THE SILVER REDUCTOR FOR ORGANIC COMPOUNDS IN GLACIAL ACETIC ACID

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Adam J. Gahn
1963

ABSTRACT

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Silver metal will not reduce the organic nitro compounds tested in glacial acetic acid. Quinone is reduced by silver due to formation of quinhydrone; however, this is a special case and not representative of most reducible organic compounds.

Dissolved silver in acetic acid may be determined accurately and rapidly by potentiometric titration with standard chloride solution using the mercury-mercurous acetate electrode in acetic acid as reference electrode and clean silver metal as the indicator electrode. The accuracy and precision of this method compare favorably with the familiar gravimetric precipitation.

The formal potential of the silver-silver(I) couple in acetic acid has not been determined. The silver species present in acetic acid from 10^{-3} M to 10^{-5} M obeys the Nernst equation with an n value of one.

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1963

ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. Kenneth G. Stone for his guidance and unfailing encouragement throughout the entire investigation and preparation of this thesis.

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INTRODUCTION

One of the most useful methods for the quantitative determination of organic compounds containing a reducible function is the reduction of that function followed by a measurement of its disappearance or the appearance of the product reduced species. Metal reductors have long been used for the determination of inorganic species in aqueous solution but have not been generally applied to organic analysis. Keller demonstrated that both lead and zinc could be used to reduce nitro compounds, with the resulting amines and metal acetates being determined as bases in glacial acetic acid by radio-frequency titration with standard perchloric acid (7).

Silver metal was proposed as a quantitative reductor of aqueous ferric ion as early as 1934 by Walden, Hammett, and Emonds (14). The subsequent extensions of this idea have been reviewed by Stegemann (12).

Since the redox potential of silver metal is lowered by the presence of an excess of precipitating anion; for example, chloride in water, the existence of similar species in acetic acid suggested that silver might be used in a reducing column in glacial acetic acid. To study the electrode reactions in this nonaqueous system, a number of reference and indicator electrodes were considered.

Conant and Hall (5) proposed an aqueous saturated calomel electrode as reference with contact to the acetic acid through a glass frit:

$$Hg \mid Hg_2Cl_2(s),\ KCl\ (sat'd\ in\ H_2O),\ frit,\ HOAc$$

Scaramo and Arnaldo (10) used mercury-mercurous acetate plated on gold and immersed in acetic acid:

$$Au,\ Hg \mid HgOAc\ (s),\ HOAc$$

The potentials of both of the above electrodes tended to drift with time. The potential of the former varied because of its liquid junction and the latter because of the thinness of the plated surface.

Reproducible, drift-free electrodes were at best secondary standards. Kolthoff and Bruckenstein (4) proposed modification of the calomel electrode for use with acetic acid solvent:

$$Hg,\ Hg_2Cl_2 \mid NaCl,\ NaClO_4,\ HOAc$$

Schwabe (11) assembled an electrode directly related to acetic acid in that the anion is acetate:

$$Hg \mid Hg_2(OAc)_2\ (s),\ NaOAc,\ HOAc$$

Since chloride ion was to be determined in the study, the chloride-free mercury-mercurous acetate system using sodium perchlorate as electrolyte was chosen as a secondary reference. The original electrode of this type was proposed by Stone and Al-Qaraghuli (1).

$$Hg \mid Hg_2(OAc)_2\ (s) \mid\mid NaClO_4\ (\text{sat'd in HOAc}),\ HOAc$$

The potential of this electrode still contains a junction potential but any variation has been minimized by the use of saturated solutions. Experimentally, the electrode has proven satisfactory.

The choice of an indicator electrode for use in glacial acetic acid was based on consideration of the literature. Hills (6) reviewed the potentiometric measurement of hydrogen ion. One of the few redox systems reported in acetic acid is the detection of ceric ion by means of a platinum indicator electrode with glass as the reference electrode at constant pH by Rao and Vasudeva (9).

Metallic indicator electrodes sensitive to either silver or halide ions in non-aqueous solvents are described by Bishop (3). Tomicek and other Czechoslovakian investigators succeeded in the potentiometric titration of chloride and bromide in acetic acid using a silver-silver chloride indicator electrode as summarized by Stock and Purdy (13). The standard electrode potential of the silver-silver chloride couple in glacial acetic acid is reported by Mukherjee to be +0.6180 volts versus a standard hydrogen on platinum reference (8). Again, a general review of indicator electrodes in acetic acid is presented by Hills (6).

EXPERIMENTAL

Chemicals

The chemicals used in this investigation were not purified unless otherwise stated. Generally, analytical reagent or A.C.S. specification grades were used. The relatively impure nitro compounds could be analyzed in the process of the determination if necessary.

The compounds used, their commercial source and labeled purity are as follows:

Acetic acid, Mallinkrodt, analytical reagent and Allied (Baker and Adamson), A.C.S. Reagent

Acetic anhydride, Matheson, Coleman, and Bell, A.C.S. Reagent

Ammonium hydroxide, Mallinckrodt, Analytical Reagent

Calcium chloride, Allied, Technical

Crystal Violet, Eastman, Certified Reagent

Erioglaucin, National Aniline, C.P.

