Substituent Effects on the Basicities of Azoxy-Compounds[1]

By Chi Sun Hahn and Hak Soo Lyu

Department of Chemistry, Yonsei University

Azoxy系化合物의 鹽基性에 미치는 置換基効果

韓 治 善* · 柳 鶴 洙**

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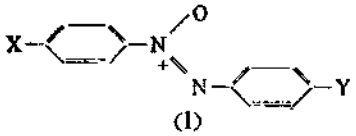
The basicities of 16 substituted azoxybenzenes have been measured by U.V. spectrophotometric method. The effects of substituents on the basicities are discussed in terms of Hammett's equation. The reaction constants, ρ_Y^X and ρ_X^Y, in a modified equation, $\log K_{XY}/K_{00}=\sigma_X\rho_X^Y+\sigma_Y\rho_Y^X$, are 2.46±0.12 and 2.25±0.26 respectively. The validity of the equation is analysed by a statistical method, and the structure of the conjugate acid of the substituted azoxybenzenes is proposed.

Although ultraviolet and visible spectrophotometric methods have been utilized for the study of substituent effects on the azoxy-group by many workers,[2-5] to date, little is known about the electron distribution in azoxybenzene compounds. The basicities of azoxy-compounds have never been reported in the literature and it is unknown which of the atoms in the azoxy-group is the basic center. Since the electron distribution within the azoxy-group is undoubtedly affected by the introduction of substituent (s) into one or both benzene nuclei, it is of interest to investigate the substituent effects on the basicities of the azoxy-compounds.

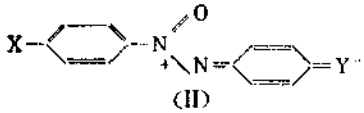
The pK's of the conjugate acids of 16 mono-and disubstituted azoxybenzenes are listed in Table I. It is apparent from the data that all the compounds substituted with electron releasing groups, such as CH_3 and OCH_3, have less negative pK values than azoxybenzene. This undoubtedly is due to the (+) E effect of the substituents, that is, protonation of compounds substituted with electron repelling group(s) is easier than that of azoxybenzene itself. On the other hand, most of the compounds less basic than azoxybenzene are substituted only with electron withdrawing groups, and the protonation of these compounds is more difficult than for azoxybenzene; this is apparently due to the (-) I effect of the groups. Each row and each column in Table I represents one reaction series to which one might be able to apply the Hammett equation. For the discussion of the data in Table I in terms of the Hammett equation,[6] the question arises as to which type of σ constants, σ, σ^+[7], or σ^-[8], is to be used. It is readily apparent that no low energy resonance structures can be written in which the azoxy group acts as an electron acceptor; hence, σ^+ values need not be considered. Similarly, it is not possible to write resonance structures delocalizing the negative charge of the oxygen atom in structure(I) into a substituent X, and hence normal σ values undoubtedly must be used for X. On the other hand, structure (II) shows that in the free base the negative charge can readily be delocalized into Y, thus suggesting the use of σ^- for Y. If we now define

* ** 延世大學校 理工大學 化學科

K_{XY}, K_{XO}, K_{OY} and K_{OO} as the equilibrium constants for 4−X−4′−Y−, 4−X−, 4′−Y− and unsubstituted azoxybenzene, respectively, the Hammett equation would take the forms where ρ_Y^X is the



(I)



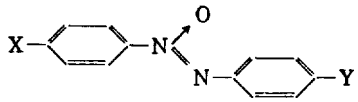
(II)

$$\log K_{XY}/K_{XO}=\sigma_Y\rho_Y^X \qquad (1)$$

$$\log K_{XY}/K_{OY}=\sigma_X\rho_X^Y \qquad (2)$$

reaction constant which measures the susceptibility of the equilibrium to the effects of substituents Y when X remains constant, and similarly for ρ_X^Y. The results of the application of equations (1) and (2) to various rows and columns of Table I are shown in Fig. I and Table II. The series in which X=H contains the only substituent, p-NO_2 for which $\sigma \neq \sigma^-$. In this case, σ^- provides by far the best fit, as seen from Fig. I. This finding suggests that σ^- is the appropriate choice for Y. For the examination of the applicability of σ^- constants, it is necessary to substitute a group possessing strong electron withdrawing power such as CN, SO_2H or $COCH_3$, besides NO_2 into the Y position and to obtain their −pK values. From the practical point of view however, it is almost impossible to measure the basicity of the azoxy group itself in each of these compounds. Since the substituent group itself can function as a basic center, the proton adds not only to the azoxy group but also to the substituent group. Accordingly, the investigation of the use of σ^- constants under these conditions can not be carried out.

