caprate solutions both in the presence and absence of mercaptan was found to be first order with respect to persulfate and independent of soap concentration over a wide concentration range. With the assumption that reaction (2) is rate-determining, the observed zero order dependence of the rate of persulfate oxidation of solubilized mercaptans on soap concentration (above the critical concentration) is consistent with the proposed mechanism.

Evidence that free radicals are formed by the reaction of persulfate with saturated fatty acid soaps is provided by the observation that compounds containing active oxygen (peroxides or hydroperoxides) are formed when sodium laurate, myristate or palmitate is oxidized by persulfate in the presence of oxygen. It is believed that the carboxylate free radicals formed by reactions (2) and (3) lose carbon dioxide to form alkyl radicals which react with oxygen to form peroxidic compounds.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 27, 1951

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Ionization Constants of Some *p*-Substituted *p*′-Dimethylaminoazobenzenes[1]

BY MAX T. ROGERS, TOD W. CAMPBELL AND RUSSELL W. MAATMAN

p-Dimethylaminoazobenzene and its *p*′-substituted derivatives add a proton in dilute acid and a second in strong acid solutions, and this work was undertaken to determine the acidity constants of the mono- and diprotonated bases. Values of pK_{1a} and pK_{2a} for the addition of the first and second protons to *p*-X-*p*′-dimethylaminoazobenzene where X = -H, -Cl, -I, $-CH_3$, $-C(CH_3)_3$, $-NO_2$, -SCN, -SeCN and $-OCH_3$, have been measured spectrophotometrically. The results provide additional evidence that the first proton is added to an azo nitrogen atom and the second to the dimethylamino nitrogen atom of the molecule. The effect of the *p*-substituents on the proton affinity of the nitrogen atoms is in the same order as the net electron affinities of the groups as measured by the Hammett substituent constant σ. The substituent constants for *p*-SCN and *p*-SeCN are nearly equal to that of the *p*-NO_2 group.

Introduction

The behavior of dimethylaminoazobenzene, and related compounds, in acid solutions has been studied for many years and various structures have been proposed for the ions; Hantzsch[2] showed that two series of mono-acid salts could be prepared—an unstable orange-yellow series in which the proton was probably on the amino–nitrogen, and a stable deeply-colored series in which the proton was considered to be on an azo nitrogen atom. Kehrmann[3] studied the spectra and showed that a second and a third proton could be added, each ion having a characteristic spectrum.

We have prepared a series of *p*-substituted dimethylaminoazobenzene derivatives and have measured their absorption spectra in 50% alcohol solution and in solutions of various known acidities.

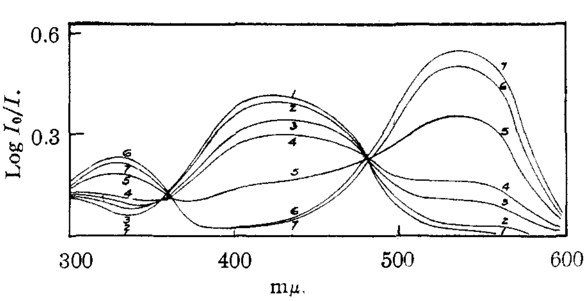
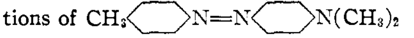


Fig. 1.—Absorption spectra of 50% aqueous ethanol solutions of 

Curve	1	2	3	4	5	6	7
*p*H	6.75	3.85	2.89	2.75	1.96	..	..
N	..	..	..	..	..	2.06	4.12

The equilibrium constants for addition of the first and second protons have been determined from the absorption spectra of the solutions and the resulting values have been correlated with the ability of the substituent groups to increase or decrease the electron density on the nitrogen atoms. The ionization exponents are approximately linear functions of Hammett's[4] substituent constants for the substituent groups and the reaction constants ρ for the first and second proton additions have been found. The behavior of the ionization constants with change of *p*-substituent is consistent with, and provides evidence for, the structures which have been assigned to the ions.

Experimental

Apparatus and Materials.—The preparation and characterization of the dyes are described elsewhere.[5] The absorption spectra were measured using a Beckman model DU spectrophotometer and 1 cm. Corex cells; spectra were recorded from 300 to 600 mμ at room temperature. A Beckman *p*H meter and glass electrode were used for *p*H measurements.