Hydrochloric acid, Mallinckrodt, Analytical Reagent

Hydroquinone, Eastman, C.P.

Lithium Chloride, Mallinckrodt, Analytical Reagent

Mercurous Acetate, Amend, C.P.

Mercury, Baker, Analyzed Reagent

Methylene Blue, Matheson, Coleman, and Bell, Certified Reagent

Neutral Red, Matheson, Coleman and Bell, C.P.

Nitric acid, Mallinckrodt, Analytical Reagent

ortho-Nitrobenzoic acid, Eastman, C.P.

Nitrogen, Liquid Carbonic, Technical

ortho-Nitrophenol, Eastman, C.P.

para-Nitrophenol, Eastman, C.P.

Perchloric acid, Baker, Analyzed Reagent

Phenosafranine, Eastman, C.P.

Potassium Acid Phthalate, Allied (Baker and Adamson), A.C.S. Reagent, Primary Standard

Quinhydrone, Eastman, C.P.

Quinone, Eastman, Practical

Silver, G. F. Smith, Reagent

Silver acetate, Baker, Purified

Silver Nitrate, Baker, Analyzed Reagent

Silver Oxide, Merck, Technical

Silver Perchlorate, G. F. Smith, Reagent

Sodium Acetate, anhydrous, Fisher, certified reagent

Sodium Acetate, trihydrate, Baker, Analyzed Reagent

Sodium chloride, Mallinckrodt, Analytical Reagent

Sodium perchlorate, G. F. Smith, Anhydrous Reagent

Zinc, Baker, to meet A.C.S. specifications.

Standard Solutions

Standard perchloric acid in acetic acid was prepared by diluting 8.5 ml. of 72 per cent perchloric acid to about 1500 ml. with acetic acid and then adding 20 ml. of acetic anhydride with constant swirling. The solution was then diluted to exactly two liters with more acetic acid. The solution was standardized by reaction with accurately weighed amounts of dried potassium acid phthalate to the blue-green endpoint of crystal violet indicator (three drops 0.1 per cent solution in acetic acid).

Standard sodium chloride solution was prepared by dissolving an accurately weighed amount of dried compound in water and diluting to one liter.

Standard sodium acetate in acetic acid was prepared by first analyzing weighed samples of sodium acetate trihydrate with previously prepared standard perchloric acid. Since the sodium acetate trihydrate appeared to be of primary standard quality, an accurately weighed amount was dissolved in acetic acid and diluted to exactly two liters. Later titrations of aliquots of this solution with standard perchloric acid agreed with the direct method of preparation. In all sodium acetate versus perchloric acid titrations, crystal violet was used as indicator.

Standard silver in acetic acid was prepared by dissolving an accurately weighed amount of silver acetate in 70 ml. of acetic acid, adding an excess of 72 per cent perchloric acid (about 5 ml.) with constant swirling and diluting the resulting solution to 100 ml. The solution was standardized by both potentiometric titration versus standard aqueous sodium chloride solution and by gravimetric precipitation of silver chloride.

Standard calcium chloride in glacial acetic acid was prepared by dissolving a weighed amount of the technical grade compound in about two liters of acetic acid. This solution was also standardized by potentiometric titration into an aliquot of the standard silver solution and by gravimetric precipitation by the addition of an excess of silver in the form of aqueous silver nitrate.

Apparatus Used

A Beckman Zeromatic pH meter equipped with a grounded solution shield, a chloride-free mercury-mercurous acetate reference electrode (1), and a commercial silver electrode, Fisher Scientific Co. No. 9-312-37, was used for all potentiometric titrations. The silver electrode was used without special preparation except for the study of its potential as a function of dissolved silver concentration.

Changes in acetic acid conductivity as a function of various salt concentrations were measured with an Industrial Instruments Corporation Model R.C. conductance bridge. The constant of the cell used in this operation was about 0.1.

A Beckman Model DK-2 spectrophotometer was used to measure the ultraviolet absorption spectra of various organic mixtures in glacial acetic acid.

Apparatus Preparation

Reference Electrode

The reference electrode used is essentially that described by Al-Qaraghuli and Stone (1) except that the jacketing solution contained saturated rather than 0.5 M sodium perchlorate in acetic acid. This change was made to facilitate preparation and gain reproducibility.

Silver Reducing Column

The silver reducing column was prepared in a typical Jones reductor column. Glass wool plugs were inserted above and below the granular silver metal packing to keep it in place and prevent fouling of the glass stop-cock.

Indicating Electrode

Throughout most of the present work, the silver electrode was used just as it arrived. The sensitive surface, dull gray in appearance, was stored in glacial acetic acid between uses.

