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The Substituent Constants of the Diazonium Ion Group

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The ionization constants of benzoic and phenylacetic acids substituted with the diazonium ion group have been measured. The Hammett substituent constants derived from these are supported roughly by rate measurements of coupling reactions of tetrazonium salts and brominations of the substituted acetophenones, yielding $\sigma_p = 1.8 \pm 0.5$ and $\sigma_m = 1.7$. A $\sigma = 3$ was obtained from the ionization constants of *p*-hydroxybenzenediazonium ion and *p*-aminobenzenediazonium ion. These results show that the diazonium ion group is the most powerful electron-withdrawing group known.

Introduction

Few reactions have been studied in which it is the substituent rather than the diazonium ion group that reacts. Before undertaking the detailed study of one such reaction, it was considered to be of some advantage to use several reactions of aromatic compounds, for which the Hammett[1] reaction constant ρ has been measured, to determine the Hammett substituent constant σ of the N_2^+ group. The strong activating effect of the diazonium ion group toward aromatic nucleophilic substitution in the *o*- and *p*-positions was observed by Hantzsch in 1897.[2,3] He observed that whereas the 3,5-dibromobenzenediazonium chloride is stable, 2,4- and 2,6-dibromobenzenediazonium chlorides rearranged in alcohol at room temperature to bromochlorobenzenediazonium bromides. Many other examples have since been noted and have led Bunnett and Zahler[4] to remark that the diazonium ion group is the most strongly activating group to such substitutions. More recently, Bolto, Liveris and Miller[5] have made quantitative measurements on the displacement of fluoride ion from substituted aromatic fluorides by methoxide ion in methanol. The extent of the activation by the diazonium ion group is shown by the substituent rate factors at 0°—$H:p\text{-}NO_2:p\text{-}N_2^+ = 1:6.2 \times 10^{10}:1.68 \times 10^{16}$. Similarly de Jonge and Dijkstra[6] observed in the titration of *p*-hydroxybenzenediazonium bisulfate against alkali, that the second ionization constant (that of the phenolic group) was of the order of 3×10^{-4}, whereas the ionization constant of *p*-nitrophenol[7] is approximately 6.2×10^{-8}. These results are insufficient to calculate reliably the Hammett substituent constants.

Experimental

Hydroxybenzenediazonium Fluoborates.—Aminophenol (4 g., 0.037 mole, either *m*- or *p*-) was dissolved in fluoboric acid (20 ml., 50%) and cooled to about −30° when liquid dinitrogen trioxide, distilled from sodium nitrite (*ca.* 0.1 mole) and excess concentrated sulfuric acid, was added. The mixture was stirred manually and the temperature was allowed to rise to about 5°, and then lowered again by addition of solid carbon dioxide, when a further quantity of dinitrogen trioxide was added. The solution was allowed to warm to 5°, and again cooled with solid carbon dioxide. The solid that separated was filtered off with suction at solid carbon dioxide temperature, and when dry was washed with absolute ether. The product was dissolved in the minimum of acetone at 0° and some activated charcoal was added. The solution was shaken for about 30 seconds and rapidly filtered into absolute ether. The solid formed was filtered, washed with absolute ether and dried *in vacuo*. The *p*-hydroxybenzenediazonium fluoborate was a white solid, yield 5.0 g. (65%). The *m*-hydroxybenzenediazonium fluoborate was light orange, yield 6.1 g. (79%), and was less stable during recrystallization than the *p*-isomer, the pale orange color probably being due to decomposition products.

***p*-Phenylenebis-[diazonium Fluoborate].**—*p*-Phenylenediamine was tetrazotized by the method described above for the hydroxybenzenediazonium fluoborates, except that twice the quantity of dinitrogen trioxide was used and the solution was filtered at 5° before the final cooling with solid carbon dioxide. No satisfactory method of recrystallization could be found, but slight improvement in product color was made by mixing the powdered product with a little 50% fluoboric acid, stirring for a few minutes, and separating and drying the product as above; yield from 4 g. of *p*-phenylenediamine was 9.1 g. (80%).

