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The Basicities of Ferrocenylazobenzenes[1]

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The pK_a values for the conjugate acids of a series of substituted m- and p-ferrocenylazobenzenes were measured in aqueous sulfuric acid containing 20 vol. % ethanol. In each case, the ferrocenylazobenzene was a weaker base than the corresponding parent azobenzene; i.e., the ferrocenyl group in this study behaves as an electron-withdrawing group, in contrast to its behavior as an electron-donating group in other studies. Evidence is presented for prior protonation of the ferrocene nucleus to account for the weaker basicity of the azo linkage in these systems. Hammett σ-constants were obtained for the protonated ferrocenyl group in the m- and p-positions, and Hammett ρ-σ correlations are discussed in the light of earlier work of Jaffé with azobenzenes.

The high electron density in the rings of ferrocene is responsible for the electron donor properties exhibited by the ferrocenyl group when it is present in a system as a substituent. Nesmeyanov[4] has demonstrated this by showing that m- and p-ferrocenylanilines are stronger bases than aniline and that ferrocenylphenols and ferrocenylbenzoic acids are weaker acids than the parent compounds. A series of m- and p-ferrocenylazobenzenes were prepared in this Laboratory,[5] and their ultraviolet and visible spectra indicated considerable resonance of the p-ferrocenyl group, as an electron donor, with the azo system.

In the light of the extensive work by Jaffé[6a-g] on the basicities of mono- and disubstituted azobenzenes, it was desirable to determine the basicities of these ferrocenylazobenzenes in order to obtain a direct comparison of substituent ferrocene with other substituents.

Jaffé[6c] has established a Hammett acidity scale for the system of aqueous sulfuric acid containing 20 vol. % ethanol for the measurement of pK_a's of the conjugate acids of substituted azobenzenes. His results showed that for monosubstituted azobenzenes,[6a] σ^+'s rather than normal Hammett σ-constants are required for a good correlation, indicating considerable resonance of electron-donating groups with the reaction site. Disubstituted azobenzenes[6d] were best treated as individual series. holding a group on one ring constant for each series and correlating the data with σ-constants for the substituent on the other ring (Fig. 1. lines Y = m-NO$_2$, Y = H, Y = p-OCH$_3$ and Y = p-OH). For a series in which the constant substituent, Y, is the most electron-donating group and is in the p-position, normal σ's are required for the correlation; for those in which the constant substituent is either a m-substituent or an electron-withdrawing group, σ^+ constants are required for the variable

substituent. Further, Jaffé showed that a good correlation can be obtained for the plot of pK_a's versus the sum of σ-constants for the two groups, provided that a σ^+ is used for but one of the two substituents, namely, the most electron-donating group. This last correlation, however, reveals a slight concavity upward (see Fig. 4).

Since a single ρ-value was required for the correlation in the mono-[6a] and disubstituted[6d] azobenzene series, Jaffé concluded that the conjugate acid of azobenzene is not a "two conjugate acid equilibrium." He proposed that the proton is symmetrically disposed between both nitrogens of the azo group, and that the azobenzene substrate in the protonated form assumes a cis structure. On the basis of this structure he has discussed the spectrum and bonding of the conjugate acid.[6d]

However, Wepster, et al.,[7] have prepared and isolated the conjugate acids of both cis- and trans-azobenzene and have convincingly demonstrated Jaffé's cis structure to be incorrect. Since π-bonding of the proton with the trans-azo linkage, suggested by Cilento,[8] meets the structural symmetry requirements of Jaffé's Hammett correlations, we have used this formulation for the structure of the conjugate acids of ferrocenylazobenzenes. The uncertainty of the structure of the azobenzene conjugate acid, however, does not alter the conclusions reached in the present work concerning the effect of ferrocene as a substituent.

