ORGANIC AND BIOLOGICAL CHEMISTRY

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Tautomeric Equilibria. IV. The Basicities of Monosubstituted Azobenzenes. An Acidity Scale in 20% Ethanolic Aqueous Sulfuric Acid[1-3]

BY H. H. JAFFÉ AND R. W. GARDNER

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The pK's of 12 monosubstituted derivatives of azobenzene have been determined by a spectrophotometric method. In spite of the presence in the molecule of two distinct basic centers, the data are well represented by a single Hammett plot, with $\rho = 2.186 \pm 0.064$. Consequently it is suggested that the structure of the conjugate acid of azobenzene involves a proton bonded simultaneously to both nitrogen atoms, rather than a localized N-H bond. An acidity scale (H'_0) in a solvent consisting of 20 vol. % EtOH and 80% H_2O-H_2SO_4 mixtures is derived.

Considerable controversy and speculation exists concerning the structure of the first conjugate acid of *p*-dimethylaminoazobenzene.[4] In particular, it has not been definitely established whether the first proton adds to this compound at the amino or at the azo group. We are now attempting to provide an unambiguous decision to this question by use of the method developed in the first paper of this series.[2a] Application of this method requires a knowledge of the basicities and of their dependence on substituents of dimethylanilines and of azo compounds. While information on dimethylanilines is available,[5] the basicities of few azo compounds not containing an amino group have been reported. The pK of *p*-nitroazobenzene is well known,[6] and the pK of unsubstituted azobenzene has been reported,[4d] although the measurements were under conditions not strictly comparable to ours.

This paper reports the determination of the basicities (throughout this paper basicities are expressed as pK_a's of the appropriate conjugate acids) of a series of 12 monosubstituted derivatives of azobenzene and the treatment of these data by the Hammett equation.[7] The pK's were determined by the spectrophotometric method of Flexser, Hammett and Dingwall,[8] but a number of technical difficulties were encountered which required special techniques. The compounds under investigation proved insufficiently soluble in water and in dilute sulfuric acid to permit spectrophotometric measurements with the available equipment. Preliminary experiments indicated that all compounds[9] were sufficiently soluble in ethanol–water–sulfuric acid mixtures containing "20% ethanol" and 80% water–sulfuric acid mixture to permit measurements in this solvent system (the exact solvent composition is described under Experimental). Initial attempts to use the Hammett acidity scale H_0[7a] with the data obtained in this solvent system failed to yield pK values independent of the B/BH^+ ratio. Consequently an H_0' scale was established for our solvent system in a manner exactly analogous to that used originally by Hammett and Deyrup.[6]

The extinction coefficients (ϵ) of many of the compounds (both for the free base and the conjugate acids) did not prove independent of acid concentration in the solvent, even in the range where $|\log B/BH^+| > 2$, so that only free base or conjugate acid was present. In these cases a best straight line was fitted empirically to the ϵ *vs.* sulfuric acid concentration curve, and extrapolated values were used in the determination of the pK. This procedure is open to criticism since there is no *a priori* reason to expect the relation between ϵ and sulfuric acid concentration to be linear, and available measurements were sufficient neither in number nor in precision to demonsrate the existence of a linear relation. The justification for the use of the procedure lies in the circumstances that the corrections made were not large and lead to consistent results. The cause of the medium dependence of ϵ has not yet been investigated; it is, however, probably related to the known *cis-trans* isomerism of azo compounds.[10] Since the isomerization appears to be rapid in hydroxylic media, it did not appear possible to perform measurements on separated isomers. Accordingly all data reported refer to *cis–trans* mixtures, presumably at equilibrium.

Experimental

Compounds.—The azo compounds were prepared by the condensation of nitrosobenzene and the appropriate substituted aniline in glacial acetic acid.[11] The compounds

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[1] This work was supported by a Grant in Aid from the American Cancer Society, and in part by the Office of Ordnance Research, U. S. Army.

[2] (a) Paper I, THIS JOURNAL, **77**, 4445 (1955); (b) paper III, *J. Org. Chem.*, **22**, 1281 (1957).

[3] Abstracted from the M.S. thesis of R.W.G.