Table I The pK's of azoxybenzenes and σ constants



Y \ X	X	MeO	Me	H	Cl	Br
		−0.268	−0.170	0	0.227	0.232
MeO	−0.268	5.23±0.03		6.10±0.04		
EtO	−0.250			6.04±0.03		
Me	−0.170		5.47±0.05	6.04±0.03		6.90±0.03
H	0.000	6.15±0.04	6.16±0.04	6.45±0.05		6.94±0.03
Cl	0.227			6.96±0.05	7.69±0.03	
Br	0.232		6.95±0.04	7.01±0.04		7.77±0.03
NO_2	1.270			9.83±0.07		

Table II Reaction constants for the protonation of substituted azoxybenzenes

	X=H	X=CH_3	X=Br		Y=H	Y=CH_3	Y=Br
ρ_Y^X	2.503	2.868	2.247	ρ_X^Y	2.199	2.857	2.113
r	0.994	0.997	0.924	r	0.980	0.999	0.932
s	0.163	0.014	0.260	s	0.088	0.020	0.233
$s\rho$	0.120	0.036	0.912	$s\rho$	0.232	0.071	0.816
$\log K_{XO}$	6.55	6.12	7.16	$\log K_{OY}$	6.53	6.06	7.11
n	7	3	3	n	4	3	3

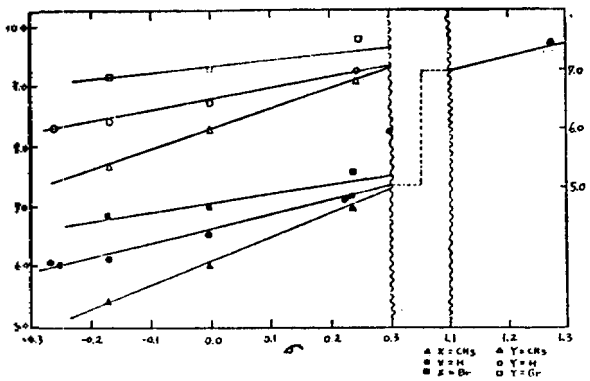


Fig. 1 plot of -pk's vs σ

When the two reaction constants, ρ_Y^X and ρ_X^Y, are not significantly different, equations (1) and (2) become as follows:

$$\log K_{XY}/K_{OO} = \rho(\sigma_X + \sigma_Y) = \rho\Sigma\sigma \qquad (3)$$

However, it appears from Table II that the two reaction constants, are not close enough in values so as to satisfy the use of the equation (3). However, Miller[9] has pointed out that the existence of a series of straight lines implies that a more general relation must exist:

$$\log K_{XY}/K_{OO} = \sigma_X\rho_X^Y + \sigma_Y\rho_Y^X + \sigma_X\sigma_Y\rho_{XY} \qquad (4)$$

When ρ_X^Y and ρ_Y^X in equation (4) are equal ρ_{XY} vanishes.

It is apparent from Table II that the ρ_Y^X are equal well within experimental error; however, for this series equation (2) does not appear to give nearly as good a fit, and examination of the s_ρ values indicates that the difference may be only apparent. Accordingly we now anticipate finding that the ρ_{XY} vanishes, the data being represented by

$$\log K_{XY}/K_{OO} = \sigma_X\rho_X^Y + \sigma_Y\rho_Y^X \qquad (5)$$

Application of this equation (5) to the data leads to $\rho_Y^X = 2.46 \pm 0.12$, $\rho_X^Y = 2.25 \pm 0.26$, $r = 0.988$, $s = 0.169$, $n = 16$.