Methods.—The absorption spectra of unbuffered solutions of *p*-methyl-*p*′-dimethylaminoazobenzene in 50% aqueous ethanol of various *p*H values are shown in Fig. 1. Two isobestic points are observed and the ionization constants can be calculated without correction for a "medium effect" by the equation[6,13]

$$pK_1 = pH - \log\left(\frac{E - E_{BH^+}}{E_B - E}\right) - \log\frac{f_B}{f_{BH^+}} \qquad (1)$$

where E_B, E_{BH^+} are the molar extinction coefficients of base and first ion and E is the apparent molar extinction coefficient at a given *p*H (all measured at one wave length). The ratio f_B/f_{BH^+} of the activity coefficients of base and ion is taken equal to unity since the dye concentrations are about 10^{-4} molar. Since the molar dye concentration and cell length are constant for a series of measurements optical den-

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[1] Abstracted from the Doctoral Thesis of R. Maatman, Michigan State College, 1950; presented at the 113th National Meeting of the Am. Chem. Soc., 1948.

[2] A. Hantzsch, *Ber.*, **41**, 1171 (1908); **52**, 509 (1919); **63**, 1760 (1930); etc.

[3] F. Kehrmann, *ibid.*, **48**, 1933 (1915).

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Ch. VII, Ch. IX.

[5] T. W. Campbell, D. A. Young and Max T. Rogers, THIS JOURNAL, **73**, Dec. (1951).

[6] A. Thiel, *Fortschr. Chem. Physik u. physik. Chem.*, **18**, 38 (1924).

sities can replace extinction coefficients in equation (1). The average value of pK_1 so obtained is shown in Table I for each of the dyes studied.

TABLE I

pK_1 AND $-pK_2$ VALUES OF p-SUBSTITUTED p'-DIMETHYLAMINOAZOBENZENES

p-Substituent	pK_1[a]	$-pK_2$[b]
$-NO_2$	1.81 ± 0.04[c]	6.69 ± 0.01
-SCN	1.81 ± .02	
-SeCN	1.83 ± .15	
-I	2.06 ± .09	4.94 ± .04
-Cl	2.00[d]	4.72 ± .03
-H	2.27 ± .07	4.50 ± .03
$-CH_3$	2.31 ± .04	3.63 ± .06
$-C(CH_3)_3$	2.27 ± .03	3.55 ± .09
$-OCH_3$	2.35 ± .03	2.13 ± .04

[a] pH range 1.96 to 3.58 (50% aqueous alcohol solutions). [b] pH range −1.13 to −7.61 (aqueous H_2SO_4 solutions). [c] All limits of error represent average deviation of values determined at four to six different acidities. The value at each acidity represents the average of the values obtained at several wave lengths; the average deviation among the different wave lengths is about the same as the average deviation of different acidities. [d] Measurement at only one acidity was made.

Since these values are all measured in 50% ethanol (to obtain sufficiently large concentrations of the less soluble dyes) they are comparable with one another but will differ from the pK_1 values observed in other media. Thus Thiel[7] found that the pK of methyl orange decreases from 3.40 in ethanol to 2.51 in 50% aqueous ethanol. Some pK_1 values previously reported for dimethylaminoazobenzene include the values pK_1 2.78 in n-butanol,[8] pK_1 3.1 in ethanol,[9] pK_1 3.4 in methanol,[9] and pK_1 3.29 in water.[10] The decrease in pK from 3.1 in ethanol to 2.27 observed here for dimethylaminoazobenzene in 50% aqueous ethanol is very close to the decrease noted by Thiel for methyl orange. From the work of White[11b] and others the pK_1 values in water would be expected to be about 1.4 ± 1.0 units smaller than the values reported here for 50% aqueous ethanol solutions. Since the pK_1 values are determined in a medium of rather low ionic strength, they should differ little from the values at zero ionic strength.[11a]

The second proton adds in more concentrated sulfuric acid solutions and pK_2 values have been determined in these solutions by a modification of the method of Hammett.[4] The equation used is

$$pK_2 = pH - \log \left(\frac{E - E_{BH^{++}}}{E_{BH^+} - E} \right) \qquad (2)$$

where pH is the value given in the extended pH scale of Michaelis and Granick[12] for a given sulfuric acid concentration; E_B, E_{BH^+} and $E_{BH^{++}}$ are the apparent molar extinction coefficient and the extinction coefficients of the first and second ions, respectively. The pH curve of Michaelis and Granick was extrapolated from 69 to 79% sulfuric acid for p-NO_2-p-dimethylaminoazobenzene. The acidity function of Michaelis and Granick has been used here since it was determined using uncharged, unipositive and dipositive bases in regions of increasing acid strength and we are concerned here with an equilibrium between unipositive and dipositive ions. Hammett's acidity function was based on equilibria between uncharged and unipositive species; values of pK_2 calculated using Hammett's H_0 function[4] differ in absolute but not relative value from those reported here.