The pK_a's of the ferrocenylazobenzenes in the present study were determined in aqueous sulfuric acid containing 20 vol. % ethanol, utilizing the method described by Reilley and Smith.[9] Fig. 2A shows typical absorption spectra of p-ferrocenylazobenzene in solutions of varying sulfuric acid concentrations. The very weak basicity of p-ferrocenylazobenzene is reflected in the fact that in 45% sulfuric acid the base is not quite half converted to the conjugate acid. Solutions of the free base and the conjugate acid in the solvent system were found to show no decomposition over a period of several hours; the reversibility of the protonation was established by dilution of solutions of the conjugate acids to give the reappearance of the free base peaks. Figure 2B shows a typical Reilley plot

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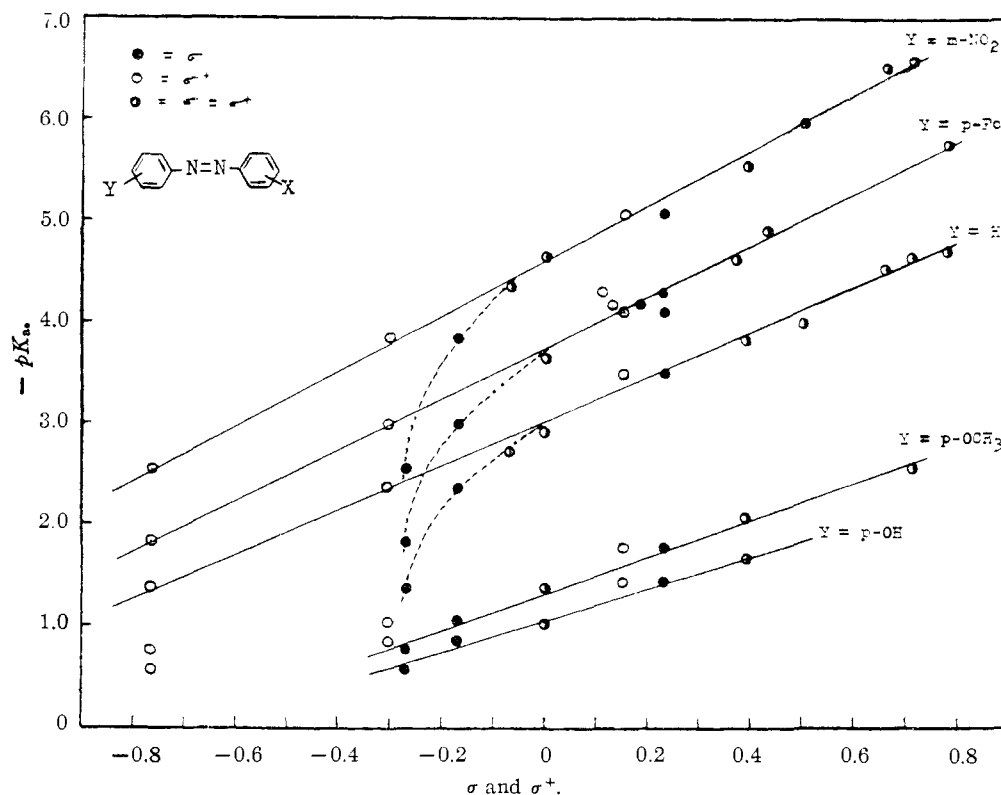(9) C. N. Reilley and E. M. Smith, Anal. Chem., 32, 1253 (1960).

