

Addition of CCl_3Br .—A mixture of CCl_3Br (1200 g. or 6 moles), benzoyl peroxide (6 g.) and $\text{CFCl}=\text{CF}_2$ (215 g. or 2 moles) was shaken in an autoclave. The temperature was slowly raised to 85° in about 2 hours, and during this period the pressure rose to a maximum of 7 to 8 atmospheres after which it dropped progressively to 2.5 to 3 atmospheres in about one-half hour, then fell to zero when the autoclave was brought to room temperature. The reacted mass was subjected to distillation; as soon as most of the excess of CCl_3Br was removed, the pressure was lowered to 6 mm. and by continued distillation a fraction of crude $\text{C}_3\text{Cl}_4\text{F}_3\text{Br}$ (285 g. or 45% yield) was collected, with b.p. $58-63^\circ$ at 6 mm., n_D^{20} 1.4673 to 1.4643. Next came a fraction $\text{C}_3\text{Cl}_4\text{F}_3\text{Br}$, b.p. $104-115^\circ$ at 6 mm., n_D^{20} 1.4532, and a residue, n_D^{20} 1.4455, which were discarded.

Fluorination to $\text{C}_3\text{F}_3\text{Cl}_3$.—Part of the C_3 obtained in the above addition (131 g. or 0.41 mole) was heated with $\text{SbF}_3\text{-Cl}_2$ (200 g. or 0.8 mole) at 100° for 48 hours in a rocking autoclave. Distillation gave 78 g. of a product b.p. 72° , which is an 80% yield if it is assumed that the reaction product is $\text{C}_3\text{F}_3\text{Cl}_3$.

Fluorination to $\text{C}_3\text{F}_3\text{Cl}_2$.—The above product ($\text{C}_3\text{F}_3\text{Cl}_3$, 78 g. or 0.38 mole) was mixed with fresh SbF_3Cl_2 (65 g.), and heated in a shaking autoclave at 150° for 48 hours. Distillation gave 62 g. of a product boiling 34 to 36° , n_D^{20} 1.3044, which is an 85% conversion on the basis of the reaction product being $\text{C}_3\text{F}_3\text{Cl}_2$.

Dechlorination to $\text{CF}_3\text{CF}=\text{CF}_2$.—The preceding product (62 g. or 0.28 mole) was mixed with an equal volume of absolute ethanol, sealed in an autoclave containing 20.2 g. of granular zinc and shaken overnight at 100° . Distillation gave 25 g. of a product b.p. -29° , which is a 59% conversion on the basis of $\text{CF}_3\text{CF}=\text{CF}_2$.

Attempted Dehalogenation of $\text{C}_3\text{Cl}_4\text{F}_3\text{Br}$.—This reaction was attempted in the hope that the addition product of CCl_3Br and $\text{CFCl}=\text{CF}_2$ would yield a mixture of $\text{CCl}_2=\text{CF-CF}_2\text{Br}$ and $\text{CCl}_3\text{CF}=\text{CF}_2$ if its formula were $\text{CCl}_3\text{CClFCF}_2\text{-Br}$, but would not react (at least not without loss of fluorine) if it were $\text{CCl}_3\text{CF}_2\text{CFCIBr}$. The reaction with zinc occurred very readily, but the reaction products were a complex mixture instead of the expected propenes, in which the main constituent seemed to be a compound, b.p. 170° , presumed to be $\text{CF}_2=\text{CFCCl}=\text{CClCF}=\text{CF}_2$. This type of "doubling up" has been observed before.^{6,7} Titration of the mixed chlorine and bromine ions in the solution corresponded to the quantity of zinc consumed, while a test for fluorine ions was only very faint.

The operating conditions were then modified by feeding $\text{C}_3\text{Cl}_4\text{F}_3\text{Br}$ to an agitated suspension of zinc in boiling alcohol; by adjusting the water flow in the reflux condenser, it became possible to allow an azeotropic mixture of alcohol and olefin to distil through, while most of the saturated halide was returned to the reaction. The distillate was washed with water, dried and distilled to yield only two fractions, the first of which boiled $32-35^\circ$ at 25 mm., n_D^{20} 1.4212, and was regarded as the desired olefin, while the second one b.p. $68-72^\circ$ at 25 mm., n_D^{20} 1.4644, was clearly recovered starting material. As the olefin was formed without loss of fluorine, it was held that a central CFCI group must have been present in the starting compound.

