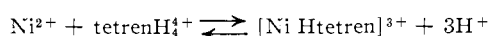


TABLE IV

FORMATION CONSTANT CALCULATED BY METHOD OF BJERRUM FOR THE EQUILIBRIUM BETWEEN NICKEL(II) PERCHLORATE AND TETREN AT 25°

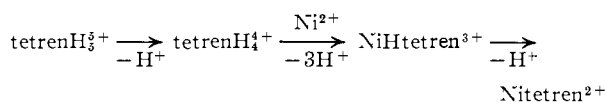
pH	$C_{Me} \times 10^4$	$C_{HCl} \times 10^2$	C_T	C_A	\bar{n}_T	pT	$C_T - C'_T$	\bar{n}_{Me}	log K
4.26	4.505	1.014	4.505	0.9590	3.547	17.91	1.801	0.40	17.73
4.29	4.484	0.9524	4.484	.9011	3.527	17.83	1.929	.43	17.70
4.33	4.464	.8929	4.464	.8461	3.502	17.71	2.048	.46	17.69
4.39	4.405	.7154	4.405	.6747	3.464	17.59	2.457	.56	17.69
4.44	4.386	.6579	4.386	.6216	3.433	17.45	2.570	.59	17.60
								Av. log K	17.68

may be illustrated by the equation



The formation constant for the "hydrogen" complex formed in this process was calculated, the results being given in Table III.

The agreement of the formation constants calculated from the "Excess-metal ion" curve and the "Equivalent" curve indicates that no polynuclear complexes are formed. Thus for the over-all neutralization process and complex formation the following equations are descriptive.



The formation constant for Nitetren²⁺ obtained by the method of Bjerrum is in excellent agreement with that obtained by the method of Schwarzenbach; however, the former method does not yield formation constants for the "hydrogen complex." Attempts also were made to measure the formation constants polarographically, but due to irreversibility of the system this method was unsuccessful.

Thermodynamic data calculated from the variation of log K with temperature are no more accurate than the reliability limits of the constants and hence are not reported.

Acknowledgments.—The authors wish to thank the Office of Ordnance Research U. S. Army for the support of this and continuing investigations.

NEW ORLEANS 18, LOUISIANA

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY AT TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. XVI. A Study of the Complex Ions Formed by the Copper(II) Ion with Triethylenetetramine, Tetraethylenepentamine and Pentaethylenhexamine¹

BY HANS B. JONASSEN, J. AARON BERTRAND, FRANK R. GROVES, JR., AND ROBERT I. STEARNS

RECEIVED APRIL 6, 1957

The complexes of the copper(II) ion with triethylenetetramine, tetraethylenepentamine and pentaethylenhexamine have been studied polarographically. It has been shown that the copper(II) ion exhibits an amine coordination number of five with these compounds and that hydrogen complexes are formed.

Introduction

The polarographic study of complex ions is a well established method² provided that the complex ion to be investigated is reduced reversibly at the dropping mercury electrode. If a plot of $E_{d.e.}$ versus the corresponding values of $\log(i_d - i)/i$ from equation I is a straight line with slope $2.303(RT/nF)$ the reduction process is reversible.

$$E_{d.e.} = E_{1/2} + 2.303 RT/nF \log(i_d - i)/i \quad (I)$$

Where

- $E_{d.e.}$ = voltage at the dropping mercury electrode
- $E_{1/2}$ = half-wave potential of the complex
- i_{d1} = diffusion current
- i = current at any $E_{d.e.}$
- n = number of electrons transferred

The composition of the complex can be determined from the equation

$$(E_{1/2})_c - (E_{1/2})_s = 2.303 RT/nF \log K_c - 2.303 RT/nF p \log C_x \quad (II)$$

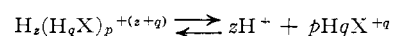
Where

- $(E_{1/2})_c$ = half-wave potential of the complex
- $(E_{1/2})_s$ = half wave potential of the simple aquo metal ion
- K_c = dissociation constant of the complex
- p = no. of moles of ligand per mole of metal ion in the complex
- C_x = concn. of ligand in moles/l. (C_x must be in considerable excess over the concn. of the metal ion in order that the concn. of the simple aquo metal ion will be negligible.)