Fig. 1.—pK_a's of substituted azobenzenes vs. Hammett and Brown σ-constants; lines Y = m-NO$_2$, H and p-OCH$_3$ from Jaffé.[6d]
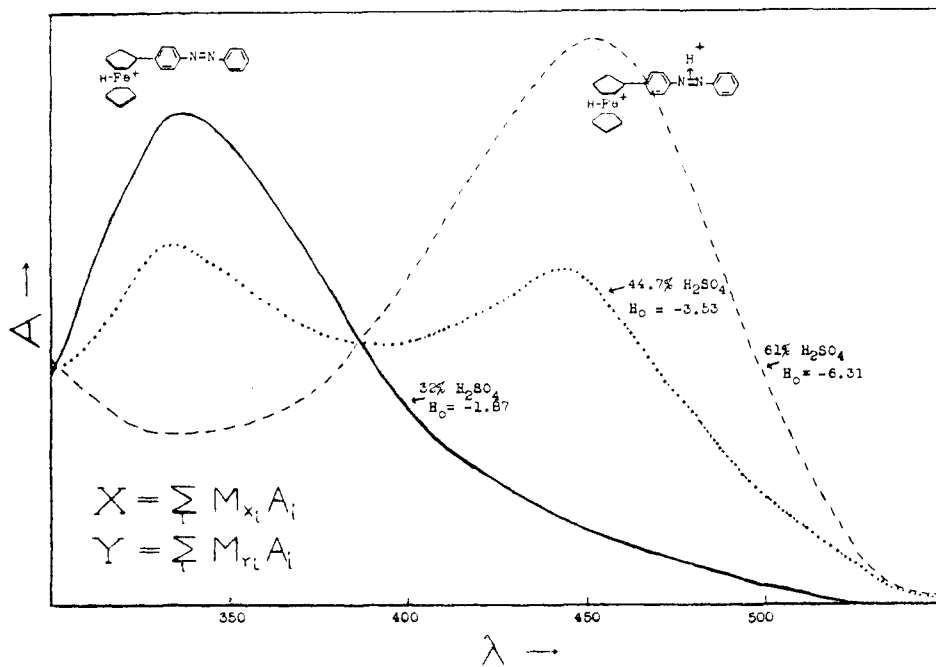

Fig. 2A.

that was used in the determination of the pK_a of the conjugate acid of p-ferrocenylazobenzene.

Table I gives the pK_a's of the conjugate acids of the m- and p-ferrocenylazobenzenes that were studied. Contrary to expectation, the compounds in both the m- and p-ferrocenylazobenzene series were weaker bases than the corresponding mono-substituted azobenzenes. This unexpected electron-withdrawing behavior of the ferrocenyl group in this system could be explained in two possible ways. Either the sulfuric acid solutions could have oxidized the ferrocenyl group to the ferrocinium ion,
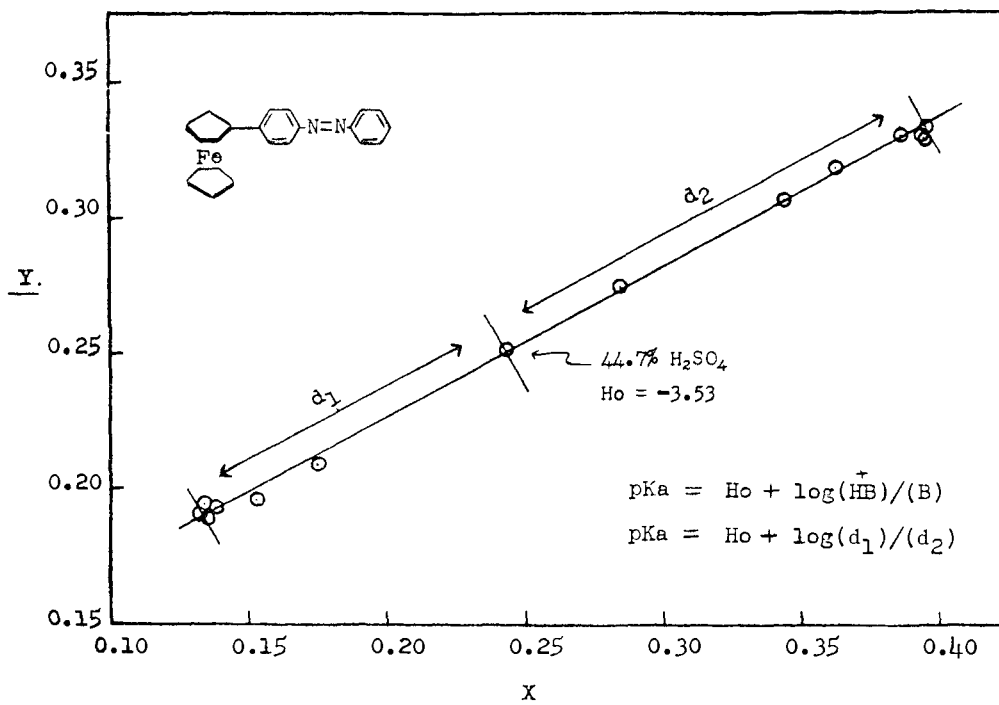
Fig. 2B.