Later, in the study of silver electrode potential, the surface of the electrode was cleaned by immersion in concentrated ammonium hydroxide followed by immersion in dilute nitric acid. After a rinse in acetic acid, the electrode appeared to have the familiar flat white surface of clean silver metal. Repeated washing as above did not change the behavior of the electrode except at very low dissolved silver concentrations as will be discussed later.

Reduction Procedures

In the Beaker

The beaker reduction procedure was devised in order to study efficiently the reducing properties of silver metal in glacial acetic acid. In this technique, a weighed amount of reducible organic compound was dissolved in about 40 ml of acetic acid in a 150 ml. beaker. The beaker was covered with a watchglass and a glass tube introduced beneath the surface of the solution to bubble dry nitrogen through the sample. After purging with nitrogen for fifteen minutes, approximately 0.1 g. of granular metallic silver washed in dilute nitric acid was introduced to the solution and allowed to stand in contact with the solution under nitrogen purge until a constant potential between the silver and mercury-mercurous acetate electrodes was observed. The general procedure was varied at times by the addition of different amounts of standard perchloric acid solution just prior to the addition of the metallic silver.

On the Column

The silver reducing column was used to reduce methylene blue by passing about 0.01 g of methylene blue hydrochloride in acetic acid plus excess perchloric acid through the column. The dye solution was eluted from the column at about one drop per second. Precaution was taken so that at no time was the column allowed to run dry lest channelling of the column or oxidation of the reduced substance occur.

Titration Procedures

Potentiometric Determination of Silver

The silver ion formed by the oxidation of silver metal was titrated with standard calcium chloride in acetic acid. The reduction mixture was decanted from the metallic silver and the latter washed with more acetic acid. The total solution including the washings was placed in a 150 ml beaker, a Teflon coated magnetic stirrer bar and the electrodes were inserted, the nitrogen purge was continued. After noting the original potential, the addition of standard chloride was followed using the ±700 millivolt scale of the pH meter. The data obtained were plotted on a graph showing the relationship of the potential as a function of the volume of standard chloride solution. The endpoint is assumed to be the mid-point of the potential jump, that is, the arithmetic mean of the potential curve before and after the equivalence point. Since the temperature of the laboratory did not vary more than two degrees C. from twenty-six degrees C. during the course of the titrations, it was felt that it was not necessary to thermostat the acetic acid solutions.

Titration of Hydrogen Ion Using an Indicator

Hydrogen ion usually present in the reduction mixture as the result of the addition of perchloric acid, was determined by the addition of two to four drops 0.1 per cent crystal violet solution and titration with standard sodium acetate. The yellow, acid crystal violet was titrated to the blue endpoint.

When standard perchloric acid was used in the reverse procedure to titrate sodium acetate, the crystal violet color change was from blue to blue-green. That is, in both cases, the acid-base endpoint with crystal violet indicator in glacial acetic acid was taken as the blue to blue-green transition.

DISCUSSION OF RESULTS

Reduction of Organic Compounds

Organic Nitro Compounds

Preliminary investigations were made to see whether silver metal in glacial acetic acid would actually reduce some of the organic compounds reported by Keller (7). It was anticipated that reduction of organic compounds would yield a corresponding oxidation of silver metal. Thus, if reduction occurred, its progress could be followed readily by potentiometric titration of dissolved silver with standard chloride. It was observed that in the presence of dissolved silver in acetic acid the mercury-mercurous acetate, silver cell yielded a positive potential. In the presence of dissolved chloride the potential was negative.

The reduction of three organic nitro compounds with silver was attempted by the beaker procedure. Para-nitrophenol, ortho-nitrophenol, and ortho-nitrobenzoic acid all failed to give positive cell potentials even after standing overnight in contact with metallic silver. Thus, no silver was oxidized to silver(I) and the results implied that silver would not reduce these compounds in acetic acid.

Quinone

Next, a more easily reduced compound was studied with the beaker reduction procedure. Quinone was apparently reduced and a substantial amount of dissolved silver detected and titrated as summarized in Table I. Upon calculation of the amount of dissolved silver titrated, it was apparent that about half as many milliequivalents of silver were oxidized as were added in the form of quinone. That is to say, because of the amount of dissolved silver titrated, approximately half of the quinone appeared to be reduced.

Table I. Volumetric Determination of Silver Oxidized by Quinone

Quinone		Cl^-		No. of meq. Ag^+ found
g.	No. of meq.	N	ml.	
0.0157	0.291	0.0100	18.00	0.180
0.0405	0.749	0.1000	4.52	0.452
0.0373	0.690	0.1000	3.40	0.340

In an effort to explain the half-complete reduction of quinone, it was postulated that two molecules of quinone react with two atoms of silver and two hydrogen ions to yield one molecule of quinhydrone and two silver ions. The overall reaction might be written as the sum of two steps:

$$2\ Ag \longrightarrow 2\ Ag^+ + 2e^-$$

$$2\ Quinone + 2e^- + 2H^+ \longrightarrow Quinhydrone$$

$$2\ Ag + 2\ Quinone + 2H^+ \longrightarrow 2\ Ag^+ + Quinhydrone$$

Examination of the ultraviolet absorption spectra of known samples in acetic acid showed the spectrum of the reduction mixture to be more like that of quinhydrone than either quinone or hydroquinone as shown in Figure 1. If the suggested reaction is correct, the reduction by silver metal would proceed because the formation of quinhydrone effectively removes product hydroquinone from the system.