(6) E. J. Young, Ph.D. dissertation, The Ohio State University, 1947.

(7) A. L. Henne, J. W. Shepard and E. J. Young, *THIS JOURNAL*, **72**, 3577 (1950).

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

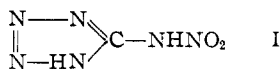
The Comparative Acidic Properties of Some 5-Substituted Tetrazoles

BY EUGENE LIEBER, SEYMOUR H. PATINKIN AND HSIANG HSIA TAO¹

The effects of substituents in the 5-position of the tetrazole ring have been determined potentiometrically. The substituents examined were hydrogen, chlorine, bromine, iodine, amino, azido and nitroamino. The potentiometric behavior of nitroguanyl azide, the open chain isomer of 5-nitroaminotetrazole, is also reported. Substitutions in the 5-position of the tetrazole ring have an effect which is quite analogous to that found in ortho-substituted benzoic acids, the acidities increasing in the order $-\text{NH}_2$, $-\text{H}$, $-\text{I}$, $-\text{Br}$ and $-\text{Cl}$, with the azido and nitramino groups having unusual effects which cannot be explained by the electronegativity properties associated with those groups. 5-Nitroaminotetrazole is a dibasic acid, the acidity of the first proton being comparable to strong mineral acids, that of the second proton having a value of approximately 10^{-7} . The comparative acidic properties of some similarly constituted 1,2,4-triazoles are presented and discussed.

Introduction

The strong acidic properties of 5-nitroaminotetrazole² (I) had previously been noted³ qualitatively by means of indicators. In order to define more precisely the effect of substitution on the tetrazole ring the comparative order of acidities and approximate dissociation constants of 5-chloro, 5-bromo, 5-iodo, 5-amino, 5-hydrogen (tetrazole), 5-azido and 5-nitroaminotetrazole, together with the mono-potassium salt of 5-nitroaminotetrazole, have been calculated from potentiometric measurements.



(1) Abstracted from a portion of the thesis submitted by Hsiang Hsia Tao to the Graduate School of the Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science.

(2) The numbering scheme for the tetrazoles is $\begin{array}{c} \text{N} \text{---} \text{N} \\ \diagdown \quad \diagup \\ \text{N} \text{---} \text{N} \end{array} \text{C}_5$. See

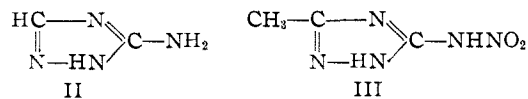
F. R. Benson, *Chem. Revs.*, **41**, 1 (1947).

(3) E. Lieber, E. Sherman, R. A. Henry and J. Cohen, forthcoming publication.

Of the large number of 5-monosubstituted tetrazoles that have been reported,² the acidic dissociation constants of only the 5-carboxy,⁴ 5-amino,⁵ 5-carboxamide⁶ and tetrazole⁶ have been determined.⁷

The dissociation constants of tetrazole and 5-aminotetrazole were redetermined in this paper, since the effect of an amino group upon the acidic properties of tetrazole seemed to be out of line in comparison with the effect of the same group on the acid properties of benzoic acid.

In order to determine the effect of altering the symmetry of the tetrazole ring by the introduction of a carbon atom in place of nitrogen on the acidity,



(4) E. Oliveri-Mandala, *Gazz. chim. ital.*, **45**, II, 303 (1915).

(5) E. Bauer, *Z. physik. Chem.*, **23**, 409 (1897).

(6) E. Oliveri-Mandala, *Gazz. chim. ital.*, **44**, II, 175 (1914).

(7) After the submission of this paper for publication a report appeared by J. S. Mihina and R. M. Herbst, *J. Org. Chem.*, **15**, 1082 (1950), presenting acidic dissociation constants for twenty-five alkyl- and aryl-5-substituted tetrazoles.

the acidic dissociation constants of 5-amino- II, and 3-methyl-5-nitroamino-1,2,4-triazole (III) were also determined by potentiometric measurement.

Experimental

Apparatus.—All determinations were carried out at room temperature in a potentiometric Precision-Shell Titrometer.

Compounds.—The purities of the compounds used in this study were determined by elementary nitrogen analysis and are summarized in Table I.