***m*-Phenylenebis-[diazonium Fluoborate].**—*m*-Phenylenediamine was tetrazotized by the method of Kosolapoff and Duncan[8] and was recrystallized by dissolving in 50% fluoboric acid at about 35° and cooling to the temperature of solid carbon dioxide, when a white crystalline solid separated; yield from 11 g. of *m*-phenylenediamine dihydrochloride was 10 g. (54%).

***p*-α-Toluic Acid Diazonium Fluoborate.**—*p*-Amino-α-toluic acid was diazotized in hydrochloric acid solution by the addition of sodium nitrite solution at 0–10°; a slight excess of sodium fluoborate solution precipitated the fluoborate. As the product was rather soluble, liquid volumes were kept to a workable minimum. The product was filtered with suction and when dry was washed with absolute ether. Suction was discontinued when most of the ether had been removed, since prolonged suction caused the product to assume a strong pink color. The remainder of the ether was removed *in vacuo*, and the product was rapidly recrystallized from acetone–ether at less than 0°, filtered, washed with ether and dried as above; yield 30%.

***p*-Aminobenzenediazonium Fluoborate.**—The hydrolysis of *p*-acetaminobenzenediazonium fluoborate with 1 *M* fluoboric acid at 70°[9] yielded *p*-aminobenzenediazonium fluoborate readily. The other diazonium salts were made by the standard procedure described above for *p*-α-toluic acid diazonium fluoborate.

Determination of Ionization Constants.—The ionization constants of the three carboxybenzenediazonium ions were determined in aqueous solution by potentiometric titration using a Beckman model D *p*H meter in conjunction with glass and calomel electrodes. A known weight of diazonium salt was dissolved in water at 0° and titrated against sodium hydroxide to the equivalence point. In each case the observed equivalence point agreed with that calculated to within 3%. The titration then was repeated by adding almost one-half an equivalent of alkali, titrating slowly over the middle range and then adding the remainder of the alkali. The value of the *pK* was taken from the *p*H at the half-equivalence point (after correction for the amount of acid ionized[10]) of the second titration, since the rapid addition kept the decomposition of the conjugate base formed to a

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

[2] A. Hantzsch, *Ber.*, **30**, 2334 (1897).

[3] A. Hantzsch and J. S. Smythe, *ibid.*, **33**, 505 (1900).

[4] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 308 (1951).

[5] B. A. Bolto, M. Liveris and J. Miller, *J. Chem. Soc.*, 750 (1956).

[6] J. de Jonge and R. Dijkstra, *Rec. trav. chim.*, **68**, 426 (1949).

[7] G. W. Wheland, R. M. Brownell and E. C. Mayo, THIS JOURNAL, **70**, 2492 (1948).

[8] G. M. Kosolapoff and J. J. Duncan, *ibid.*, **77**, 2419 (1955).

[9] Badische Anilin- & Soda-Fabrik, Ludwigshafen, German Patent 205,037; *C. A.*, **3**, 1595 (1909).

[10] J. E. Ricci, "Hydrogen Ion Concentration," Princeton University Press, Princeton, N. J., 1952, p. 67.