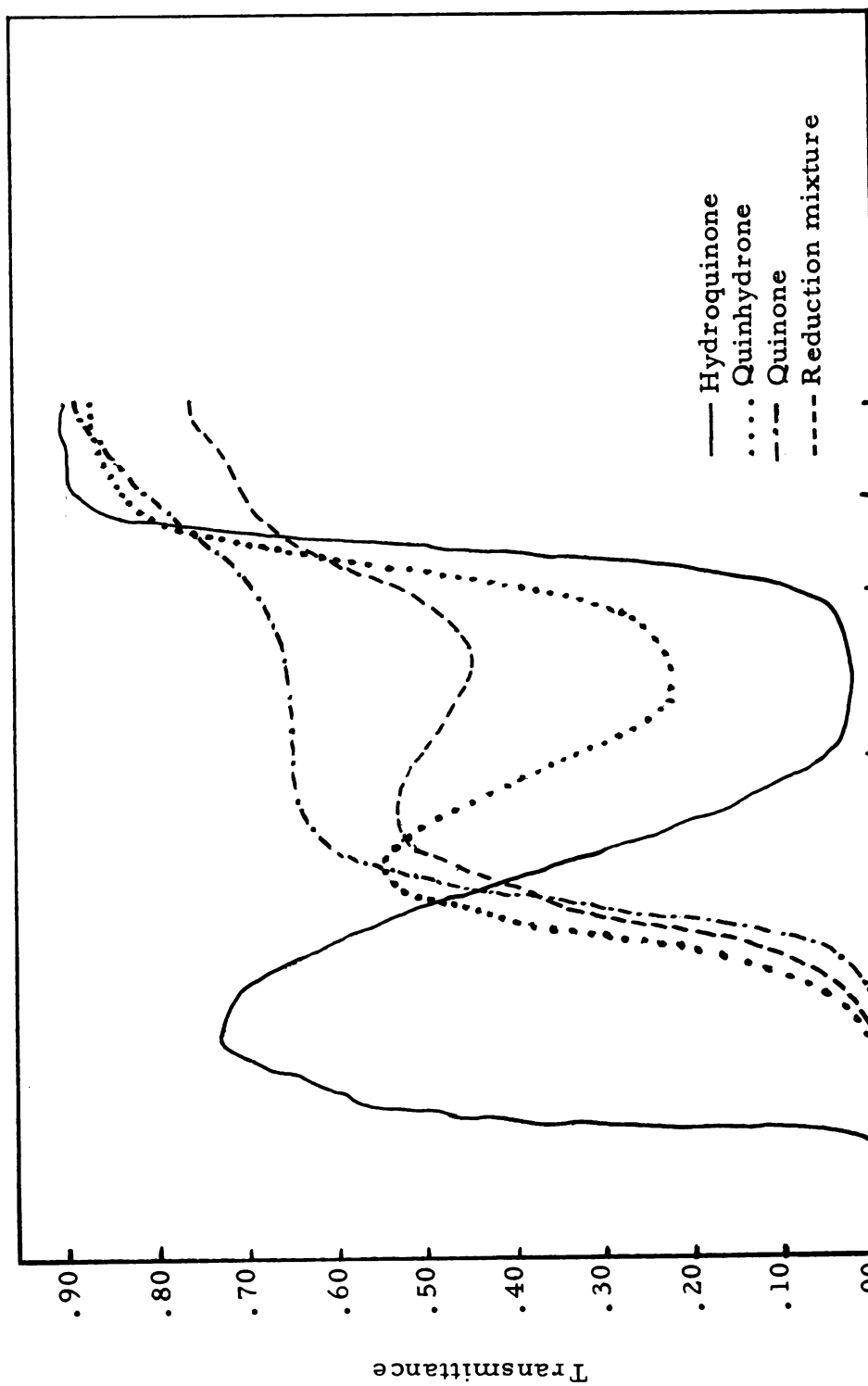

Figure 1. Ultraviolet Spectra in Acetic Acid.

Determination of Dissolved Silver

Standard Chloride Solution

Since calcium chloride appears to be one of the most soluble inorganic chloride salts in glacial acetic acid (2), standard solutions were prepared at approximate concentrations by weighing the salt and dissolving in acetic acid. The resulting solutions were then standardized by gravimetric precipitation of silver chloride with excess aqueous silver nitrate solution. That the standardizations yielded results quite close to the concentrations anticipated by weighing out 8-mesh reagent grade anhydrous calcium chloride is substantiated by Table II.