[4] (a) M. Rogers, T. Campbell and R. Maatman, THIS JOURNAL, **73**, 5122 (1951); (b) G. Badger, R. Buttery and G. Lewis, *J. Chem. Soc.*, 2143 (1953); (c) H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953); (d) I. Klotz, H. Fiess, J. Y. Chen Ho and M. Mellody, THIS JOURNAL, **76**, 5136 (1954); (e) E. Sawicki and F. Ray, *J. Org. Chem.*, **19**, 1686 (1954); (f) A. Pullman and B. Pullman, *Compt. rend.*, **243**, 1322 (1956); (g) E. Sawicki, *J. Org. Chem.*, **22**, 365 (1957).

[5] (a) W. C. Davies, *J. Chem. Soc.*, 1865 (1938); (b) W. C. Davies and H. W. Addis, *ibid.*, 1622 (1937).

[6] L. P. Hammett and M. A. Paul, THIS JOURNAL, **56**, 827 (1934).

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

[8] (a) L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935); (b) L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932); (c) ref. 7a, p. 267.

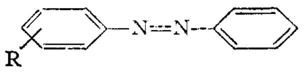
[9] As a single exception, at low sulfuric acid concentration, *p*-bromoazobenzene did not form stable solutions in the solvent used. The rate of crystallization, or more probably the rate of nucleation, from solutions prepared in the manner described under Experimental, however, was so slow that the solutions were in practice stable long enough to complete the measurements.

[10] G. M. Badger, R. G. Buttery and G. E. Lewis, *J. Chem. Soc.*, 2143 (1953).

[11] A. Baeyer, *Ber.*, **7**, 1638 (1874); K. Ueno and S. Akiyoshi, THIS JOURNAL, **76**, 3670 (1954).

TABLE I

THE pK'S OF MONOSUBSTITUTED AZOBENZENES



R	M.p., °C.	Wave length used λ_1, mμ	 λ_2, mμ	pK^b	σ^{7b}	σ^{+15}
H	68-69.5	320	420	−1.64 ± 0.02	0	0
p-C_2H_5O	77.5–78.5	350	462	−0.02 ± .03	−0.250	(−0.764)
p-CH_3O	54-55	348	458	−0.11 ± .02	− .268	− .764
p-CH_3	68.5–69.0	336	430	−1.11 ± .07	− .170	− .306
m-CH_3	165[c]	326	420	−1.47 ± .01	− .069	− .069
p-Br	89–89.5	334	430	−2.22 ± .02	.227	.148
m-Br	67-69.0	324	416	−2.55 ± .02	.391	.391
p-CH_3CO	115	330	420	−2.71 ± .01	.516	.516
p-CN	120.5–121.5	328	416	−3.19 ± .02	.628	.628
p-NO_2	135–136	338	418	−3.35 ± .00	.778	.778
m-NO_2	95–96.5	328	408	−3.30 ± .04	.710	.710
p-$(CH_3)_3N^+$[a]	....	326	408	−3.44 ± .10	.859	.859

[a] This compound was prepared by Mr. L. A. Jones. The pk is not included in the calculations since use of the H_0 function is not completely valid. [b] The uncertainties given are standard errors. [c] Boiling point at 15 mm.

were repeatedly recrystallized, usually from aqueous alcohol, and emphasis was placed on purity rather than yield. All compounds were analyzed for nitrogen[12] and the analyses agreed to within 1% with calculated values; melting points compared well with literature values and are listed in Table I.

Solutions.—Stock solutions of the azo compounds were prepared in commercial 95% ethanol at a concentration of about 10^{-4} M. Ten-ml. aliquots (measured throughout this work with a single pipet) were transferred to volumetric flasks thermostated at 25° and diluted to 50 ml. with a premixed water–sulfuric acid mixture of the appropriate concentration. Thus the solvent was reproducible and solutions were conveniently prepared. All solutions contained the same amount of ethanol, about 19% by volume.

Analysis for Sulfuric Acid.—For solutions in the critical B/BH^+ range, the sulfuric acid concentration had to be determined accurately. A calibration curve was prepared by determining the density of solutions prepared as above, but without base, and by titrating aliquots of the same solutions. The calibration curve then permitted determination of sulfuric acid by density determination. (*Cf.* Table II.) The solute base was present in sufficiently low concentration not to affect the density.