minimum. The ionization constant of *p*-α-toluic acid diazonium fluoborate was determined in a similar manner to that described above except that decomposition was more rapid; even in aqueous solution, before addition of alkali, a red color was produced and gradually increased in intensity. The *pK* was therefore determined as rapidly as possible by placing exactly one-half of an equivalent of alkali in a beaker flushed with carbon dioxide-free air just beneath the two electrodes. The weighed quantity of diazonium salt was quickly dissolved in water and poured into the alkali. The solution was thoroughly mixed by manual swirling and the *p*H was observed immediately following this mixing. For about the first five seconds after mixing the *p*H rose slightly (*e.g.*, 3.18–3.29) and then remained constant for the next 20–30 seconds. Further observation of the *p*H was not made to avoid the deposition of solid decomposition products on the surface of the glass electrode. No complete titration could be carried out. The *pK* was taken from the steady value of the *p*H (after correction[10]) approximately 15 seconds after mixing. The ionization constant of *p*-hydroxybenzenediazonium ion was determined as described for the carboxybenzenediazonium ions. However, no exact value could be obtained for the *m*-isomer as its decomposition was too rapid. A rough plot of apparent *p*H at the half-equivalence point against time showed that the *pK* was greater than 4.5, but no reasonable extrapolation could be made to zero time. The ionization constant of the *p*-isomer was also determined spectrophotometrically using a Cary model 14 spectrophotometer. The ultraviolet spectrum of the diazonium salt was observed in buffer solutions of *p*H ranging from 2.2 to 3.8 (Clark and Lubs[11]) and also in 1 *M* perchloric acid solution and at *p*H 8.6.[12] From the latter two solutions the extinction coefficients of the two forms were determined at 310 mμ (λ_{max} hydroxydiazonium ion, ε 2.27 × 10^4) and at 349 mμ (λ_{max} diazooxide, ε 4.2 × 10^4) and from the former solutions the *p*H at which the two concentrations were equal was therefore determined. The reversibility of the reaction was also demonstrated. The ionization constant of *p*-aminobenzenediazonium ion was determined spectrophotometrically in solutions of sulfuric acid from 20–99% in the same manner, but using the wave lengths 354 mμ (λ_{max} aminobenzenediazonium ion) and 247 mμ (λ_{max} conjugated acid). One-half of the amine was protonated in 63.4% sulfuric acid.

Determination of Coupling Rates with 2-Aminonaphthalenesulfonic Acid.—The rates of these reactions were determined by a method based on that of Zollinger and Wittwer,[13] but the extreme reactivity of the diazonium salts used necessitated the development of a spectrophotometric method. Solutions of the aminosulfonic acid (approximately 10^{-6} molar) were made in perchloric acid (1.74 and 0.872 molar), and 25 ml. of one of these solutions was placed in a 10-cm. spectrophotometer cell thermostated at 20.0°. A solution of *p*-phenylenebis-[diazonium fluoborate] (*ca.* 3 × 10^{-3} molar) was accurately prepared in 8.72 molar perchloric acid and cooled to 0°. One ml. of the cold diazonium solution was added to the spectrophotometer cell and the spectrum of the product was observed in the visible region. The experiment was then repeated with the wave length fixed at 575 mμ (λ_{max} of the azo compound formed), and the change in optical density with time was observed. Since the tetrazonium salt was in large excess, its concentration remained virtually constant, so the reaction followed a first-order course, and the apparent rate constant was a function of the fraction of the aminosulfonic acid in the unprotonated form and of the concentratation of *p*-phenylenebis-[diazonium fluoborate]. Correction was made for a statistical factor of 2 in the rate constant. The amount of heat liberated on addition of 1 ml. of 8.72 molar perchloric acid to the solution in the cell was about equal to the heat necessary to bring the same amount of perchloric acid from 0–20°; the final temperature of the solution was therefore 20.0 ± 0.1°. An attempt to duplicate this experiment with *m*-phenylenebis-[diazonium fluoborate] was unsuccessful, as the decomposition of the diazonium salt masked the coupling at the acidities used. By making the concentration of the aminosulfonic acid approximately 100 times that of the diazonium salt, the coupling reaction was made to predominate. A rate constant could be obtained for the pseudo first-order formation of one of the peaks in the spectrum of the azo compound, but another peak was seen to increase rapidly and then to decrease at about the same rate that the first peak had increased. This suggested that there is an intermediate in the formation of the azo-compound, possibly the diazoamino compound, the rates of formation and decomposition of which are comparable. The rate constant obtained may therefore be unsuitable for comparison with similar constants obtained where no such intermediate has been observed, *i.e.*, in the reactions studied by Zollinger.[14]