Standard Silver Solutions

Dissolved silver solutions of known concentration in glacial acetic acid proved somewhat more difficult to prepare. First, as shown in Table III, known dissolved silver was prepared by solution of weighed silver acetate in acetic acid with excess perchloric acid. The resulting solution was standardized gravimetrically via silver chloride which was precipitated by the addition of excess aqueous sodium chloride. Titration of the above silver solution potentiometrically showed no change in the amount of silver detected regardless of the amount of excess perchloric acid present (see Table IV).

A second approach was the preparation of a neutral solution of silver in acetic acid by dissolving silver acetate in acetic acid containing a deficient amount of perchloric acid. Aliquots of this solution had to be drawn from the top so as not to disturb the undissolved silver acetate which settled to the bottom. The potentiometric titrations summarized

Table II. Analysis of Calcium Chloride in Acetic Acid

Number	$CaCl_2$		g. AgCl	Std. Ag^+		Normality $CaCl_2$	
	g.p.l.	Cal'd. N	from 10 ml.	N	ml.	Precipitation	Titration
1	5.5550	0.1001	0.1430	0.0785	10.00	0.0998	0.1002
2	5.5550	0.1001	0.1444	0.0785	10.00	0.1007	0.1000
3	7.0828	0.1259	0.1680	0.0997	9.95	0.1172	0.1178
4	7.0828	0.1259	0.1672	0.0997	9.96	0.1166	0.1171
5	7.0828	0.1259	0.1677	0.0997	9.98	0.1170	0.1174
6	7.0828	0.1259	0.1676	0.0997	9.96	0.1169	0.1171

Table III. Analysis of $AgClO_4$ from AgOAc (dissolved by excess $HClO_4$)

Number	AgOAc		g. AgCl	Std. Cl^-		N Ag^+	
	g.p.l.	Cal'd. N	from 10 ml.	N	ml.	Precipitation	Titration
1	12.7160	0.0762	0.1118	0.1002	7.85	0.0780	0.0787
1'	12.7160	0.0762	0.1133	0.1002	7.83	0.0791	0.0785

Table IV. Titration of $AgClO_4$ in Acetic Acid (effect of varied excess of $HClO_4$)

Number of meq. AgOAc added	Number of extra meq. $HClO_4$	Number of meq. AgOAc found
0.0693	11.5700	0.0693
0.0693	11.5700	0.0690
0.0693	1.1504	0.0697
0.0693	1.1504	0.0696
0.0693	1.1504	0.0697

in Table V show dissolved silver equivalent to the perchloric acid added in the preparation of the solution.

Third, known silver solutions were prepared by the solution of silver(I) oxide in acetic acid with excess perchloric acid. Table VI shows this solution reacts similarly to the acid silver acetate solution discussed above.

Finally, known dissolved silver solutions were prepared by direct solution of apparently soluble silver perchlorate. It was observed that silver perchlorate solutions greater than 1.0 M gave a yellow, acid reaction with crystal violet indicator. More dilute solutions turned the indicator the blue-green transition color, and solutions below 10^{-3} M gave neutral, blue reactions. Potentiometric titrations of silver perchlorate with standard chloride gave sharp endpoints and generally good reproducibility as tabulated in Table VII.

An example of the titration curve resulting from the titration of known silver with standard chloride in acetic acid is given in Figure 2. A series of titrations are summarized in Table VIII. It would appear that this method of determining dissolved silver in acetic acid is as accurate as the customary gravimetric precipitation procedure and it is certainly more rapid.

Study of the Potential of the Silver Electrode in Glacial Acetic Acid

Since silver metal does not reduce the organic compounds examined, but does appear to have redox properties since it yields an electrode sensitive to the concentration of monomeric silver, an attempt was made to investigate the oxidation-reduction characteristics of silver metal in acetic acid.

Table V. Analysis of $AgClO_4$ (from AgOAc dissolved by measured amount $HClO_4$)

H^+ Titration Std. NaOAc		Ag^+ Titration Std. Cl^-		Number of meq. $HClO_4$ added	Number of meq. $AgClO_4$ detected [a]
N	ml.	N	ml.		
0.1003	0.69	0.0100	6.95	0.0697	0.0695
0.1003	0.69	0.0100	6.93	0.0697	0.0693
0.1003	0.69	0.0100	6.92	0.0697	0.0692

[a] Theoretical based on AgOAc 0.626 meq.

Table VI. Analysis of $AgClO_4$ in Acetic Acid (from Ag_2O)

Ag_2O taken		Std. Cl^-		N Ag_2O found
g.p.l.	Cal'd. N	N	ml. [a]	
9.7810	0.0844	0.1000	4.35	0.0870
9.7810	0.0844	0.1000	4.38	0.0876
1.4740	0.0127	0.0100	6.48	0.0129
1.4740	0.0127	0.0100	6.52	0.0130
0.8480	0.0073	0.0100	3.82	0.0076
0.8480	0.0073	0.0100	3.82	0.0076

[a] Five ml. sample aliquots.