A plot of $(E_{1/2})_c$'s of several solutions of varying C_x versus $\log C_x$ will yield a straight line of slope $2.303 RT/nF p$ from which p can be calculated.

Using the value of p established in equation II pK_c can be calculated.

The polyamines which become protonated to varying degrees depending upon the pH of the solution become a special case. Their dissociation occurs as shown in the reaction



(1) Abstracted in part from the Master's Theses submitted to Tulane University, New Orleans, Louisiana, by J. Aaron Bertrand, 1956, Frank R. Groves, Jr., 1951, and Robert I. Stearns, 1955.

(2) I. M. Kolthoff, "Polarography," Interscience Publishers, New York, N. Y., 1952.

Where

z = no. of protons dissociated from the acid amine
 q = no. of protons associated with the amine in the complexes formed

The equilibrium constant of this dissociation is

$$K_a = \frac{[H^+]^z [H_q X^{z-q}]^p}{[H_z(H_q X)_p]} \quad (III)$$

According to this notation the ligand is $H_q X^{z+q}$ and the term C_x of equation II is given by $[H_q X^{z+q}]$. Also

$$[H_z(H_q X)_p] = \Sigma [(HX)_p]^{-1} + [(H_2 X)_p]^{-2} + \dots + [H_{z-q}(X)_p] \quad (IV)$$

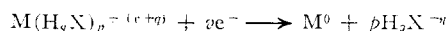
Solving (III) for $p \log [H_q X^{z+q}]$

$$p \log [H_q X^{z+q}] = zpH + \log K_a + \log [H_z(H_q X)_p] \quad (V)$$

Substituting (V) into (II)

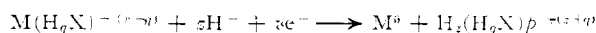
$$(E_{1/2})_c - (E_{1/2})_s = 2.303 \frac{RT}{nF} \log K_c - 2.303 \frac{RT}{nF} (zpH - \log K_a + \log [H_z(H_q X)_p]) \quad (VI)$$

The reduction of a complex ion of a protonated polyamine occurs then as



M denotes the metal and v its oxidation state.

Combining this with the dissociation of the protonated amine the over-all reaction occurs



A series of solutions may be prepared in which all the factors are constant except the pH and the $(E_{1/2})_c$'s which are measured and plotted *versus* each other. By equation VI such a plot will be a straight line of slope $2.303(RT/nF)z$ from which the value of z may be calculated.

Approximate thermodynamic values can be calculated by the usual equations.³

Experimental

The technical grades of triethylenetetramine (trien), tetraethylenepentamine (tetren) and the mixture of amines designated "Polyamine H" were obtained from Carbide and Carbon Chemicals.

I. Purification of Triethylenetetramine.—Stock solutions of trien were made by weighing out accurately proper amounts of trien which had been purified previously.⁴ More dilute solutions were prepared by diluting aliquot portions of this stock solution.

II. Purification of Tetraethylenepentamine.—Tetren pentahydrochloride was obtained in the pure state by adding 100 g. of technical grade tetren to 100 ml. of benzaldehyde slowly and with vigorous stirring so as to avoid overheating. After the addition of the benzaldehyde the mixture was allowed to cool to room temperature with occasional stirring. At this point the mixture became quite viscous. The Schiff base separated when about 15 to 20 times its volume of water was added.

The water layer containing some unreacted tetren and other water-soluble impurities was separated from the oily Schiff base at the bottom of the beaker. About 200 ml. of concentrated HCl was then added slowly to the Schiff base. The mixture was heated after dilution with 100 ml. of water until it dissolved.

After cooling the solution in an ice-bath the tetren pentahydrochloride was precipitated with methanol. This recrystallization was repeated several times until a pure white product was obtained. The product was then washed with acetone and finally with ether, and then dried in the oven at about 80°.

(3) F. Daniels, "Outline of Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1948.

(4) H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm and R. M. Rogan, THIS JOURNAL, **72**, 2430 (1950).

Tetren pentahydrochloride was prepared similarly by using nitric acid.