TABLE I

ACIDIC DISSOCIATION CONSTANTS OF 5-MONOSUBSTITUTED TRIAZOLES, NITROGUANYL AZIDE AND 5-SUBSTITUTED

Compound	1,2,4-TRIAZOLES		k_{c1}	$10^6 K$	k_{c2}
	Nitrogen, % Calcd.	Found			
Tetrazole	79.97	79.79	1.3 ^b		
5-Chlorotetrazole	53.59	53.12	850		
5-Bromotetrazole	37.61	38.01	740		
5-Iodotetrazole	28.89	29.33	140		
5-Aminotetrazole	82.23	82.18	0.1 ^c		
5-Azidotetrazole	88.29	88.20	Strong		
Potassium 5-nitroaminotetrazole	49.98	50.39		0.08	
5-Nitroamino-tetrazole	64.62	64.12	Strong	.09	
Nitroguanyl azide	64.62	64.95		.05	
3-Methyl-5-nitroamino-1,2,4-triazole ^d	48.94	49.41	1.6		Too weak
5-Amino-1,2,4-triazole	59.51	59.73	Too weak		

^a Micro analyses by Micro Tech Laboratories, Skokie, Illinois. ^b Value identical to that reported by Oliveri-Mandala, reference (6). ^c The value reported by Bauer,⁵ was 6.8. ^d Sample furnished by Dr. Ronald A. Henry, U. S. Naval Ordnance Test Station, China Lake, California.

Method and Calculation.—The acidic dissociation constants of the compounds described in Table I were determined by titration of a weighed sample of the compound in aqueous solution with standard alkali. From the data the apparent acid dissociation constants were calculated in the usual way using points at or near the region of half neutralization.

Results

The following order of acidities was found (Table I): $-\text{NH}_2 < -\text{H} < -\text{I} < -\text{Br} < -\text{Cl} \ll -\text{NHNO}_2, -\text{N}_3$. Figure 1 graphically summarizes the potentiometric data obtained for potassium 5-nitroaminotetrazole, 5-aminotetrazole, tetrazole and 5-bromotetrazole and makes quite obvious the comparison in acid strengths. Figure 2 summarizes the potentiometric data obtained for the dibasic acid, 5-nitroaminotetrazole.

The approximate acidic dissociation constants for the dibasic acid, 5-nitroaminotetrazole (I) were obtained (Table I, Fig. 2). The first acid hydrogen was found to act as a strong acid, giving the theoretical pH for a completely ionized acid. The calculated and observed pH values are summarized below, the data being taken from Fig. 2.

Ml. NaOH added	0.0	1.0	2.0	3.0	5.0
Calcd. pH	2.16	2.28	2.36	2.44	2.68
Obsd. pH	2.15	2.20	2.30	2.40	2.65

It will be noted from Fig. 2 that both protons can be detected potentiometrically. The second acidic dissociation constant was found to be about $9 \times$

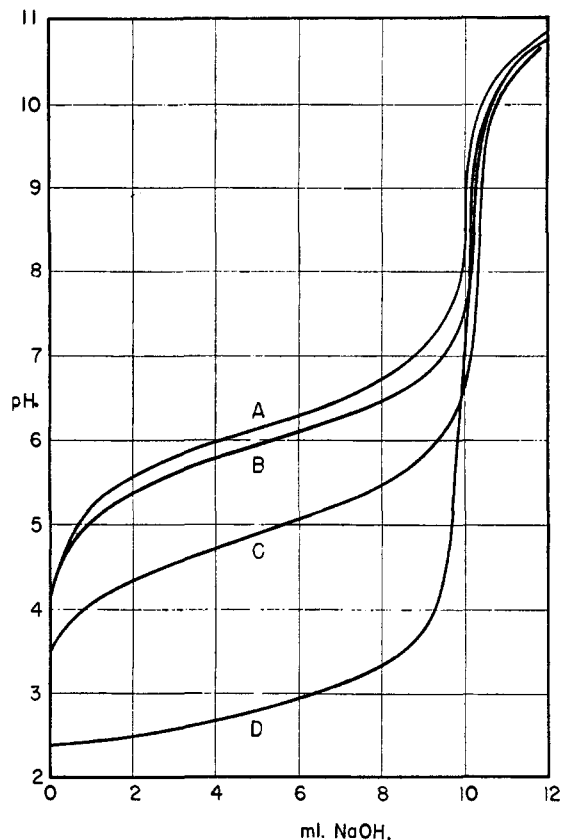


Fig. 1.—Potentiometric titration of 5-monosubstituted triazoles: A, potassium 5-nitroaminotetrazole, 1.032 millimole in 135 ml. water; B, 5-aminotetrazole, 1.052 millimole in 135 ml. water; C, tetrazole, 1.053 millimole in 135 ml. water; D, 5-bromotetrazole, 1.032 millimole in 135 ml. water. All solutions were titrated with 0.1022 N NaOH.