generating a cation that would result in lower basicity (dilute sulfuric acid is known to oxidize ferrocene[10]); or a prior protonation of the iron in the ferrocenyl group could likewise decrease the ease of protonation of the azo linkage (Fig. 3). Protonation of the iron in ferrocene has been studied,[11] and such protonation in sulfuric acid solution has been used by Berger, et al.,[12] in explaining the course of acid-catalyzed decomposition of ferrocenylcarbinyl azide.

TABLE I

pK_a VALUES FOR THE CONJUGATE ACIDS OF AZOBENZENES IN AQUEOUS SULFURIC ACID SOLUTIONS CONTAINING 20 VOL. % ETHANOL AT 25°

X	Y = H (Jaffé[9a])	Y = p-Fc	Y = m-Fc
p-OCH₃	−1.36 ± 0.03	−1.82 ± 0.08	
p-CH₃	−2.35 ± .02	−2.98 ± .02	
H	−2.90 ± .02	−3.63 ± .02	−3.62 ± 0.01
p-Cl		−4.28 ± .01	−4.29 ± .01
m-Cl		−4.62 ± .02	
p-Br	−3.47 ± .02	−4.07 ± .05	−4.26 ± .02
p-I		−4.14 ± .03	−4.18 ± .03
m-CF₃		−4.91 ± .02	
p-NO₂	−4.70 ± .02	−5.74 ± .12	−5.92 ± .09

Three experiments were performed in order to distinguish between these two possible explanations. First, deliberate attempts were made to

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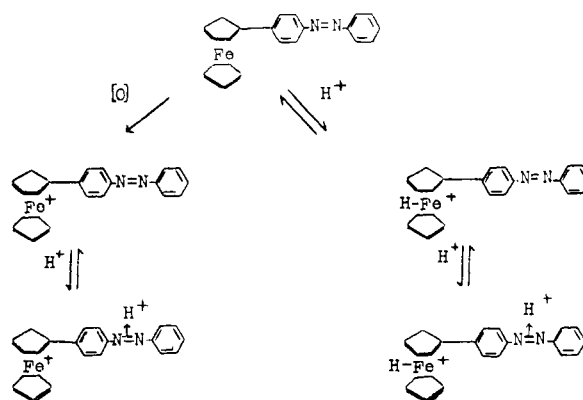(12) A. Berger, W. E. McEwen and J. Kleinberg, ibid., 83, 2274 (1961).

Fig. 3.

oxidize the ferrocene in several ferrocenylazobenzenes solutions by adding hydrogen peroxide to both neutral and acidic solutions of the ferrocenylazobenzenes. No change could be observed in the ultraviolet spectra of the solutions after the addition of the peroxide. This indicated a resistance of ferrocene in these compounds to oxidation.