The products were analyzed for primary amine nitrogen content by the Van Slyke method⁵; calcd. for tetren·5HCl, 7.54%; observed, 7.48%. Calcd. for tetren·5HNO₃, 5.56; observed, 5.65.

III. Purification of Pentaethylenehexamine.—About 1.5 l. of "Polyamine H" was distilled under a pressure of 10 to 20 mm. with about 1 l. of distillate being collected. Four hundred ml. of this distillate was redistilled and the fraction boiling at 220–250° (10–20 mm. pressure) was collected.

Forty milliliters of this fraction was dissolved in 250 ml. of methanol and cooled in an ice-bath. Concentrated HCl was added dropwise while stirring and a precipitate formed after the addition of about 50 ml. This was filtered, washed with acetone and ether and dried in a vacuum desiccator.

By the method of Van Slyke⁶ the primary amine nitrogen content was determined; calcd. N, 6.21%; observed, 6.26%. By means of a potentiometric determination against NaOH the equivalent weight was determined; calcd., 75.19; observed, 75.13.

Aqueous stock solutions using boiled distilled water of tetren pentahydrochloride, tetren pentahydrochloride and hexen hexahydrochloride were prepared and standardized potentiometrically against NaOH. Other solutions of these amines were prepared by dilution of these stock solutions.

Stock solutions of cupric perchlorate (G. Frederick Smith Chemical Co.) and cupric nitrate were prepared using boiled distilled water and standardized electrolytically.

A carbonate-free solution of NaOH was obtained by first preparing a saturated solution of NaOH and letting it stand about a week. This was then filtered and diluted with distilled water and standardized against potassium acid phthalate.

Concentrated HCl and HNO₃ were diluted with distilled water and the stock solution standardized against NaOH.

The solutions used in the polarographic determinations of the trien and hexen complexes were prepared with the stock acid amine solutions to which a calculated amount of NaOH was added to neutralize the acid. By the addition of HNO₃ the pH for the trien complexes was varied.

The pH determinations were made with a Beckman Model G pH meter, standardized with Beckman buffer solutions (pH 's of 4, 7 and 10).

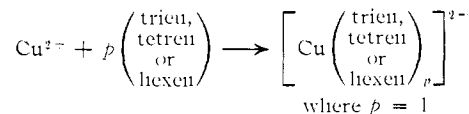
The polarograph was one assembled according to the Leeds and Northrup technical manual 77-12-0-8, using Leeds and Northrup parts.

Results and Discussion

Stability Studies.—Polarograms were determined in the usual way. The $E_{1/2}$ (S.C.E.)'s for the various solutions are listed in Table I.

The polarographic data which showed reversible reduction were then used to determine the constitution of the complexes, the dissociation constants, and other thermodynamic functions. It was also shown that the reduction occurs in one step involving the transfer of two electrons.

A plot of the values of $(E_{1/2})_c$ *versus* the corresponding values of $\log C_{\text{trien}}$, C_{tetren} and C_{hexen} resulted in a straight line whose slope indicated a value of 1 for p in the formation equation



Using equation II and the $E_{1/2}$ values listed in Table I, the dissociation constants of the complex ions $[Cu\text{trien}]^{2+}$, $[Cu\text{tetren}]^{2+}$ and $[Cu\text{hexen}]^{2+}$ were calculated. In these calculations the value of $(E_{1/2})_s$ was taken to be +0.04.⁶ The results of these calculations are shown in Table II.

(5) D. D. Van Slyke, *J. Biol. Chem.*, **83**, 425 (1929).

(6) H. H. Willard, L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand, Inc., New York, N. Y., 1952.

TABLE I
MEASUREMENT OF HALF-WAVE POTENTIALS

$C_{\text{Cu(II)aq}},$ $M \times 10^{-2}$	$C_{\text{suppr}},$ M	$E_{1/2}$			
		25°	30°	35°	45°
(a)					
trien	NaNO ₃				
2.0	0.1		-0.542		
5.0	.1		-.538		
7.5	.1		-.553		
8.7	.1		-.555		
(b)					
tetren	KCl				
0.5	0.1	-0.607		-0.610	-0.609
1.0	.1	-.617		-.620	-.610
1.5	.1	-.622		-.622	-.615
2.0	.1	-.630		-.630	-.621
(c)					
hexen	NaCl				
0.5	0.1	-0.638		-0.647	-0.647
1.0	.1	-.643		-.660	-.652
1.5	.1	-.648		-.654	-.660
2.0	.1	-.652		-.668	-.660