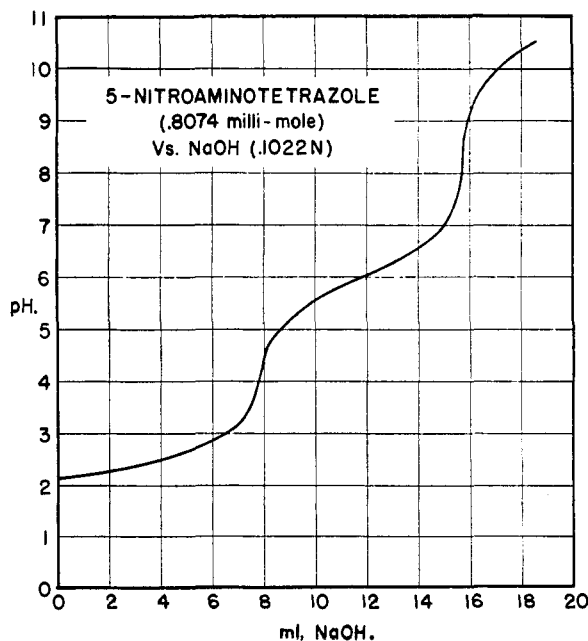


Fig. 2.—Potentiometric titration of 5-nitroaminotetrazole, 0.8074 millimole in 135 ml. of water.

10^{-7} as determined both from the free acid (I) and the mono-potassium salt.

The calculated and observed pH values for 5-azidotetrazole considering complete ionization are:

Ml. NaOH added	0.0	3.0	5.0	9.0	11.0
Calcd. pH	2.93	3.03	3.12	3.34	3.50
Obsd. pH	2.97	3.08	3.23	3.50	3.61

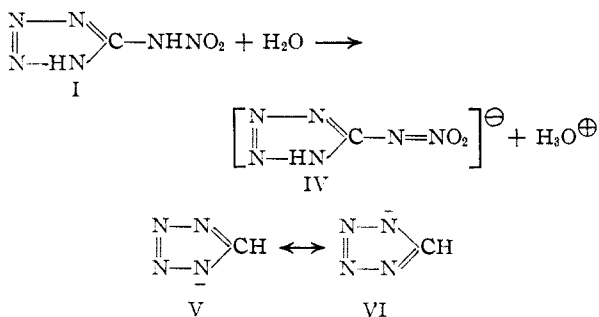
Discussion

Substitution in the 5-position of the tetrazole ring has been found to bring about an effect which is quite analogous to that found in ortho-substituted benzoic acids, except for the 5-nitroamino- and the 5-azidotetrazoles. This is clearly brought out in the following comparison in which the data for the ortho-substituted benzoic acids are taken from Dippy³ and those for 5-methyl- and 5-phenyl-tetrazoles from Mihina and Herbst.⁷ The com-

Ortho substituent	Tetrazole	$10^4 K$	Benzoic acid
H	1.3		6.27
Cl	850		114
Br	740		140
I	140		137
NH ₂	0.1		1.0
CH ₃	27.4		12.3
C ₆ H ₅	29.8		34.7

parisons are made with ortho substituted benzoic acids since in the tetrazoles the substituent group is ortho to the nitrogen attached to the active hydrogen.