Determination of Rates of Bromination of Acetylbenzenediazonium Ions.—The rates of bromination of the substituted acetophenones were determined in acid solution in the manner described by Emmons and Hawthorne.[15] The method depended upon the spectrophotometric determination of the concentration of bromine as a function of time in the presence of a large excess of the substituted acetophenone. The plot of bromine concentration was therefore a straight line, since the reaction is zero order with respect to bromine. Slight curvature in the plots was attributed to a change during the reaction in the extinction coefficient of the total bromine due to the reaction

$$Br_2 + Br^- = Br_3^-$$

This was overcome by carrying out the reactions in the presence of an excess of bromide ion. The reactions were carried out in 50% acetic acid 2 molar in hydrochloric acid, containing 2.5 × 10^{-2} molar sodium bromide, and the temperature was 25 ± 0.4°. In the bromination of *p*-acetylbenzenediazonium fluoborate slight curvature was observed, whereas identical runs on acetophenone and its *m*-nitro and *p*-methyl derivatives showed no such curvature. This was even more marked with the *m*-isomer, and is ascribed to the presence of small amounts of the corresponding undiazotized amine or of the corresponding phenol, since these would certainly be very much more reactive toward bromine. Recrystallization of the diazonium salt from methanol or acetone did not help the plots. Besides producing curvature in the plots, the above impurities would also be expected to add to the over-all observed constant for the disappearance of bromine, which can therefore be considered only as a maximum possible rate for the enolization of the acetylbenzenediazonium ion. This is particularly so in the case of the *m*-isomer, where decomposition of the diazonium group to the reactive phenol would be expected to be fairly rapid and to occur to a significant extent during the bromination reaction.

Results

In Table I are shown the results obtained, and the corresponding values of σ.

The *pK*'s of the phenols and carboxylic acids have been corrected for the amount of ionized acid present at the mid-point of the titration.[10] No correction has been made for the effect of ionic strength because the exact magnitude and direction of this effect are uncertain. However, it is to be expected that to a first approximation the effect will be small, since the reactions are of the charge type

$$HA^+ + H_2O = H_3O^+ + A$$

in which there is no change in the number of ions or of the total charge.[16]

The value of the *pK* for the anilinium ion is not accurate, since the value −4.71 used for the *pK* is the Hammett acidity function[17] for 63.4% sulfuric acid in which the amine is 50% protonated. As the base is positively charged, it would be more appropriate to use an acidity function H_+, but this unfortunately has never been determined. The coupling rates shown in Table I are values extrapolated to $\mu = 0.25$ from measurements made in approximately 1.0 and 2.0 molar solutions. The

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[11] H. T. S. Britton, "Hydrogen Ions," Vol. 1, 3rd edition, D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 303.

[12] Reference 11, p. 307.

[13] H. Zollinger and C. Wittwer, *Helv. Chim. Acta*, **35**, 1220 (1952).

[14] H. Zollinger, *ibid.*, **36**, 1730 (1953).

[15] W. D. Emmons and M. F. Hawthorne, THIS JOURNAL, **78**, 5593 (1956).

[16] Reference 1, p. 260.