- (a) $[\text{Cu}^{2+}] = 5.0 \times 10^{-4} M$; maximum suppressor was methyl red
 (b) $[\text{Cu}^{2+}] = 4.0 \times 10^{-4} M$; maximum suppressor was gelatin
 (c) $[\text{Cu}^{2+}] = 4.0 \times 10^{-4} M$; maximum suppressor was gelatin

TABLE II
AVERAGE pK_c VALUES

	25°	30°	35°	45°
$[\text{Cutrien}]^{2+}$		20.7		
$[\text{Cutetren}]^{2+}$	24.25		23.58	22.64
$[\text{Cuhexen}]^{2+}$	25.13		24.74	24.22

The approximate thermodynamic data of these complexes are listed in Table III. The data for the $[\text{Cutrien}]^{2+}$ complex are added for comparison.⁷

TABLE III

APPROXIMATE THERMODYNAMIC VALUES IN KCAL./MOLE	25°	30°	35°	45°
$[\text{Cutrien}]^{2+}$				
ΔH^0		22.0		
ΔF^0		28.6		
$[\text{Cutetren}]^{2+}$				
ΔH^0	32.69		32.69	32.69
ΔF^0	33.07		33.24	32.95
$[\text{Cuhexen}]^{2+}$				
ΔH^0	19.62		19.62	19.62
ΔF^0	34.28		34.86	35.26

It has been shown that for most polyamines the amine coordination number of the copper(II) ion is less than six.^{7,8}

Since a relatively large increase of the stability of the $[\text{Cutetren}]^{2+}$ ion over that of the $[\text{Cutrien}]^{2+}$ ion occurs, it is indicated that the coordination number of the copper(II) ion is greater than four, possibly five.

The pK_c of the $[\text{Cuhexen}]^{2+}$ ion is about the same as that of the $[\text{Cutetren}]^{2+}$ which seems to

(7) H. B. Jonassen, G. G. Hurst, R. B. LeBlanc and A. W. Meibohm, *J. Phys. Chem.*, **56**, 16 (1952).

(8) H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, *THIS JOURNAL*, **72**, 4968 (1950).

indicate that in both cases five copper to nitrogen bonds exist. The ΔH^0 values, however, indicate that the $[\text{Cuhexen}]^{2+}$ ion is less thermally stable than the $[\text{Cutetren}]^{2+}$ ion since its dissociation is accompanied by endothermic ΔH^0 of 19.62 kcal./mole, whereas the ΔH^0 of $[\text{Cutetren}]^{2+}$ is 32.69 kcal./mole. This would be expected since an additional amine group is present which does not seem to be bound to the copper(II) ion.

pH Studies.—Plots of $(E_{1/2})_c$ versus pH (Figs. 1, 2, 3) give the value of z of equation VI. For all

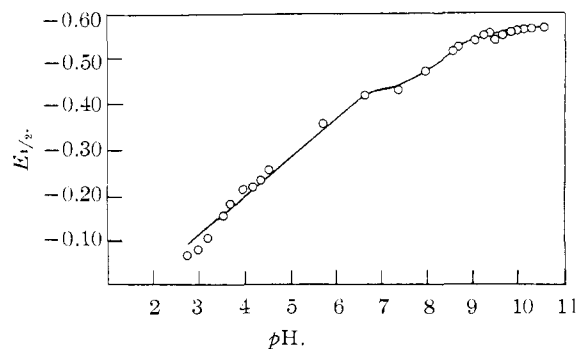


Fig. 1.—Cu(II)-triethylenetetramine system: each solution $4 \times 10^{-4} M \text{Cu}(\text{ClO}_4)_2$, $1 \times 10^{-2} M$ triethylenetetramine, $0.1 M \text{KCl}$, 0.01% gelatin; slope = 0.086.