Table VII. Analysis of $AgClO_4$ in Acetic Acid (from solid $AgClO_4$)

$AgClO_4$		Std. Cl^-		N $AgClO_4$
g.p.l.	Cal'd. N	N	ml.	found
2.3790	0.0115	0.0100	5.92[a]	0.0118
2.3790	0.0115	0.0100	5.90[a]	0.0118
2.3790	0.0115	0.0100	5.90[a]	0.0118
20.9400	0.1010	0.1169	8.48[b]	0.0991
20.9400	0.1010	0.1169	8.49[b]	0.0993
20.9400	0.1010	0.1169	8.51[b]	0.0995
20.9400	0.1010	0.1169	8.49[b]	0.0993

[a] vs. a 5.00 ml. aliquot

[b] vs. a 10.00 ml. aliquot

Table VIII. Comparison of Gravimetric and Volumetric Methods

Std. Cl^- [a]		N Ag^+ Solution	
N	ml.	by precipitation	by titration
0.1002	7.85	0.0780	0.0787
0.1002	7.83	0.0791	0.0785
0.1169	8.48	0.0995	0.0991
0.1169	8.49	0.0999	0.0993
0.1169	8.51	0.0999	0.0995
0.1169	8.49	0.0994	0.0993

[a] 10 ml. sample aliquots

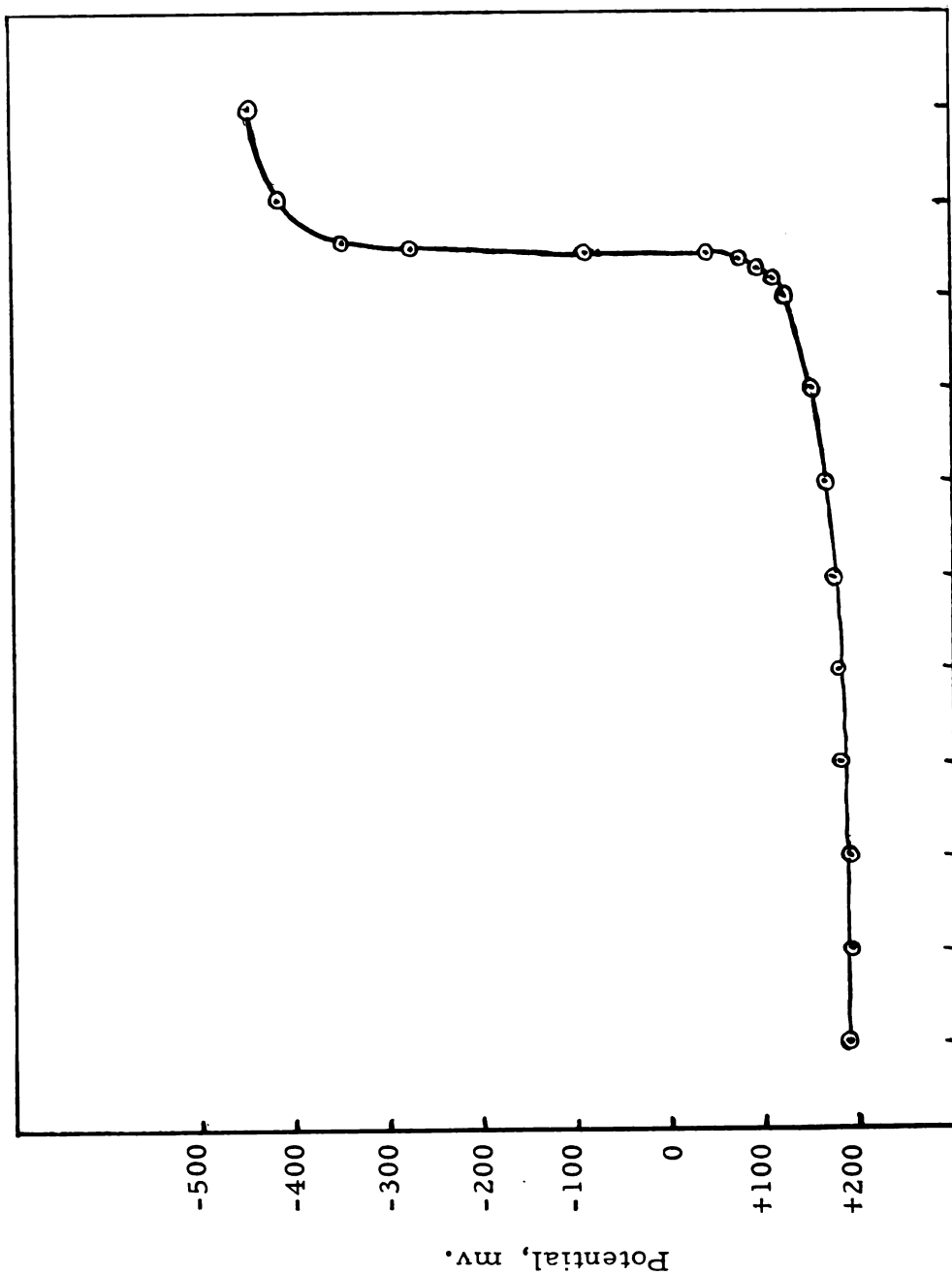

Figure 2. Potentiometric Titration of Ag^+ with Cl^-.

