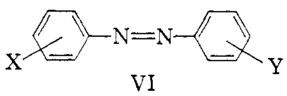
tive to substituent effects (*i.e.*, that the reaction constant $\rho_T \approx 0$), and that the scatter of *p*-compounds is due to a failure of Sawicki's approximation. The *p*-arylazo-N,N-dimethylanilines are being investigated further.

The value $\rho_T \approx 0$ derived in the preceding paragraph is of considerable interest. We had at one time argued that the structure of the conjugate acid of *p*-dimethylaminoazobenzene must be the ammonium form III because of the small ρ-value for the second basicity.[3b] It now appears on the basis of two lines of evidence that our argument was fallacious. We believe that we have now shown conclusively that a tautomeric equilibrium between the two possible forms exists, and if, as proposed, $\rho_T \approx 0$, it follows that no appreciable difference can exist in susceptibility of the equilibria I + H$^+ \rightleftarrows$ II and I + H$^+ \rightleftarrows$ III to substituent effects. Alternately, we can estimate the ρ-value for the second of these processes from the correlation between the ρ-values of the basicities of series of compounds with constant Y and the σ-values of the apropriate Y.[2a] Such an estimate leads to $\rho_{III} \approx 1.0$, not quite twice the magnitude expected for the ρ-value of the corresponding ammonium ion dissociation.[3b,10] Hence again $\rho_T = \rho_{III} - \rho_I$ is quite small.



VI

It then only remains to ask ourselves why the ρ-value for protonation of the azo group is so low in these cases. If one remembers, however, that the Hammett equation is really concerned with electronic effects, it becomes apparent that the factor affecting ρ most strongly is not the site of attachment of the proton, but the energy required to localize the positive charge. Since it seems very likely that the quinoid structure IIIb makes a very important, if not the predominant contribution to III, ρ_{III} then measures not so much the effect of substituents on the ease of addition of a proton at the nitrogen atom alpha to the substituent, but on the ease of placing a positive charge on the amino group. That this quantity is of a similar magnitude as ρ_{II} for the protonation of the amino group is not surprising since in both processes the charge is placed on the same atom. These arguments seem to provide an alternate explanation of the variability of ρ values with Y in the series of compounds VI. In a preceding paper we have proposed that this magnitude of ρ is dependent on the asymmetry of the proton position in the parent compound of each series. It now seems very likely that the value is ρ is more importantly dependent on the extent to which the positive charge is displaced from the azo group to the end of the ring or to Y by the intervention of quinoid structures.

Experimental

***p*-Dimethylaminoazobenzene.**—A product of the Hilton-Davis Chemical Co.[11] was recrystallized twice from 95% ethanol; m.p. 119–120° (uncor.), lit.[3a] m.p. 119–120°.

***p*-Phenylazo-N,N,N-trimethylanilinium Methylsulfate.**—Ten grams of *p*-dimethylaminoazobenzene, recrystallized from ethanol, was placed in a 500-ml. round-bottomed flask fitted with a reflux condenser. After 100 ml. of dimethyl sulfate was added to the flask, the mixture was refluxed in a water-bath for 5 hours. On standing, the red *p*-phenylazo-N,N,N-trimethylanilinium methylsulfate crystallized out. The crystals were washed with anhydrous ether until the filtrate was clear, and dried under vacuum.

Anal.[12] Calcd.: C, 54.66; H, 6.03; N, 11.97; S, 9.13. Found: C, 54.41; H, 6.26; N, 11.74; S, 9.03.

***pK* Determinations.**—All *pK*'s were determined by a standard spectrophotometric method using a Beckman DU quartz spectrophotometer.[13] The general procedure for the determination of concentration ratios, c_B/c_{BH^+} and $c_{BH^+}/c_{BH_2^{++}}$ and the calculation of *pK*'s were described elsewhere.[6] The *p*H of the solutions was measured by a Beckman model G *p*H meter calibrated with standard buffer solutions.

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[10] S.-J. Yeh and H. H. Jaffé, THIS JOURNAL, **81**, 3287 (1959).

[11] We are grateful to the Hilton-Davis Chemical Co. for a generous gift of this compound.

[12] Microanalyses were performed by A. Bernhardt, Mühlheim (Ruhr), Germany.

[13] L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Transmission of Electronic Effects through the —N=NC$_6$H$_4$— Group[1]

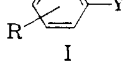
BY SI-JUNG YEH AND H. H. JAFFÉ

RECEIVED DECEMBER 20, 1958

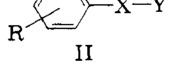
The acid dissociation constants in 20% ethanol of a series of *p*-arylazophenols are reported, and shown to obey the Hammett equation with $\rho = 0.516$. Comparison of this value with an interpolated value for phenols gives a ρ-ratio of 0.16, in fair agreement with a theoretical estimate of 0.14, and an experimental value of 0.13 from the *p*-arylazo-N,N-dimethylanilines.[2]

Some years ago we have proposed that the reaction constants (ρ)[3] for identical reactions occurring at a reaction center Y under identical conditions in two series of compounds I and II can be related by the equation

$$\rho_{II}/\rho_I = \pi' \qquad (1)$$



I



II

in which the constant π' is independent of the group

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[1] This work has been jointly supported by the Office of Ordnance Research, U. S. Army, and by the American Cancer Society through a Bonita Geho Memorial Grant for Cancer Research. This support is gratefully acknowledged.

[2] H. H. Jaffé, *J. Chem. Phys.*, **23**, 415 (1953).