However, a comparison of these ρ values with those obtained from the single linear correlation is not sensitive enough to discuss the validity of equations (1)-(5). Accordingly, the variance of the entire set of row pK values was analysed by a statistical method to investigate whether a significant improvement could be achieved by the use of equation (5) over the simpler equation (3). The results of analysis of variance are shown in Table III. Since the pK values of 15 of the 16 compounds were measured at two different wavelengths, the number of different groups is 31. By random sampling, three pK's were chosen from each of the groups, so that the total number of degrees of freedom (DF) was 93. Substracting one DF for the mean from 93 DF, there remain a total of 92 DF. These 92 DF were then divided as indicated in the first column of Table III. It can be seen from Table III that the variance between the two different wavelengths is not significant; however, the variance between the various compounds is highly significant. The most striking fact is that equation (5) yields an appreciable improvement over the simple Hammett correlation given by equation (3). Also, this improvement is evident from the fact that the variance ratio, F=77.7, for the derivation from equation (3) is quite sigificant. The variance due to the interaction between the wavelengths and the compounds is so small that the result of the use of either of the two wavelengths for each compound would not differ appreciably from the above analysis. It can be presumably concluded that equation (5) should be used for the correlation of the effect of the substituent(s) on the basicities of azoxybenzenes.

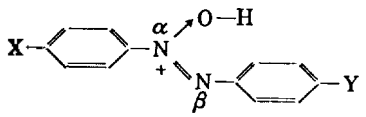
Table III

Analysis of variance of pK's of azoxybenzenes

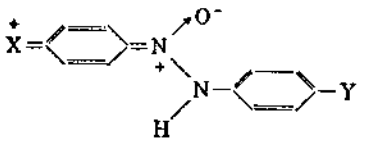
Source	D.F.	Sum of Squares	Mean Squares	F[a]
Total	92	100.58935	—	—
Between Wavelength	1	0.01126	0.01126	4.83*(n.s.)
Between Compounds	15	100.39995	6.69330	2872**
Due to Eq. (5)	2	98.04616	49.02308	10000**
Due to Eq. (1&2, 3)	1	97.96146	97.96146	10000**
Improvements Eq. (5) over Eq.(3)	1	0.08470	0.08470	36.4**
Derivation from Eq. (5)	13	2.35379	0.18106	77.7**
Wavelengths and compound Interaction	14	0.03344	0.00223	1
Error	62	0.14470	0.00233	—

(a) Significance at the 96% level is indicated by one asterisk, at the 99% level by two.

Regarding the protonation of azoxybenzenes, it must be considered which of the three atoms of the azoxy group is the basic center. It is immediately obvious that it could not be the α-nitrogen atom bonding the oxygen atom, since it already bears a positive charge, not lone pair of electrons. The following two forms are possible structure for the conjugate acids of substituted azoxybenzenes. Structure (IV) seems to have considerably higher energy than structure (III).

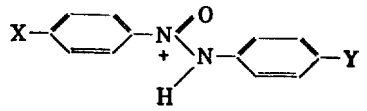


(III)

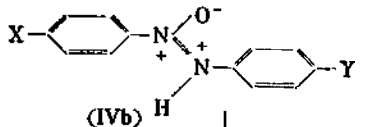


(IV)

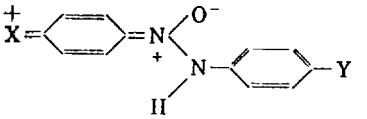
It would receive contribution from at least the three resonance forms, (IV_{a-c}). Structure (IV_a) has no separation of charges; however, the two benzene rings are not conjugated. Structures (IV_b) and (IV_c) involve charge separations, and hence are of relatively high energy. Thus, structure (III) is the most probable form for the conjugate acids



(IVa)



(IVb)

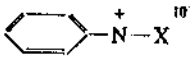
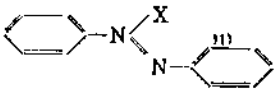


(IVc)

of azoxybenzenes. A study dealing with the structure of the conjugate acid of pyridine-1-oxide, in connection with the basicities of substituted pyridines (cf. Table IV) and their 1-oxides by Jaffe and Doak[10] is further evidence to support the probability of structure (III).