Initially, silver metal previously washed with dilute nitric acid was placed in nitrogen purged solutions of various redox indicators. Table IX shows that while the standard potentials of these indicators ranged from 0.24 to 1.00 volts, none of them were changed from oxidized to reduced form by contact with metallic silver. To prove the method used was conducive to the reduction of these indicators, identical runs using metallic zinc rather than silver produced expected changes in color as the indicators changed from oxidized to reduced form. From this evidence we further conclude that the potential of silver metal in acetic acid is not sufficient to reduce most commonly reducible species.

Next, the potential of the silver electrode was studied as a function of dissolved silver concentration. In order that no additional substances be present, the dissolved silver was prepared by solution of the apparently soluble salt, silver perchlorate.

The highly concentrated mixture of silver perchlorate in acetic acid produced by the addition of solid crystals to solvent until no more would dissolve was obviously not a true solution. The mixture was found to be about 2.95 M in silver perchlorate. It was pink, viscous, and somewhat cloudy. As it was diluted with more acetic acid, the pinkish cast diminished but the cloudiness increased. Observations of the silver electrode potential during dilution yielded erratic and obviously non-ideal behavior. The mixture finally became clear about 10^{-1} M but upon further dilution the potential appeared to pass through a maximum.

In order to assure reproducibility of the observed potentials, the silver electrode which was stored in contact with glacial acetic acid was washed in concentrated ammonium hydroxide, wiped, washed in dilute nitric acid, wiped again, and finally rinsed with acetic acid.

Table IX. Reaction of Redox Indicators in HOAc vs. Silver

Indicator in HOAc + $HClO_4$	π_o volts (water)	Color		
		Ag Immediate	Ag 12 hrs.	Zn 2 hrs.
Neutral red	0.24	blue	blue	red
Phenosafranine	0.28	blue-violet	blue-violet	red-orange
Methylene blue	0.53	blue	blue	pale blue
Erioglaucin	1.00	yellow	yellow	green

Repeated determinations of the potential of this washed electrode as a function of the dissolved silver concentration yielded no maximum in the region where the mixture appeared to be a true solution. Indeed, Figure 3 shows the Nernst equation plot of volts versus log of the molar silver concentration which yields a straight line of slope 0.06. The observed potentials varied slightly with different solutions of approximately the same silver concentration so no claim can be made as to the reproducibility of the electrode potential nor can a formal potential be determined. However, for a series of runs, the slope approximates 0.06. This is assumed to be representative of a one electron change with respect to dissolved silver. The linearity is observed from 10^{-3} M to 10^{-5} M silver and it would appear that in this region, the dissolved silver species behaves as though it were monomeric.

Finally, it must be said that due to the non-ideal behavior of silver(I) in glacial acetic acid, it is not possible to determine the formal potential for the silver-silver ion couple. Since none of the organic compounds studied are reduced except the special case of the complex