The effect of change of solvent on the absorption curves was corrected for by the isobestic point method.[13] Since it is difficult to prepare solutions containing only the first ion pK_2 values were usually calculated in a region of the spectrum (400–470 mμ) where its absorption is small to minimize the uncertainty in the absolute molar extinction coefficient. The absorption curves for p'-methyl-p-dimethylaminoazobenzene in strong sulfuric acid solutions are shown in Fig. 2. The average pK_2 values so obtained are shown for seven compounds in Table I; the dyes with X = —SCN and —SeCN decomposed in strong acid solution and are not included. Since sulfonation occurs in fuming H_2SO_4 solutions the spectra of the triprotonated ions were not studied.

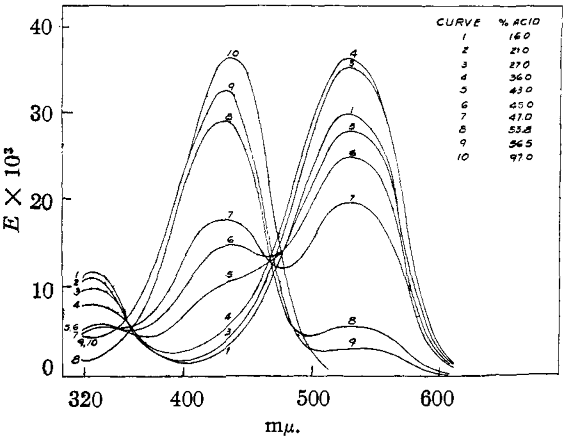
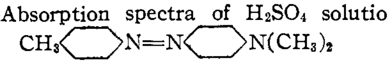


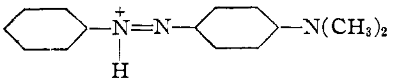
Fig. 2.—Absorption spectra of H_2SO_4 solutions of



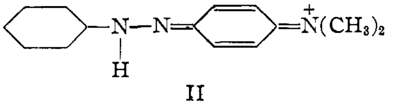
Curve	1	2	3	4	5
Acid, %	16.0	21.0	27.0	36.0	43.0
Curve	6	7	8	9	10
Acid, %	45.0	47.0	53.8	56.5	97.0

Discussion

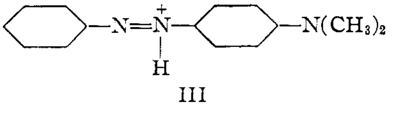
The deepening of the color when the first proton is added has been attributed[3,14] to resonance between the two nearly equivalent structures I and II. The possibility has been suggested[15] that the tautomer III is also present and resonates principally between structures III and IV.



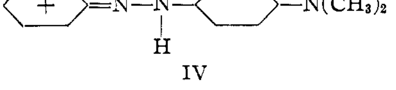
I



II



III



IV

Since the latter resonance would be less effective in stabilizing the ion, it seems likely that the tautomer with structure I represents the first ion. A similar conclusion is reached if the electron density on each azo nitrogen atom, as a result of resonance in the uncharged base, is considered. The extra stabilization from structures of type V should

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[7] A. Thiel and W. Springemann, *Z. anorg. allgem. Chem.*, **176**, 64 (1928).

[8] R. B. Mason and M. Kilpatrick, THIS JOURNAL, **62**, 1949 (1940).

[9] I. M. Kolthoff and L. S. Guss, *ibid.*, **60**, 2516 (1938).

[10] E. Guntelberg and E. Schiodt, *Z. physik. Chem.*, **135**, 393 (1938).

[11] (a) I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930); (b) J. R. White, THIS JOURNAL, **72**, 1859 (1950).

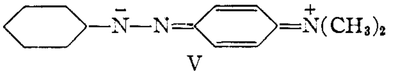
[12] L. Michaelis and S. Granick, *ibid.*, **64**, 1861 (1942).

[13] L. A. Flexner, L. P. Hammett and A. Dingwall, *ibid.*, **57**, 2103 (1935).

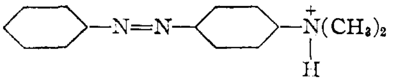
[14] C. R. Bury, *ibid.*, **57**, 2115 (1935).

[15] S. E. Sheppard and P. T. Newsome, *ibid.*, **64**, 2937 (1942).

make the azo nitrogen further from the amino group the stronger proton acceptor in all the molecules studied.



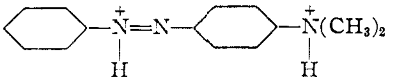
V



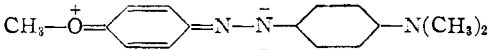
VI

The third possible tautomer (VI) should have a spectrum similar to azobenzene itself since no important additional resonance structures can be written for it. Hantzsch[2] has indeed shown that the methiodide with structure analogous to VI, and an unstable tautomeric form of the solid mono-hydrochloride with structure VI (presumably), both have spectra similar to azobenzene itself. It is difficult to decide whether appreciable amounts of both tautomers I and III are present in dilute acid solutions. It seems likely that if this were the case there would be a difference in their spectra and a continuous change in the general appearance of the spectra of dilute acid solutions, resulting from changes in the proportions of the tautomers, as the para substituent ranges from $-NO_2$ to $-N(CH_3)_2$; no such changes are observed even in the $-N(CH_3)_2$ derivative where I and III become identical for the first ion.