Prior protonation of the ferrocene should be reversible by dilution and hence the ferrocenylazobenzene could be recoverable unchanged by dilution and extraction. On the other hand, oxidation of the ferrocene should be irreversible toward dilution and the substrate should not be extractable with a non-polar solvent. Extraction of a solution of 0.22 mg. of p-ferrocenyl-p'-bromoazobenzene in 25 ml. of 50 wt. % H₂SO₄, 20 vol. % ethanol, with CCl₄ failed to extract any of the ferrocenylazobenzene. After dilution of the solution with 100 ml. of water (to 2.7 M H₂SO₄), CCl₄ still failed to extract any of the ferrocenylazobenzene, suggesting that
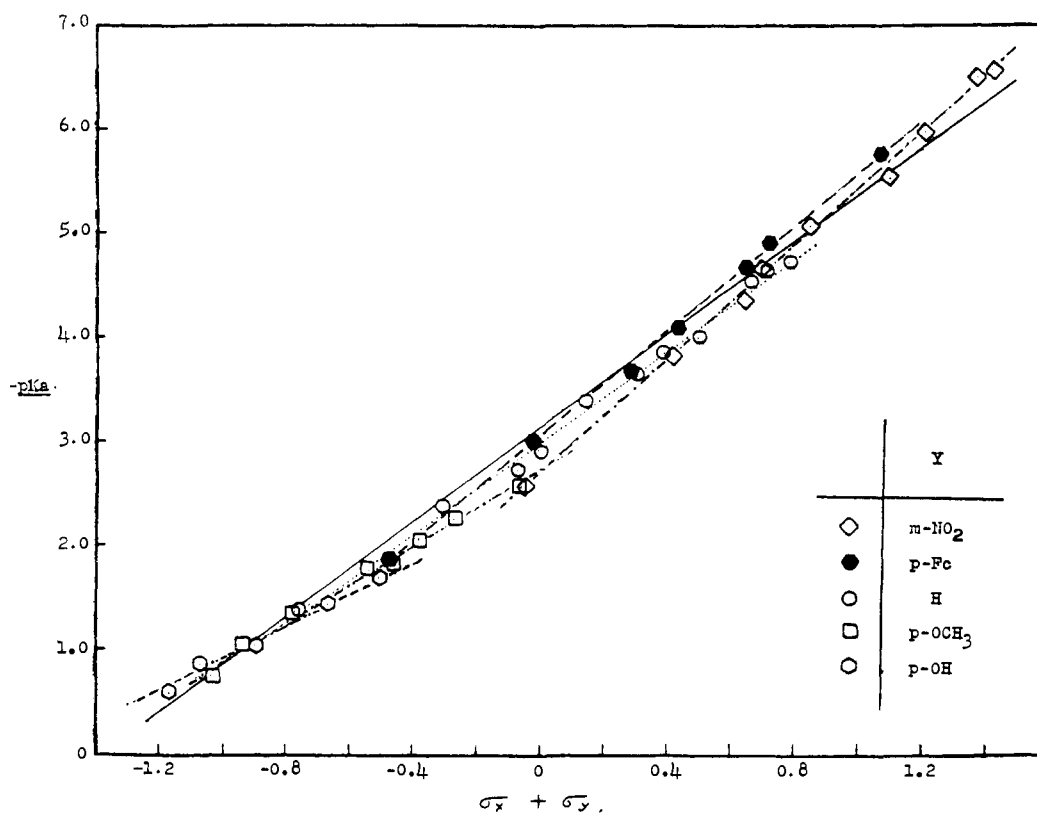
Fig. 4.—Jaffé's plot of pK_a vs. summation of σ's with p-ferrocenylazobenzene data included.

protonation of iron was still virtually complete at this dilution. However, further adjusting of the pH to 6 with 6 N NaOH resulted in recovery of 75% of the ferrocenylazobenzene by CCl_4 extraction, indicating that prior protonation rather than oxidation was occurring in these solutions.

One further experiment was performed in which measurement of pK_a's of three ferrocenylazobenzenes was attempted in a non-oxidizing medium, HCl in 20 vol. % ethanol. Hammett acidity values were obtained for several solutions of HCl in water–ethanol using azobenzene as an indicator. These solutions were used for the attempted pK_a measurements. It was found, however, that ferrocenylazobenzenes were unstable in this solvent system, as seen in a general disappearance of the ultraviolet spectral peaks. Both p-ferrocenylazobenzene and p-ferrocenyl-p'- methylazobenzene decomposed too rapidly for a pK_a measurement. Only m-ferrocenylazobenzene decomposed sufficiently slowly to afford a measurement. The value of -3.70 was obtained, which is reasonably close to the value determined in sulfuric acid. This can be taken as additional evidence for protonation of the ferrocenyl group, rather than oxidation, prior to the protonation of the azo linkage in these compounds.