[3] (a) L. P. Hammett, "Physical Organic Chemistry," Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

Y, of the reaction and the conditions under which it occurs, as long as these are the same for ρ_I and ρ_{II}.[2] In connection with work on the basicities of substituted azo compounds and on an H_0 function in 20% ethanol,[4] we have had occasion to prepare a series of *p*-arylazophenols. We have now determined the acid dissociation constants of the phenolic function of these compounds in an attempt to gain information concerning the transmission of electronic effects through the group X = —N=N-C_6H_4—. Such information was of special interest for two reasons; it provided an additional test of the proposed method of calculating the constant (π') of eq. 1 by molecular orbital theory, and it provided an interesting comparison with the data available from the consideration of the *p*-arylazo-N,N-dimethylanilines.[2,4d]

Experimental

Compounds.—The preparation and physical properties of the *p*-arylazophenols have been reported in a previous paper.[4b]

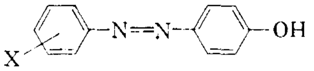
***pK* Determinations.**—The *pK*'s of the *p*-arylazophenols were determined in about 10^{-5} *M* solution in 20% ethanol by a standard spectrophotometric method.[5] Standard phosphate and borate buffers made in 20% ethanol were used,[6] and no ionic strength corrections were made. *pK*'s were determined with a Beckman model G *p*H meter, and spectroscopic measurements were made with a Beckman DU quartz spectrophotometer.

Results and Discussion

The *pK*'s of the *p*-arylazophenols in 20% EtOH are listed in Table I. They are well correlated with the σ-values[3b] of the substituents in the aryl group with a $\rho = 0.515 \pm 0.019$, $s = 0.011$, $r = 0.998$, $n = 5 \log k^0 = 8.393$.[7]

TABLE I

pK_2 OF *p*-(ARYLAZO-)-PHENOLS



IN 20% ETHANOL AT 25°

X	σ	pK_2
4-OCH_3	−0.268	8.54 ± 0.02
4-CH_3	−0.170	8.48 ± .04
H	0	8.38 ± .04
4-Br	0.232	8.27 ± .02
3-Br	0.391	8.20 ± .02

No data appear to be available for the acid dissociation of simple phenols in the same solvent. Interpolation between reported values yields $\rho_I = 3.10$, $\rho_{II}/\rho_I = 0.16$.[3b] This value is in satisfactory agreement with the molecular orbital value $\pi' = 0.14$[2] for the same group X, and with the value obtained from the basicities of the *p*-aryl-N,N-dimethylanilines $\rho_{II}/\rho_I = 0.13$.[2,8] This latter value, however, requires further comment; it was derived from the ρ-value for the first protonation of these bases on the assumption that this reaction involves only the amino group. We have, however, now demonstrated that the conjugate acid of the bases under discussion are tautomeric mixtures of ammonium and azonium forms,[4d] and hence cannot expect a straightforward application of the Hammett equation to these equilibria. Only since substituents do not appear to affect the position of tautomeric equilibrium (*i.e.*, $\rho_T \approx 0$) is our use of the ρ from the basicities of the *p*-aryl-N,N-dimethylanilines for a determination of ρ_{II}/ρ_I for X = —N=NC_6H_4— justified, and our comparison of this value with the value from the *p*-arylazophenols and the theoretical value meaningful.

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[4] (a) H. H. Jaffé and R. W. Gardner, THIS JOURNAL, **80**, 319 (1958); (b) S.-J. Yeh and H. H. Jaffé, *ibid.*, **80**, 3274 (c) 3279, (d) 3283 (1959).

[5] L. A. Flexser, L. P. Hammett and A. Dingwall, *ibid.*, **81**, 57, 2103 (1935).

[6] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 3rd. ed., 1928, p. 200.

[7] All symbols have their usual significance; *cf.* ref. 2b.

[8] *Cf.* M. T. Rogers, T. W. Campbell and R. W. Maatman, THIS JOURNAL, **73**, 5122 (1951).

CINCINNATI, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Oxygen Oxidation of Triphenylsilyllithium

BY M. V. GEORGE AND HENRY GILMAN

RECEIVED DECEMBER 27, 1958

Oxidation of triphenylsilyllithium using molecular oxygen has been studied at different temperatures, in tetrahydrofuran as the solvent. Triphenylsilanol, triphenylsilane and small amounts of hexaphenyldisilane were formed in each case, though the yields of these products varied depending on the reaction temperature. A change of the solvent medium to tetrahydropyran did not affect the nature of the reaction products. The oxidation is assumed to proceed through an unstable hydroperoxide salt, followed by the radical decomposition of this intermediate.

Since the early investigations of Bodroux[1] and Bouveault,[2] numerous investigators have studied the reaction of Grignard reagent with molecular oxygen.[3] Wuyts[4] postulated that the oxidation reactions proceed through the formation of peroxide intermediates, and later Porter and Steele[5] suggested the reaction scheme

$$\mathrm{RMgX} + \mathrm{O_2} \longrightarrow \mathrm{ROOMgX} \xrightarrow{\mathrm{RMgX}} 2\mathrm{ROMgX}$$

Experimental evidence for this sequence was provided by Walling and Buckler,[6] who in an elegant study, have isolated several intermediate

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[1] F. Bodroux, *Compt. rend.*, **136**, 158 (1903); *Bull. soc. chim.*, [3] **31**, 33 (1904).

[2] L. Bouveault, *ibid.*, [3] **29**, 105 (1903).

[3] For an extensive review on the oxidation of Grignard reagents see, M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 1264–1274.

[4] H. Wuyts, *Bull. soc. chim. Belg.*, **36**, 222 (1927); *Compt. rend.*, **148**, 930 (1909).

[5] C. W. Porter and C. Steele, THIS JOURNAL, **42**, 2650 (1920).

[6] C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).