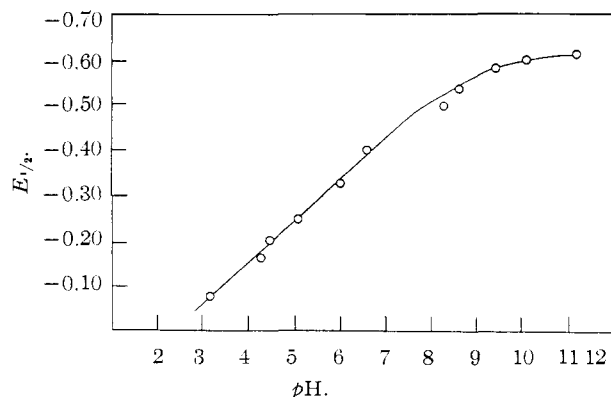


Fig. 2.—Cu(II)-tetraethylenepentamine system: each solution $4 \times 10^{-4} M \text{Cu}(\text{ClO}_4)_2$, $1 \times 10^{-2} M$ tetraethylenepentamine, $0.1 M \text{KCl}$, 0.01% gelatin; slope = 0.093.

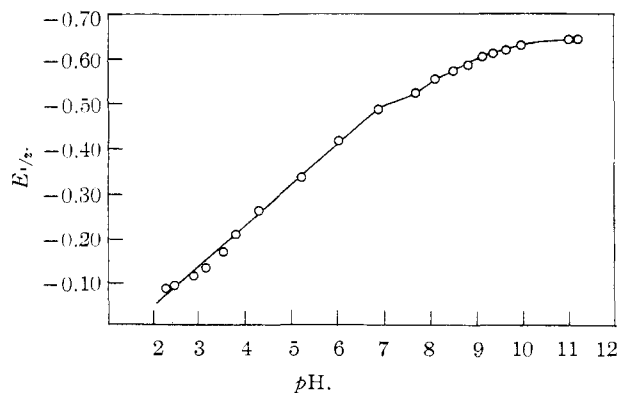
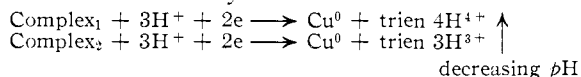


Fig. 3.—Cu(II)-pentaethylenhexamine system: Each solution $4 \times 10^{-4} M \text{Cu}(\text{ClO}_4)_2$, $1 \times 10^{-2} M$ pentaethylenhexamine, $0.1 M \text{NaCl}$, 0.01% gelatin; slope = 0.093. For each system for $z = 3$, theoretical slope = 0.089.

three complexes the maximum slope found in the pH regions of about 3 to 6 corresponded to a value of 3 for z .

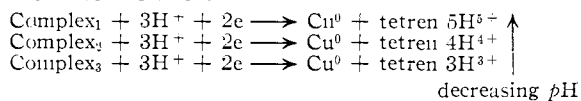
Considering the species of the protonated amines existing in the pH regions of the study the following reactions are indicated:

For the Cu(II)-trien complexes with decreasing pH two reactions may occur

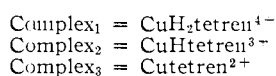


This would fit the data if $\text{Complex}_1 = [\text{CuH-trien}]^{2+}$ and $\text{Complex}_2 = [\text{Cutrien}]^{2+}$

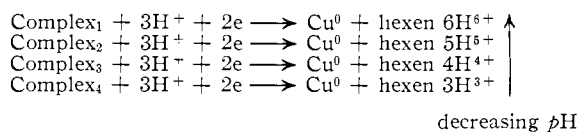
For the Cu(II)-treden complex these three reactions fit the data.



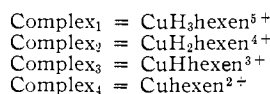
if



For the Cu(II)-hexen system four reactions would explain the data



If



This also seems to indicate that three of the copper to amine bonds in the copper(II) polyethylene-amine complexes are of about the same order of strength, far greater than the strength of the proton to amine bond. The other copper to amine bonds are of about the same order of strength as the proton to amine bond and an equilibrium is set up between them. At least three of the amine groups are bound to the copper(II) ion, the rest are protonated depending upon the pH of the medium.

Acknowledgment.—The financial support of part of this work by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

NEW ORLEANS, LA.