Two possible explanations can be offered to account for the strong acid properties of 5-nitroaminotetrazole. First, one can consider that the nitramine group, $-NHNO_2$, acts to withdraw electrons from the ring and hence causes an increase in the acidity of the ring hydrogen. The second possibility suggests that the hydrogen of the nitramine group is the strong acid hydrogen. The removal of the hydrogen from the nitramine group will result in a large increase in resonance (I \rightarrow IV) which would mean a large increase in stabilization of the anion with respect to the free acid. The acidity of tetrazole, the parent compound, undoubtedly lies in the symmetry of the resonance forms of the anion (V and VI) and for which two other symmetrical anion forms may exist derived from the tautomeric tetrazole in which the



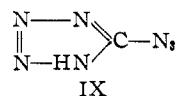
active hydrogen is in the 2-position in the ring. This is strikingly brought out by considering the acidic dissociation constant found for 3-methyl-5-nitroamino-1,2,4-triazole, and the inability to determine potentiometrically the acidity of 5-

amino-1,2,4-triazole, and also by comparing the relative acidities of 1,2,4-triazole (VII) and tetrazole (VIII). The triazole (VII) has a basic dissociation constant,⁹ albeit weak, while the tetra-



zole (VIII) is an acid of the strength of the usual organic acids. Triazole (VII) does exhibit some acidic properties due to the imino hydrogen atom as shown by the formation of a silver salt.¹⁰ It seems improbable that the negative effect of the nitramine group is sufficient to account for the large increase in acidic properties of 5-nitroaminotetrazole (I) over that of the parent compound, tetrazole (VIII). It appears, therefore, that the large increase in acidity over that of the unsubstituted tetrazole must be due to an increase in the stability of the anion because of resonance considerations and it is thus postulated that the first strong proton is that liberated by the nitramine group (I \rightarrow IV). Assuming this thesis to be correct the authors know of no other example in which the acidic property of a parent, which we now take to be nitramide, NH_2NO_2 , for which the acidic dissociation constant has been determined¹¹ to be 2.55×10^{-7} , has been increased to such an extent by the introduction of a negative substituent of the order of acidity of 10^{-5} .

Further evidence for the argument that the strong proton of 5-nitroaminotetrazole is that evolved from the nitramine group due to increased stability of the anion from resonance and symmetry considerations is found in the surprisingly strong acid properties of 5-azidotetrazole (IX)



in which only the ring hydrogen can be involved. Here again the increase in acid properties over that of tetrazole (VIII) is too great to be explained on the basis of the electron-withdrawing effect of the azido-group. The linearity of the azido-group¹² preserves the symmetry of the molecule such that all the resonance forms of the anion are nearly equivalent. 5-Azidotetrazole (IX) is an acid of properties equal to that of the usual strong mineral acids. This large increase in acidity over that of the 5-halogen substituted tetrazoles must then be due to the superposition of the resonance of the azido-group to that of the tetrazole ring. Further consideration of the acidic dissociation constant of phenylnitramide, $C_6H_5NHNO_2$, which has been determined¹³ to be 2.3×10^{-5} leads to the conclusion that the tetrazole ring affords much greater opportunities for resonance than the benzene ring.

Nitroguanyl azide (X) is known⁸ to cyclize with

(8) E. Buchner, *Ann.*, **273**, 218 (1893).

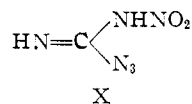
(10) H. H. Strain, *This Journal*, **49**, 1566 (1927).

(11) J. N. Brønsted and C. V. King, *ibid.*, **59**, 193 (1927).

(12) L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933).

(13) A. Hantzsch, *Ber.*, **35**, 266 (1902).

(9) J. F. A. Dippy, *Chem. Revs.*, **28**, 206 (1939).



rapidity on addition of a base to form salts of 5-nitroaminotetrazole. Hence it is of considerable interest that nitroguanyl azide can be titrated potentiometrically with a base and that the form of the curve shows only one break which is equivalent to the complete neutralization of 5-nitroaminotetrazole to the di-acid salt. Using the half-neutralization point as corresponding to the second proton of 5-nitroaminotetrazole a value of k_{c_2} of 5×10^{-7} is obtained which is in very good agreement with the value obtained by titration

of the acid itself. It is interesting to note that the initial pH of a water solution of nitroguanyl azide is acidic to the extent expected for an acid with a K_c of about 10^{-6} . This can only be due to the dissociation of the proton from the nitramide group.