The second proton would not be expected to add to the other azo-nitrogen atom because of the instability of adjacent positive charges; it must therefore add to the dimethylamino-nitrogen atom and structure VII is considered to be the structure of the dipositive ion.

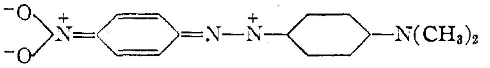


VII

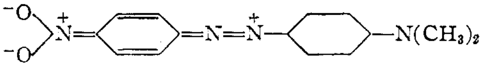


VIII

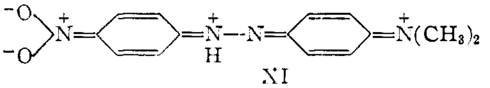
The effect of substituent groups on the values of pK_1 and pK_2 is shown in Figs. 3 and 4 in which the values of the first and second ionization exponents are plotted against Hammett's[4] substituent constants σ for the groups. The σ values for para substituents in the benzene ring were used. In each case approximate linearity between pK and σ is observed and the negative slopes of the lines give the values $\rho_1 = 0.55$ and $\rho_2 = 4.35$ of the reaction constants ρ for the addition of the first and second proton, respectively. The value of ρ measures the susceptibility of the reaction to change of substituent. The value of ρ for the addition of the first proton may be small because the important resonance structures VIII and IX do not affect the electron density on the azo nitrogen accepting the proton, but only on the atom next to it. Structure X might be expected to be less favorable than IX because a linear configuration is the stable one for adjacent double bonds. On the other hand, important resonance structures in the first ion, such as XI for the p-NO_2 derivative, have a direct effect on the electron density of the amino-nitrogen which accepts the second proton. Both the large value of ρ_2 and the electric moment data[5] indicate that structures of type XI are important. The choice made for the tautomeric forms of the first and second ions is thus in agreement with the magnitudes of the reaction constants; if the first ion had structure III then ρ_1 should be larger.



IX



X



XI

The value of the substituent constants σ of the p-SCN and p-SeCN groups are close to that of the p-NO_2 group (about +0.78); these groups are thus strongly electron attracting in the compounds studied here. This would not be expected from the ease with which phenyl selenocyanate and phenolthiocyanate substitute in the o- and p-positions; it does agree, however, with the results of electric moment measurements.[16]

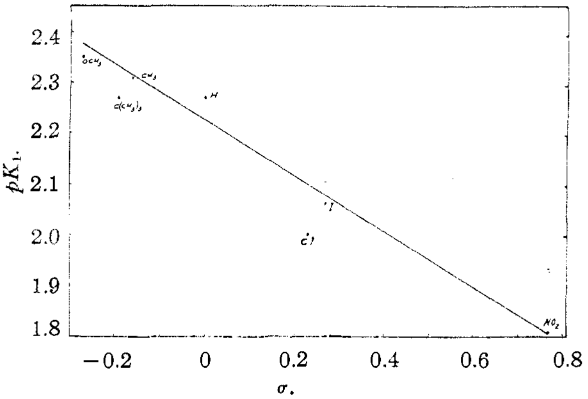


Fig. 3.—σ, the substituent constants *vs.* pK_1 of seven related azo dyes.

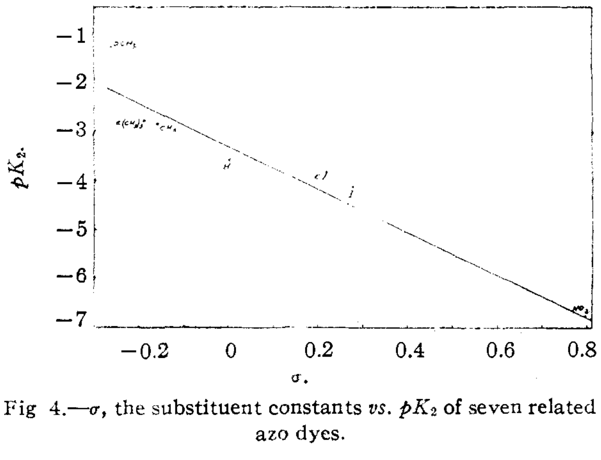


Fig 4.—σ, the substituent constants *vs.* pK_2 of seven related azo dyes.

EAST LANSING, MICHIGAN

RECEIVED FEBRUARY 2, 1951

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(16) T. W. Campbell and M. T. Rogers, THIS JOURNAL, **70**, 1029 (1948).