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY AT TULANE UNIVERSITY]

Studies of Metallated Dye Complexes. III. Copper(II)-*o*-Azophenol Complexes

By HANS B. JONASSEN AND ELWOOD J. GONZALES¹

RECEIVED APRIL 22, 1957

Spectrophotometric and conductometric evidence indicates that the copper(II)-*o*-azophenol complex forms a copper(II) complex with propylene glycol in alkali in which the glycol and copper(II)-dye react in a 1:1 mole ratio. The complexes $\text{K}[\text{Cu}-o\text{-azophenol}-\text{OH}]$ and $\text{Cu}(\text{II})-o\text{-azophenol}-\text{H}_2\text{O}$ were isolated from ethanolic solution.

Introduction

o-Azophenol, a dye containing hydroxy groups *ortho* to the azo group, readily forms a dye complex with transition metal ions in which the metal ion is bound to the two oxygen atoms and to the azo linkage as shown by investigations of Morgan and co-workers,²⁻⁸ Drew and Landquist,⁹ Wilson,¹⁰ and Oliver.¹¹ In the present investigation dihydroxy compounds, propylene glycol (pngl) and *l*-2,3-butanediol, having free rotation of the hydroxy groups, are used to show their effect on the unsaturation of the copper(II) complex coordination sphere.

Experimental

A. Reagents.—Pngl (99+ % pure), white label, Eastman Kodak Company was used without further purification.

(1) Abstracted in part from a thesis submitted by Elwood J. Gonzales to the Tulane University in partial fulfillment of the requirements for the degree of Master of Science.

(2) G. T. Morgan and J. D. Main-Smith, *J. Chem. Soc.*, 704 (1921).

(3) G. T. Morgan and J. W. Porter, *ibid.*, 645 (1915).

(4) G. T. Morgan and E. D. Evans, *ibid.*, 1126 (1919).

(5) G. T. Morgan, *J. Soc. Dyers and Colourists*, **37**, 43 (1921).

(6) G. T. Morgan and J. D. Main-Smith, *J. Chem. Soc.*, 2866 (1922).

(7) G. T. Morgan, *ibid.*, 1731 (1924).

(8) G. T. Morgan and J. E. Moss, *J. Soc. Chem. Ind.*, 461T (1923).

(9) H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, 292 (1938).

(10) J. S. Wilson, Doctoral Dissertation, Tulane University, 1952.

(11) J. Oliver, *THIS JOURNAL*, **79**, (1957).

A sample of dye prepared according to Willstätter and Benz¹² was kindly furnished by Mr. Gayle Strickland. The melting point was found to be 172-173° (lit. value 172°).

l-2,3-Butanediol, kindly furnished by Dr. R. E. Reeves, was used in polarimetric studies, $[\alpha]_D -12.8^\circ$.

Formamide, C.P. grade, Fisher Scientific Company, was distilled at 8 mm. pressure and the fraction boiling at 89-90° collected. The refractive index at 23° was 1.4468.

Molar solutions of pngl, *l*-2,3-butanediol, and the dye were prepared by direct weighing and dilution to volume with oxygen-free 95% ethanol prepared by bubbling nitrogen deoxygenated by alkaline pyrogallol into ethanol for at least one hour.

Aqueous molar solutions of copper(II) chloride were prepared by weighing directly reagent grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, dried over partially dehydrated $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and diluting to volume.

A molar solution of copper(II) nitrate was prepared by dissolving reagent grade $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in one liter of distilled water. A drop of C.P. concd. nitric acid was added to suppress hydrolysis. The copper(II) ion concentration was determined by electrolysis.

Aqueous molar potassium hydroxide solutions were prepared by weighing the appropriate quantities of potassium hydroxide. Standardization was against potassium acid phthalate using phenolphthalein as indicator.

B. Spectrophotometric Studies.—Absorption measurements in the visible spectral region were made with a Beckman Model B spectrophotometer using 1-cm. matched Corex cells. All solutions were diluted to 100 milliliters with oxygen-free 95% ethanol prepared by bubbling nitrogen deoxygenated by alkaline pyrogallol into ethanol for at least

(12) R. Willstätter and M. Benz, *Ber.*, **39**, 3492 (1906).