Table IV

Comparison of pK between pyridine, azo and azoxybenzene

X	 [10]	 [11]	Difference
H	5.29	-2.90[11]	8.19
OH	0.79	-6.45	7.24
Difference	4.50	3.55	

Experimental

Compounds.— Symmetrical 4,4'-disubstituted azoxybenzenes were prepared by the oxidation of the corresponding azobenzenes with hydrogen peroxide in glacial acetic acid.[12] The preparation of the azobenzenes followed Mill's method,[13] that is condensation of 4-substituted nitrosobenzenes with 4-substituted anilines. The 4-substituted nitroso-benzenes were synthesized by Coleman's method.[14] Unsymmetrical 4- and 4,4'- disubstituted azoxybenzenes were also obtained by the same method. The isomers, α- and β-form, of 4-monosubstituted azoxybenzenes were separated using an alumina chromatography column. The chromatogram was developed with ligroin(60—90° fraction) and eluted with organic solvents in the following order: ligroin, carbon tetrachloride, cyclohexane, benzene, $(Et)_2O$, EtOH and MeOH. Fractions of the first four solvents were collected together and condensed.

The crystals obtained in such a way were recrystallized from warm ethyl alcohol until a constant melting point was obtained (α-form). The rest of the fraction of $(Et)_2O$, EtOH and MeOH were mixed together and condensed, and then crystallized in an ice-box. The crystals resulted were washed with a cold ligroin 3 times, and recrystallized from EtOH until a constant melting point was obtained (β-form). The purity of all the azoxy-compounds used was confirmed by comparison of their melting points with that given in the literature which are listed in Table V.

Table V

Melting points of azoxy-compounds.

X	Y	m.p.(obsd.)	m.p. (lit).
H	H	36°	36°
CH_3	CH_3	71—72	70.5—71.5
Cl	Cl	154—155	155
Br	Br	175—176	175
OCH_3	OCH_3	117—118	117.4—118.5
H	CH_3	46—48	46
CH_3	H	65	65
H	Cl	62—63	62—63
H	Br	73—73.5	73
Br	H	92—92.5	92
H	OCH_3	66.5—67.5	a
OCH_3	H	42—43	a
H	OC_2H_5	72	72
H	NO_2	152—153	153
CH	Br	114	112
Br	CH_3	122—123	a

(a) Not previously reported.

Preparation of Solution.——A $1.0\times10^{-4}M$ solution was obtained from as $1.0\times10^{-2}M$ stock solution by 1 : 10 dilution prodeture.[1] Since the addition of H_2SO_4 solution of concentration higher than 40% evolves an intense heat, which might be caused the Wallach rearrangement,[1] the preparation of the solutions for higher concentration of H_2SO_4 was carried out by a stepwise procedure using a dry ice acetone bath. For example, 60% H_2SO_4 solution was prepared as follows: 5 ml. of a cold 30% H_2SO_4 solution were added slowly into a cold 50 ml. volumetric flask containing the stock solution of appropriate concentration and then another 5 ml. of 50% H_2SO_4 solution were added into the flask in cold. In the same manner, ca. 9 ml. of 60% H_2SO_4 and ca. 18 ml. of 70% H_2SO_4 solution were added. After warming to 25°±0.1, the solution was made up to the mark with 60% H_2SO_4 solution, so that the final concentration of the solution was 60% approximately.

Determination of pK—The ratios of concentration were measured by the standard method.[6a] and pK values were calculated by least square method.[6b] Since the solvent system was 20 Vol.% EtOH and 80 Vol.% H_2SO_4 H_2O mixture, Yeh and Jaffe's H_0 function[11] was used in stead of Hammett's H_0 function.[6a] A Cary Model 11 automatic recording spectrophotometer and Beckmann Model DU quartz spectrophotometer were used for the measurement of the absorption coefficient at the specified wave length. The cells used were either 1 cm. or 10 cm. silica cells.

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