Procedure.—The spectra of the azo compounds in "20% ethanol" and of their conjugate acids in about "20% ethanol" containing 65 wt. % sulfuric acid were determined in the usual manner. Two wave lengths, usually the 320 mμ peak of the free base, and the 420 mμ peak of the conjugate acid were then chosen for further work and are listed in Table I. The region of sulfuric acid concentration in which B/BH^+ is near unity was determined by measurement of the absorption at the wave lengths selected of a series of base solutions in solvent containing varying sulfuric acid concentration. Further measurements on solutions in this region finally gave data on 8 solutions in the region of $|\log B/BH^+| \leq .7$ and approximately symmetrically distributed around $B/BH^+ = 0$. Finally, the absorption of several base solutions in low and high acid concentration was also determined to provide data for the extrapolation of ε-values for free base and conjugate acid into the critical region. All spectral measurements were performed using a Beckman model DU spectrophotometer with 1-cm. quartz absorption cells. Samples were thermostated to 25.0 ± 0.5° using a thermospacer assembly.

Calculations.—From the data obtained in this manner for p-nitroazobenzene and using $pK = -3.35$[6] for this compound, it was then readily possible to calculate eight H_0' values for our solvent system.[12a] Several of the B/BH^+ values in the range between 0.2 and 5 for m-nitroazobenzene fell at sulfuric acid concentrations in the range for which H_0' values had thus been determined and could be used to calculate the pK for this compound. The B/BH^+ values for sulfuric acid values outside this range were then used to extend the H_0' scale. This process was repeated for all compounds, and sufficient overlap was encountered to permit the use of this procedure, until p-methoxy- and p-ethoxyazobenzene were reached. At this point, the H_0' scale had to be extrapolated a short distance. Since all determinations were performed at two wave lengths, duplicate values were obtained for each solution and agreed within narrow limits. Further, 3 to 4 independent pairs of determinations of the pK of each compound were available and agreed among each other within a few hundredths of a unit in each case.

Results and Discussion

The Acidity Scale.—The H_0' scale derived for the "20% ethanol" solvent system used in this work, shown in Fig. 1 and Table II, is considerably steeper than the original Hammett scale, which is shown for comparison. This fact is due undoubtedly to the continuing increase of the non-polar component of the non-acidic part of the solvent as the sulfuric acid concentration increases. This H_0' scale should be of considerable usefulness in the determination of basicities of other weak bases, since the solubility problems encountered in this work undoubtedly are not unique. The scale obviously cannot be extended to or beyond 100% sulfuric acid, which provides a rather serious limitation, but the convenience of preparation of solutions should balance this limitation for many applications. Determination of H_0' is now being carried to lower and higher acidities. The internal consistency of the results obtained in this investigation confirms that the acidity function concept is valid

TABLE II

THE H'_0 SCALE IN "20% ETHANOL"

Wt. % H_2SO_4	Density	H_0, relative values
20	1.085	0.58
25	1.127	+0.10
30	1.165	−0.425
35	1.204	−1.00
40	1.244	−1.625
45	1.283	−2.28
50	1.324	−2.995
55	1.369	−3.79

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(12) Micro analyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Mühlheim (Ruhr), Germany.

(12a) In the expectation that the new H_0' scale would provide estimates of pK's in dilute aqueous solution (*cf.* ref. 12b), the known pK of p-nitroazobenzene was used as reference point. Since this expectation was not confirmed, the calculated values are relative to an arbitrary reference point.

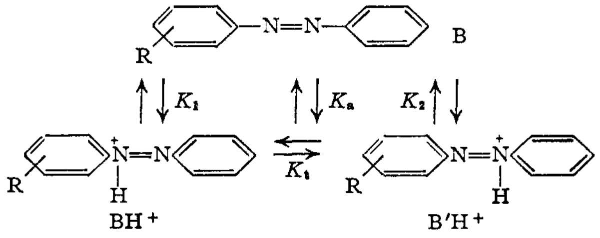
in our solvent system,[12b] at least in the narrow and closely related group of indicators used. The *pK*-values obtained, however, cannot be regarded as estimates of *pK*'s in aqueous solution. The reasons for this discrepancy are now under investigation.