Fig. 1 includes the plot of the pK_a's of p-ferrocenylazobenzenes (Y = p-Fc) versus σ and σ^+.[13] It can be seen that correlation of the data requires the use of σ^+-values for the second substituent. Since resonance of the second substituent with the

reaction site in the ferrocenylazobenzenes is important, it can be inferred from Jaffé's work with disubstituted azobenzenes[6d] that resonance of the p-ferrocenyl group with the azo linkage is not important under these conditions of high acidity, $i.e.$, the protonated ferrocenyl group does not resonate significantly with the azo system ($i.e.$, $\sigma = \sigma^+$).

Figure 5 shows the plot of the m-ferrocenylazobenzenes versus σ^+-constants of the second substituents, giving a good correlation.

From the pK_a values for p- and m-ferrocenylazobenzenes and the curve for monosubstituted azobenzenes (Fig. 1, line Y = H), it is possible to obtain Hammett σ-values for the protonated ferrocenyl group in the p- and m-positions. These values are very close: 0.291 and 0.286, respectively.

Using the value for the protonated ferrocene group in the p-position, the pK_a's of the p-ferrocenylazobenzenes were found to fit well into Jaffé's composite plot of pK_a's of disubstituted azobenzenes versus the sum of σ-constants (Fig. 4). It can be seen that the slopes (ρ-values) of the disubstituted azobenzenes, treated as individual series, are not identical (Fig. 1), and that this gives rise to the curvature in Fig. 4. Jaffé[6d] has demonstrated that the ρ-values for the individual series can be correlated with the σ^+-constants of the groups held constant in the series. Figure 6 shows Jaffé's correlation with the values of the p-ferrocenyl series included.

Experimental

The ferrocenylazobenzenes were prepared by the method described by Little and Clark.[5] Only the preparation of p-ferrocenyl-p'-methoxyazobenzene was not previously re-

(13) The Hammett σ-constants used were taken from the compilation by D. H. McDaniel and H. C. Brown, $J.$ $Org.$ $Chem.$, 23, 425 (1958); the σ^+-constants were taken from H. C. Brown and Y. J. Okamoto, $J.$ $Am.$ $Chem.$ $Soc.$, 79, 1913 (1957).
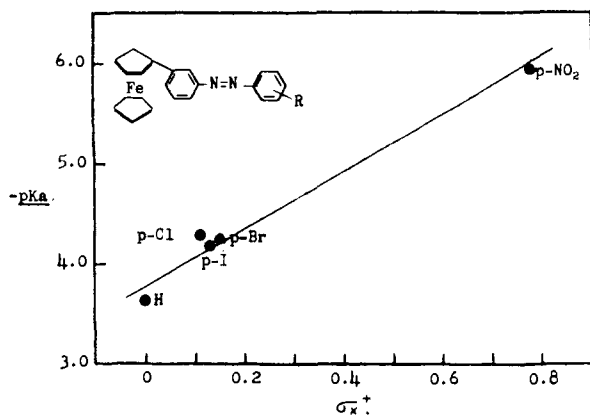
Fig. 5.

Fig. 6.

ported. While the earlier efforts to obtain this compound were not successful, it was found that the compound could be obtained in very low yields.

A solution of 0.8 g. of p-methoxynitrosobenzene in 10 ml. of glacial acetic acid was added slowly to a solution of 1.5 g. of p-ferrocenylaniline in 40 ml. of glacial acetic acid at room temperature. After standing at room temperature for 24 hours, the resulting dark brown suspension was poured into 100 ml. of water and filtered. The black precipitate so obtained was worked up for the desired compound, but only intractable materials were obtained. The filtrate from the original filtration, however, upon neutralization with NaOH yielded a black precipitate (1.2 g.) which was taken up in benzene and chromatographed on Florisil. After an initial yellow band, a second band (red) was collected and rechromatographed on Florisil. From the eluent was obtained 100 mg. of p-ferrocenyl-p'-methoxyazobenzene that was recrystallized from ethanol; m.p. 182–184° (uncor.); ultraviolet max. 362 mμ.