TABLE I

MEASURED VALUES

Reaction	Temp., °C.	*meta*	*para*	σ *meta*	σ *para*	ρ[17]	$-\log k_0$[17]
pK of benzoic acids[a]	0	2.55	2.41	1.76	1.91	0.947	4.221
pK of phenylacetic acids	25		3.24		2.18	0.487	4.297
Rates of coupling μ 0.25 *M* $10^{-5}k$, l. mole^{-1} sec.$^{-1}$	20	(9.3)[b]	9.32	(1.3)[b]	1.32	4.26[14]	0.350[14]
Rates of bromination 10^5k, sec.$^{-1}$	25	<13.1	<5.11	>0.2	>1.1	−0.423[17]	3.801[c]
pK of anilinium ions	25		−4.71[d]		3.43[g]	2.767	4.557
pK of phenols[e]	25		3.40		3.04[g]	2.113	9.847
pK of phenols[f]	0	>4.5	3.47	<2.1	3.02[g]		

[a] *pK* for *o*-carboxybenzenediazonium ion = 1.47. [b] Uncertain values; see text. [c] Determined by a separate experiment. [d] The Hammett acidity function[18] H_0 for 63.4% sulfuric acid. [e] Spectrophotometric determination. [f] Potentiometric determination. [g] Values for σ^*.[17]

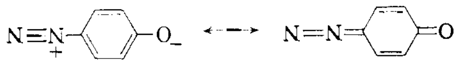
large ρ for this reaction renders the errors in σ by this extrapolation very small. On the other hand, the small negative ρ for the bromination reaction renders the errors in σ very large, and as the rate constants are only the maximum possible values, the σ's determined for this reaction must be considered to be inaccurate minimum values.

Discussion

It has been pointed out by Roberts, Clement and Drysdale[19] that ionic substituents will be particularly subject to interaction with the solvent. Theoretically, therefore, the comparison of the rate of a reaction of a compound containing a charged group with those of compounds containing no charged group is hardly valid as a method of determining σ unless the reaction takes place in a medium of infinite dielectric. In aqueous solution, therefore, a variation must be expected in σ-values obtained from different reactions. If we ignore the values 3.02 and 3.04 obtained in this work for the reactions of the phenol and the amine, the variation in $\sigma_{p\text{-}N_2^+}$ from 1.32 to 2.18 is not unreasonable, and compares favorably with the variation in σ from 0.664 to 1.112 observed for the *p*-trimethylammonium ion group.[16,17] That this range is hardly different from those for neutral groups has been taken as practical evidence for the applicability of the Hammett equation to reactions of compounds carrying charged substituents.[17,19] It is certainly justified therefore to compare the σ's for one charged group with those for other similarly charged groups, and comparison is probably justified to a lesser precision with σ's obtained for uncharged groups.

As only one dependable value could be obtained for the *m*-diazonium ion group, this is best discussed in terms of the particular reaction involved, *i.e.*, the ionization of the substituted benzoic acids. The values of σ for the *meta* (1.76) and *para* (1.91) diazonium ion groups are both considerably higher than the corresponding σ's (1.02 and 0.88, respectively) for the trimethylammonium ion group, indicating a greater tendency to withdraw electrons by the former group. With the trimethylammonium ion group the ratio $\sigma_{\text{para}}/\sigma_{\text{meta}}$ is less than unity, whereas the corresponding ratio for the diazonium ion group is greater than unity. The former ratio has been explained[19] as due to the stronger direct or inductive effect of the trimethylammonium ion group in the *m*-position and the complete lack of any resonance effect in the *p*-position. The reversal of this ratio for the diazonium ion group thus suggests the retention of the above direct effect, but coupled here with an extremely strong resonance effect which is most important at the *p*-position, with the result that both *meta* and *para* σ's for this group are greater than those for the trimethylammonium ion group. The presence of a strong resonance effect is supported by the much higher values of σ obtained for the phenol and anilinium ion ionizations. This is quite parallel to the use of a special σ for these reactions by Hammett[20] and Jaffé,[17] who proposed the term σ^*. Both authors ascribe the need for this special substituent constant to the important resonance with NH_2 or O^- groups, in our case represented by the important contribution of the diazo-oxide structure Ia, as well as the ordinary structure Ib.

Ib Ia



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[17] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[18] Reference 1, p. 267.

[19] J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2181 (1951).

[20] Reference 1, p. 193.