Absorption Spectra.—The absorption spectra of all the azobenzene derivatives used in this work have been reported previously, usually in neutral and much less polar media. The discrepancies we observed between the spectra obtained by us and those previously reported are probably closely related to the medium effect on the spectra discussed above. The spectra of these compounds and of their conjugate acids will be discussed in a later paper.

Basicities.—The *pK* values found for the 12 compounds investigated are listed in Table I. Since Hammett's value of −3.35 for the *pK* of *p*-nitroazobenzene was used to fix our H_0' scale, this value provides no comparison. Klotz, Fiess, Chen Ho and Mellody[4d] reported −2.48 for the *pK* of azobenzene; their calculations were based on the acidity scale of Michaelis and Granick.[13] Recalculation on the basis of the Hammett H_0 scale leads to $pK_a = -2.3$. The *pK* of the methyl sulfate of trimethylammonioazobenzene (*p*-phenylazo-N,N,N-trimethylanilinium methyl sulfate) was also determined in this work in our solvent system ($pK = -3.44$) and was independently determined in this Laboratory in water ($pK = -3.04$). The discrepancies between the values in water and in our solvent system indicate that our values cannot be considered as estimates of values in dilute aqueous solution, and, consequently, our use of *p*-nitroazobenzene as reference is arbitrary and the values reported in this paper are only relative values. Extension of the H_0' scale to solutions very dilute in sulfuric acid and direct determination of a *pK* in such solutions will be necessary before the data achieve absolute significance.

The Structure of the Conjugate Acid and Substituent Effects.—Azobenzene contains two nitrogen atoms, each of which may be considered as a basic center. Since these atoms are equivalent, the same conjugate acid is formed by proton addition to either of them. In monosubstituted derivatives of azobenzene (B), however, the two nitrogen atoms are not equivalent, and accordingly two tautomeric conjugate acids of B (BH^+ and $B'H^+$) may be formed. The entire equilibrium scheme is shown in Chart I.

CHART I



K_a is the measured acid dissociation constant of the equilibrium mixture of BH^+ and $B'H^+$, ($K_a = [B][H^+]/\{[BH^+] + [B'H^+]\}$), K_t the tautomeric equilibrium constant for the equilibrium between BH^+ and $B'H^+$ ($K_t = [B'H^+]/[BH^+]$) and K_1 and K_2 are, respectively, the acid dissociation constants of BH^+ and $B'H^+$ ($K_1 = [B][H^+]/[BH^+]$, $K_2 = [B][H^+]/[B'H^+]$).

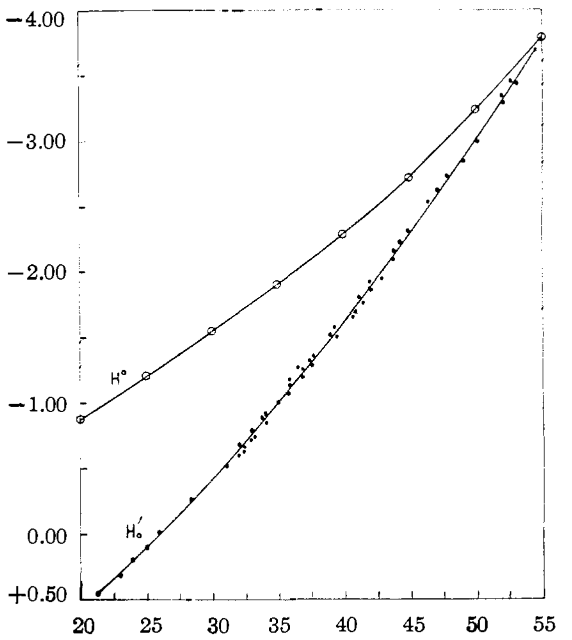


Fig. 1.—The H_0' scale in comparison with Hammett's H_0 scale.