Anal. Calcd. for $C_{23}H_{20}ON_2Fe$: N, 7.07. Found: N, 7.12.

Determination of pK_a's.—Solutions of the ferrocenylazobenzenes were prepared at 25° in aqueous solutions of sulfuric acid containing 20 vol. % ethanol in the same manner described by Jaffé[6e]. The solutions were approximately 10^{-5} M in the ferrocenylazobenzenes and ranged in sulfuric acid wt. % from 15% to 75%. The absorbance of these solutions did not change on standing over a period of several hours. Stability tests were performed on a number of the ferrocenylazobenzenes over the entire range of sulfuric acid concentrations.
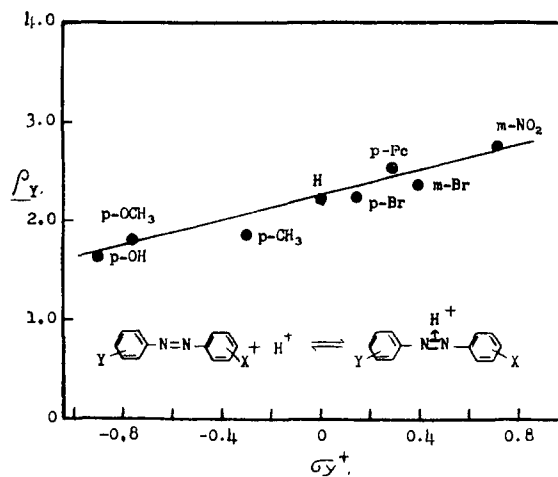
The spectra were obtained with a Cary model 14 instrument. The spectra were recorded over a range from 300 to 550 mμ. For each compound, ten arbitrary wave lengths were selected in the regions of maximum change for the determination of the pK_a's. The pK_a's were determined by the treatment described by Reilley and Smith.[9] The procedure was checked by re-examining several of the compounds studied by Jaffé,[6d] and excellent agreement with Jaffe's values was found. For example, Jaffé found for azobenzene and p-nitroazobezene −2.90 ± 0.02 and −4.70 ± 0.02; our values were −2.93 ± 0.05 and −4.70 ± 0.01.

Recovery of p-Ferrocenyl-p'-bromoazobenzene.—A solution of p-ferrocenyl-p'-bromoazobenzene, typical of the solutions used in the pK_a measurements, was prepared from 0.22 mg. of the azo compound in 25 ml. of 50 wt. % H_2SO_4 containing 20 vol. % ethanol. This solution contained approximately half the azo compound converted into the protonated form. After dilution of the solution with 100 ml. of water, CCl_4 extraction failed to remove any of the azo compound from solution. However, after adjusting the pH to 6 with 6 N NaOH, 75% of the azo compound was extracted with two 10-ml. portions of CCl_4. This estimate was made from the absorbance of the extract solution after dilution to 25 ml.

Synthesis of Boron Heterocycles from Biguanide

BY J. E. MILKS, G. W. KENNERLY AND J. H. POLEVY

Biguanide has been found to react with aminoboranes and boron acids to give heterocyclic compounds containing tetravalent, rather than trivalent, boron. Structures with an hydroxyl group on the boron atom were shown to hydrolyze reversibly, whereas a spiro compound and a compound with two phenyl groups on boron were unaffected by water. The heterocyclic system, which bears a positive and a negative charge, is related to the resonance stabilized biguanide conjugate acid.

Recent studies by Dewar and others[1] have shown that boron heterocycles with aromatic properties could be derived from normal aromatic compounds by replacing a pair of carbon atoms with a boron

and a nitrogen atom. Aromaticity in the heterocycles was demonstrated from ultraviolet data and from the unusual stability of the B–N bonds to hydrolysis as compared to simple aminoboranes. This stability was attributed to considerable

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hedron Letters, No. **23**, 8 (1960); (e) P. M. Maitlis, *J. Chem. Soc.*, 425 (1961); (f) J. M. Davidson and C. M. French, *ibid.*, 191 (1960).