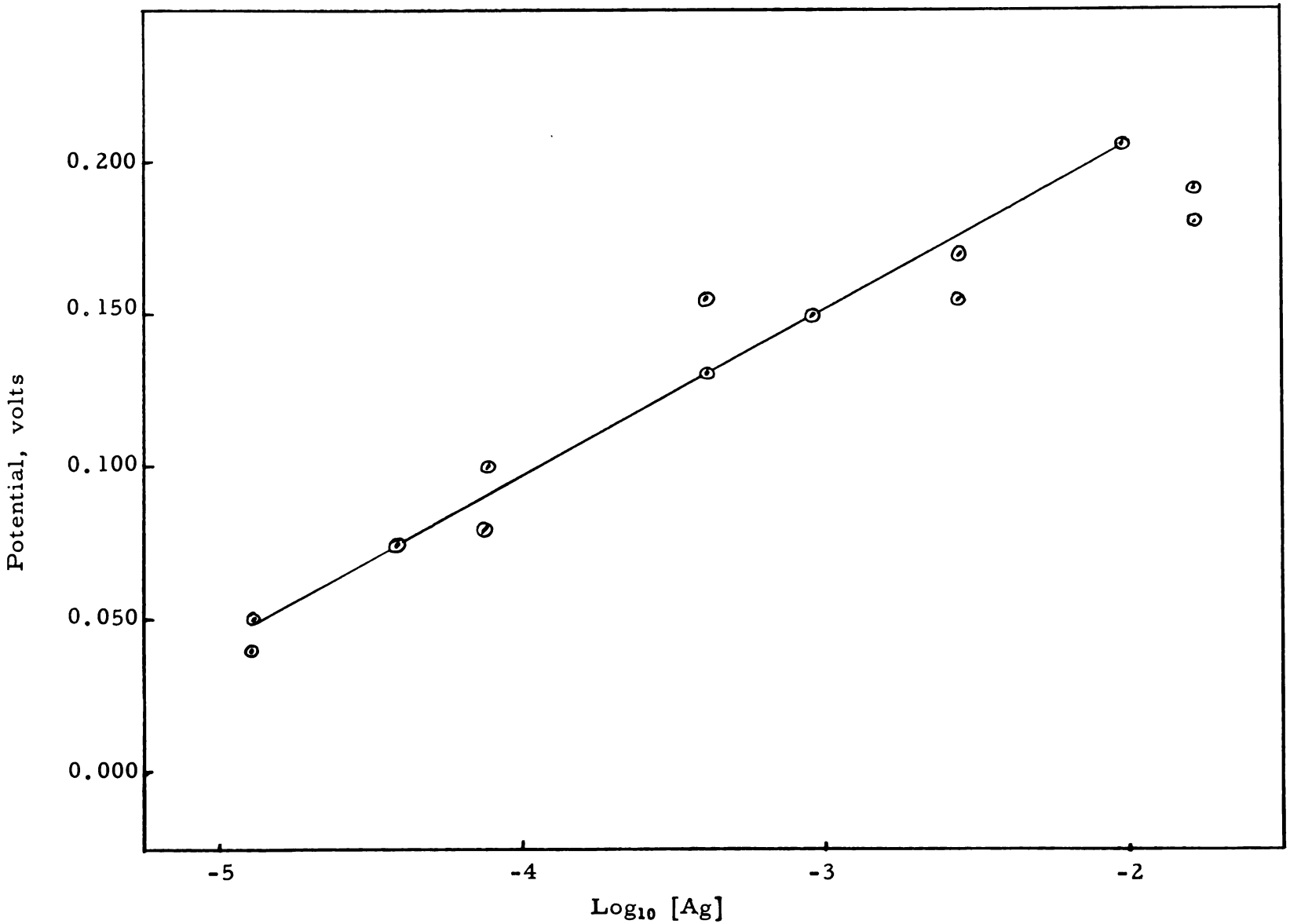

Figure 3. Electrode Potential vs. log Silver Concentration.

former, quinhydrone, the formal potential of silver metal must be too high for straightforward reductions. In an aqueous chloride system, silver reduces many substances due to the lowering of the silver ion activity by precipitation of insoluble silver chloride. It would appear from this investigation that none of the silver salts present in glacial acetic acid are insoluble enough to have analogous effect. Thus, reduction via the silver reductor is observed only when there is an effective means of removing the product materials from the reaction.

In a final attempt to explain behavior of dissolved silver in acetic acid, the conductance of a series of solutions was measured as a function of the silver concentration. However, because of the low conductivity of acetic acid solutions, most of the measurements were necessarily made near the end of the conductance bridge scale where readings are known to be erratic. Therefore, from the data in Table X, one may conclude only that conductance decreases as the dissolved silver concentration decreases.

Table X. Conductance of $AgClO_4$ Solution vs. Concentration

Molar $AgClO_4$ Concentration	Observed Conductance in $ohms^{-1} \times 10^6$
1.60×10^{-2}	7.40
9.00×10^{-3}	2.90
2.75×10^{-3}	1.60
8.18×10^{-4}	0.70
4.58×10^{-4}	0.66
3.90×10^{-5}	0.18
1.27×10^{-5}	0.10

SUMMARY AND CONCLUSIONS

Silver metal will not reduce the organic nitro compounds tested in glacial acetic acid. Quinone is reduced by silver due to the formation of quinhydrone; however, this is a special case and not representative of most reducible organic compounds.

Dissolved silver in acetic acid can be determined accurately and rapidly by potentiometric titration with standard chloride solution using the mercury-mercurous acetate electrode in acetic acid as reference electrode and clean silver metal as the indicator electrode. The accuracy and precision of this method compare favorably with the familiar gravimetric precipitation of silver chloride. Further, use of the method is indicated whenever the solution being titrated develops a color which may mask chloride indicators.

While a formal potential for the silver-silver(I) couple in acetic acid cannot be readily determined, the silver specie present from 10^{-3} M to 10^{-5} M would appear to be monomeric. In that region, the potential of the silver electrode obeys the Nernst equation with an n value of one.

Finally it must be said that many questions remain to be answered with regard to the silver system in glacial acetic acid. Thus, one might propose to determine the true nature of the monomeric silver species, whether it is silver ion or an ion pair. Further work would certainly investigate the reducing properties of silver metal in chloride medium to see if the potential is lowered in a method precisely analogus to the Walden reductor. Finally, the determination of silver using complexing agents other than chloride, such as iodide, bromide, thiocyanate, or cyanide, might be undertaken.

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