From these definitions follow

$$K_t = K_1/K_2$$

$$\frac{1}{K_a} = \frac{[BH^+]}{[B][H^+]} + \frac{[B'H^+]}{[B][H^+]} = \frac{1}{K_1} + \frac{1}{K_2} = \frac{1}{K_1} + \frac{1}{K_1}K_t$$

$$K_a = K_1K_2/(K_1 + K_2) = K_1/(1 + K_t) \quad (1)$$

For unsubstituted azobenzene, $K_1 = K_2 = K°$, $K_t = 1$ and $K_a = K_1/2 = K_2/2$. Now, it appears reasonable to believe that the Hammett equation should be separately applicable to K_1, K_2 and K_t. With this assumption, setting $\delta = \rho_2 - \rho_1$[14] and dividing both sides of equation 1 by $K°$, we obtain

$$K_a/K° = 10^{\sigma\rho_1}\,10^{\sigma\rho_2}/(10^{\sigma\rho_1} + 10^{\sigma\rho_2}) = 10^{\sigma\rho_1}/(1 + 10^{\sigma\delta}) = 10^{\sigma\rho_1}/(1 + 10^{\sigma\rho_t}) \quad (2)$$

whence $\rho_t = \rho_2 - \rho_1$. Corresponding to this relation, for $\rho_t \neq 0$, $\rho_1 \neq \rho_2$, a plot of log K_a (or pK_a) *vs.* σ should be a curve, asymptotically approaching the lines log $(K_a/K°) = \sigma\rho_1$ and log $(K_a/K°) = \sigma\rho_2$ at large and small σ. At $\sigma = 0$, these asymptotes would intersect, while the experimental curve passes 0.3 unit below the intersection point.

There appears no *a priori* reason that substituents should influence the two basic centers in azobenzene equally. Consequently, we fully anticipated finding the curved *pK vs.* σ plot described in the preceding paragraph. If the data of Table I are plotted against σ, however, the curve shown in Fig. 2 (dotted line) results. It is seen that the points representing azobenzene and its *m*-methyl derivative lie on a single straight line together with all compounds involving an electron-withdrawing substituent. *p*-Methoxy-, *p*-ethoxy- and *p*-methylazobenzene deviate in the expected direction.

[12b] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

[13] L. Michaelis and S. Granick, THIS JOURNAL, **64**, 1861 (1942).

[14] Subscripts on ρ refer to the appropriate equilibrium.

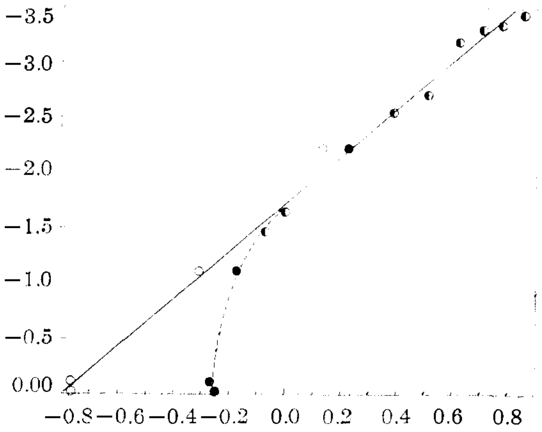
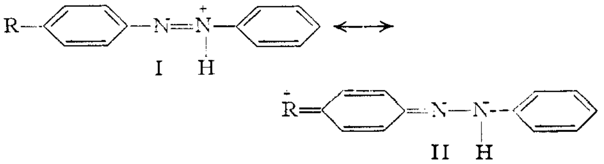


Fig. 2.—The pK *vs.* σ and σ^+ plots: open circles, σ-values; full circles, σ^+-values; half-filled circles, $\sigma = \sigma^+$.

However, the fact that azobenzene and *m*-methylazobenzene lie on the straight line indicates that this curve does not represent the case anticipated above but that we are more likely dealing with one of the deviations from the Hammett equation not uncommonly observed for *p*-alkoxy substituents.[7h]

The tautomer $B'H^+$ of the conjugate acids of substituted azobenzenes, when R is an electron-repelling substituent, should receive an appreciable stabilization from resonance between the structures I and II. Consequently, the new σ^+ substituent constants recently proposed by Brown and Okamoto[15] should be applicable to the equilibrium constants K_2. The solid curve in Fig. 2 shows a plot of pK *vs.* σ^+. The excellence of the fit is indicated by the statistical measures, the standard deviation from regression, $s = 0.110$, and the correlation coefficient, $r = 0.996$. Thus there can be no question that the basicity of monosubstituted azobenzenes is represented by a single term Hammett equation, using the σ^+ constants, with $\rho = 2.186 \pm 0.064$ and $\log k^0 = 1.73$. This finding has some far-reaching implications, which will now be examined.



