μ, possibly from an N-nitroso group. Reasonable model compounds do not resolve the problem. Thus the infrared peak is also shown by N-nitroso-N-methylaniline, but the ultraviolet of this model has λ_{max} 310 mμ (log ϵ 4.2), and its O-methylated isomer ($p\text{-}NO_2C_6H_4N{=}NOCH_3$) shows λ_{max} 281 mμ (log ϵ 4.1), but did not show a peak at 6.7 μ. The substance apparently contains no *syn*-diazo structures, for it does not couple with naphthol derivatives without prior treatment with acid. An *anti,anti*-diazoanhydride or N-nitrosodiaryltriazene are conceivable structures which we can no more than suggest.

Experimental Section

Potassium *anti-p*-Nitrobenzenediazotate. The method of Schraube and Schmidt[30] gave dark red prisms which changed to yellow powder on drying.

Anal. Calcd for $C_6H_4N_3O_3K$: K, 19.05. Found: K, 19.08 (as tetraphenylboride).

Substituted Phenylhydrazines. Diazonium salts were reduced with stannous chloride following McPherson and Stratton.[31]

2-Chloropyridine. Diazotization of 2-aminopyridine in concentrated hydrochloric acid yielded this substance contaminated with the higher boiling 2-pyridone.[32]

2-Hydrazinopyridine. The method of Fargher and Furness[33] yielded the hydrazine in only 14.5% yield from 2-chloropyridine.

***anti*-Diazotates.** These were made from the hydrazines following Thiele[14] and Stolle.[15] The following preparation of sodium *anti-m*-chlorobenzenediazotate is typical. Sodium methoxide (3.08 ml of 3.25 *M* methanolic solution, 0.01 mole), *m*-chlorophenylhydrazine (0.48 g, 0.01 mole), and amyl nitrite (2.75 ml, 0.02 mole) were combined in cold anhydrous ether (20 ml). The mixture was stirred briefly and evolution of gas started. The mixture was allowed to stand 4 hr in the refrigerator. The resulting suspension of white solid was centrifuged and the solid was washed with ether and then vacuum dried. The yield was 1.1 g (62%) which was not improved by attempted recrystallization from ethanol, dimethylformamide, or various other mixtures.

2-Pyridinediazotate. In addition to the above preparation, the method of Chichibabin and Rjazancev[32] by diazotization of the sodium salt of 2-aminopyridine with amyl nitrite was tried. The product appeared to be the same but less pure than that from the hydrazine.

Acidification Product of Diazotates. When cold concentrated water solutions of *anti-p*-nitrobenzenediazotate or the *p*-chloro compound were acidified with 1 equiv of hydrochloric acid, a crystalline precipitate formed rapidly. This was separated by filtration on a sintered glass funnel. The product from the *p*-chloro compound immediately decomposed to a brown tar, the *p*-nitro compound was dried under vacuum for 15–20 min, and the ultraviolet spectrum was measured in isopropyl alcohol, the infrared spectrum in a mull in Nujol or fluorocarbon, but only a peak at 6.77 was not common either to the diazonium salt or the diazotate. The solution in isopropyl alcohol did not couple with sodium 2-naphthol-3,6-disulfonate unless acid was added. The substance detonated when struck.

Model Compounds for Spectra. The method of Meldola and Salmon[34] was used to prepare N-methyl-N-nitroso-*p*-nitroaniline. *p*-Nitrobenzenediazomethoxide was prepared in 26% yield by the method of von Pechmann and Frobenius.[35] The intermediate silver diazotate is hazardous; a sample detonated on handling.

Titration of *anti*-Diazotates. A sample of the diazotate (0.1–0.2 g) was weighed into a 100-ml beaker and dissolved in 60 ml of chilled, carbon dioxide free, distilled water. The beaker was placed in an ice bath and stirred magnetically, and nitrogen was blown over it to prevent absorption of carbon dioxide. The titration using 0.01 *N* hydrochloric acid or 0.01 *N* bromoacetic acid was followed potentiometrically with a glass–calomel electrode system. The pH readings toward the end of the titration were less erratic when bromoacetic acid was used.

Hydrolysis of *anti*-Diazotates. A sample of diazotate was weighed into a 10-ml volumetric flask and diluted to the mark with freshly distilled, carbon dioxide free water. The pH was measured using a Beckman Model H-2 pH meter with a glass–calomel electrode system. The meter was calibrated in the expected pH region with buffers made up according to the directions of Britton.[36]

Spectrophotometric Ionization Constant of the Conjugated Acid of *anti-p*-Nitrobenzenediazotate. The method of Lewis and Suhr[3] was followed, except that in determining the spectrum of the conjugate acid all spectra were extrapolated back to the time of mixing assuming a pseudo-first-order course. The result was K_a = 4.4 ± 0.4 ± 10^{-7} at an ionic strength of 0.06 *M*.

Rate Measurements. Rates were measured by following absorption changes in the visible or ultraviolet on a Cary Model 14 spectrophotometer. Temperature control was achieved by circulating water from a thermostat. All reactions were followed essentially to completion, and first-order rate constants were calculated from a plot of log $(A - A_\infty)$ or log $(A_\infty - A)$ *vs.* time. The rate constants were calculated by the method of least squares from several points well distributed on the curve. The numbers following the ± figures in Table II are rough estimates of uncertainty based upon average deviations from the mean of about 2–5% in 2–5 replicate experiments at each point on curves such as that of Figure 1. The method of initiating the reaction depended on the rate; the fastest method was to mix the dry diazotate (*ca.* 0.5 mg) with 5 mg of coupling compound (in the cases where it was used; see footnotes to Table II). Reaction was then started by filling the cell with buffer solution at the thermostat temperature; the mixture was shaken in the cell to complete solution and then placed in the cell compartment, and readings could be obtained in as little as 15–20 sec after mixing.

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