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CHICAGO 16, ILLINOIS

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF PORTLAND]

Surface and Interfacial Tension Titrations of Long Chain Quaternary Salts in Brom Phenol and Brom Thymol Blue Solutions

BY EUGENE L. COLICHMAN

Surface tension and drop time (effective interfacial tension) results of a series of long chain quaternary salts in titrations vs brom phenol and brom thymol blue are reported herein. These properties, ordinarily intrinsic, are applied here to the quantitative analysis of surface-active materials. These results show the micellar nature of the quaternary-dye "ion-pair" compound as formed in aqueous solutions. The relation of the presently observed phenomenon to polarography and to determinations of critical micelle concentrations is noted.

The effective conductometric titrations previously reported¹ showed that the known^{2,3,4} affinity of brom phenolate blue anions for long chain cations is due to "ion-pair" formation in dilute aqueous solutions probably followed by aggregation into micelles. These results suggested the possibility of quantitative determinations of long chain quaternary salts, by employing the specific reactants, brom phenol and brom thymol blue, in surface and "effective" interfacial tension titrations. Furthermore, the present results establish the nature of the state of aggregation of the "ion-pair" compound in solution.

Surface and interfacial tension measurements on all types of surface-active materials as a means of detecting critical micelle concentrations have been reported^{5,6,7} frequently. The minima in these surface tension-concentration curves, earlier attributed to time effects, is now known^{8,9,10} to be due to the presence of impurities. However, the analytical possibilities of such measurements have not been explored previously. That metathesis reactions (*viz.* long chain quaternary cations and brom phenolate or brom thymolate blue anions) can be characterized by surface and "effective" interfacial tension titrations is shown here.

Experimental

Octab (Rhodes Chemical Co.) is 100% octadecylbenzyl-dimethylammonium chloride. Cepacol (Wm. S. Merrell Co.) is a proprietary antiseptic solution, 250 p.p.m. cetyl pyridinium chloride. The other quaternary salts used here were described previously¹ as were the purification and standardization procedures. The 0.100% brom phenol (B.P.B.) and brom thymol (B.T.B.) blue standard solutions were prepared from C.P. chemicals by recognized procedure.¹¹

The buffer solutions¹² were prepared from C.P. materials as follows: pH 2.00-4.00, potassium acid phthalate and hydrochloric acid; pH 4.00-5.50, potassium acid phthalate and sodium hydroxide; pH 6.00-8.05, potassium dihydrogen phosphate and sodium hydroxide. A Beckman pH Meter, Model G, was used in checking the pH values.

Surface tension measurements (uncor.), by the ring method, were made using a Cenco-DuNuoy Interfacial Tensiometer, No. 70540.

The "effective" interfacial tension measurements were obtained by using a functional dropping mercury electrode¹³; however, polarographic measurements were not involved. As in polarographic work, the drop times, recorded with a stop watch, were obtained as average values by counting ten drops. Capillaries, 0.03-0.05 mm. internal diameters, employed at 3 to 6 second drop times, as recommended¹³ in polarography, were found satisfactory and necessary here. Drop times greater than 6 seconds were erratic and not reproducible.

Twenty-five to one hundred ml. of the various buffer solutions and aliquot portions of the 0.100% dye solutions were added to cylindrical dishes in establishing the desired initial concentrations of ionic dye species. Portions of standard quaternary solutions were added dropwise from microburets. Mechanical stirring in between increment additions was found to be desirable. About two minutes was required for turbulence to subside after each addition

(11) Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 4th ed., p. 942.

(12) Britton, "Hydrogen Ions," D. Van Nostrand Co., Inc., New York, N. Y., Vol. I, Chap. 16.

(13) Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., Revised Reprint, 1946, pp. 240-243.

(1) Colichman, *THIS JOURNAL*, **72**, 1834 (1950).

(2) (a) Auerbach, *Anal. Chem.*, **15**, 492 (1943); (b) **16**, 739 (1944).

(3) Colichman, *ibid.*, **19**, 430 (1947).

(4) (a) Hartley and Runnicles, *Proc. Roy. Soc. (London)*, **168A**, 420 (1938); (b) Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

(5) Adam and Shute, *ibid.*, **34**, 758 (1938).

(6) Nutting, Long and Harkins, *THIS JOURNAL*, **62**, 1496 (1940).

(7) Tartar, Sivertz and Reitmeier, *ibid.*, **62**, 2375 (1940).

(8) Miles and Shedlovsky, *J. Phys. Chem.*, **48**, 57 (1944).

(9) Miles, *ibid.*, **49**, 71 (1945).

(10) Brady, *ibid.*, **53**, 56 (1949).