I

II

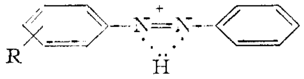
The most plausible interpretation would be to conclude that $\rho_1 = \rho_2$ and $\rho_t = 0$, although we can see no *a priori* reason why this should be so. But while we have seen that σ^+ should be applicable to the correlation of K_2-values, there is no reason why the same constant should apply to K_1-values. Accordingly, equation 2 would become

$$K_a/K^0 = 10^{(\sigma+\sigma^+)\rho}/(10^{\sigma\rho} + 10^{\sigma^+\rho}) = 10^{\sigma^+\rho}/(1 + 10^{(\sigma^+-\sigma)\rho})$$

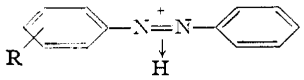
With ρ about 2.2 and $\sigma^+ - \sigma$ almost 0.5, $10^{(\sigma^+ - \sigma)\rho}$ in the denominator is far from negligible with respect to 1, and the *p*-methoxy- and *p*-ethoxyazobenzene points, and probably also the *p*-methylazobenzene point should not lie on the straight line in the *pk vs.* σ^+ plot. Consequently the postulate $\rho_1 = \rho_2$, $\rho_t = 0$ must be abandoned.

An alternate postulate explaining why the latter three points fall on the line is that the stabilization of $R'H^+$ due to the resonance I ⟷ II is sufficient to overcome the larger ρ-value (ρ_1) for the pK of RH; in other words that $|\sigma^+\rho_2| > |\sigma\rho_1|$, even though $|\rho_2| < |\rho_1|$. Considering the differences between σ and σ^+ for *p*-CH_3O, *p*-C_2H_5O and *p*-CH_3, such a postulate would not be untenable. However, for *m*-CH_3, $\sigma^+ = \sigma$ and consequently $|\sigma^+ \rho_2| < |\sigma\rho_1|$ would follow from $|\rho_2| < |\rho_1|$. Also, since $\sigma^+ = \sigma = 0$ for the unsubstituted compound, it follows that the points for azobenzene and its *m*-methyl derivative would have to lie below the line for the remaining points by 0.3 unit and more than 0.3 unit, respectively. Figure 2 shows that this is not the case. Hence, the postulate made at the beginning of this paragraph must also be rejected.

Thus, the experimental results appear to permit only one rational interpretation, for which, unfortunately, so far no direct evidence can be advanced. We now feel forced to propose that the structure of the conjugate acid of azobenzene is neither RH^+ nor $R'H^+$ but some intermediate structure alternatively represented by the equivalent structures[16] III or IV.

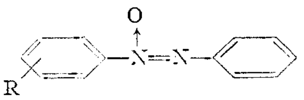


III

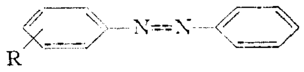


IV

An argument against this structure lies in the known isomerism of the azoxybenzenes, which exist as α- and β-isomers V and VI.[17]



V



VI

On the other hand, delocalized bonds, such as postulated in III and IV, have been encountered repeatedly in recent years[16,18] and cannot today be rejected on the basis that they form an entirely new type of bonding. Structures III and IV would be in accord with the experimental findings if it is assumed that the proton is not symmetric to the azo nitrogen atoms, but that, depending on the character of the substituent, structures resembling BH^+ and $B'H^+$, but with the hydrogen atom in a single position, make varying contributions to the actual state of the conjugate acid. The magnitude of the ρ-value found in this work is also in accord with this proposal. From qualitative considerations one might expect ρ_1 to be of the same order of

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[15] H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957).

[16] H. H. Jaffé, *Z. Elektrochem.*, **59**, 823 (1955).

[17] H. E. Bigelow, *Chem. Revs.*, **9**, 117 (1931).

[18] W. H. Eberhardt, B. Crawford and W. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).