OXIDATION OF SODIUM AZIDE AND HYDRAZINE WITH CERIUM(IV) IN GLACIAL ACETIC ACID

By

William Charles Harris

A THESIS

Submitted to the School of Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1958

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. K. G. Stone for his encouragement and stimulating guidance throughout the course of this investigation.

Appreciation is also due to various other members of the Department of Chemistry who have given helpful advice from time to time, and especially to Dr. J. C. Sternberg for his very kind help with the gas identification.

The author also wishes to express his thanks to his wife, Joan, for her help in the preparation of this manuscript.

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Approved R. G. Stone Assoc. Prof. Chemistry

ABSTRACT

The oxidation of sodium azide, hydrazine acetate, acethydrazide, and symmetrical diacethydrazide can be affected by cerium(IV) in glacial acetic acid. Of these materials only the sodium azide is quantitatively oxidized. This oxidation to nitrogen was achieved by dissolving the sample in glacial acetic acid, adding an excess of the cerium(IV) reagent, allowing the mixture to stand for one-half hour and then determining the excess cerium(IV) with sodium oxalate. This determination may also be done as a direct titration with the cerium(IV) reagent, provided the glacial acetic acid used as a solvent is made one normal in perchloric acid.

The oxidation of both hydrazine acetate and symmetrical diacethydrazide resulted in odd values for the stoichiometry. In both cases the stoichiometry values were quite reproducible. The stoichiometry values obtained in the oxidation of the symmetrical diacethydrazide were more consistant than those obtained in the oxidation of hydrazine acetate. This would be expected because of the instability of a solution of hydrazine acetate in glacial acetic acid.

In each case it appeared that the oxidation resulted in the formation of nitrogen as the only product. In the

oxidation of hydrazine acetate and symmetrical diacethydrazide the amount of nitrogen produced is not quantitative at first glance. However, if the amount of nitrogen collected is compared to the ratio of the number of milliequivalents of cerium(IV) actually used to that required for oxidation to nitrogen, the evolution is quantitative.

Under standardized conditions, the stoichiometry achieved in the oxidation of hydrazine acetate was 2.21 ± .09 equivalents of cerium(IV) per mole of hydrazine acetate. Similarly, the oxidation of symmetrical diacethydrazide required 3.37 ± .03 equivalents of cerium(IV) per mole of diacethydrazide. For the latter oxidation the following route is proposed:

$$CH_3\overset{\overset{O}{\|}}{C}NHNH\overset{\overset{O}{\|}}{C}CH_3 + 2\ Ce(IV) \longrightarrow CH_3\overset{\overset{O}{\|}}{C}N{=}N\overset{\overset{O}{\|}}{C}CH_3 + 2\ Ce(III) + 2\ H^+$$

$$CH_3\overset{\overset{O}{\|}}{C}N{=}N\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3 + N_2$$

$$CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3 + 2\ OH^- + 2\ Ce(IV) \longrightarrow 2\ CH_3COOH + 2\ Ce(III)$$

Hydrazine acetate and acethydrazide were found to be titratable with perchloric acid in glacial acetic acid using the blue-green color of crystal violet as an indication of the end point. Both materials behave as monobasic substances and require one equivalent of acid per mole.

A colorimetric determination of hydrazine based on reaction with salicylaldehyde was also developed. The reaction produces a yellow colored solution which was measured at 418mμ. The apparent limit of concentration of hydrazine is determined by the solubility of the reaction product, disalicylalhydrazine.

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I. INTRODUCTION

I. INTRODUCTION

The study of organic oxidations in non-aqueous solutions from an analytical point of view has been very limited. There has been some work using lead tetra-acetate, bromine, chromic acid, sodium permanganate, titanium(III) chloride, iodine monochloride, and iodine monobromide in glacial acetic acid, as reviewed by Kolthoff and Belcher (13).

Hinsvark (12) found that cerium(IV) in glacial acetic acid could be used for the quantitative oxidation of certain organic oxygenated compounds, notably some dibasic acids.

It was deemed desirable to extend his work to nitrogen compounds to see if a feasible method for their determination might be developed. Sodium azide and hydrazine were the nitrogen compounds to be investigated.

The literature yields various oxidative measurements for azides. Among the reagents which have been used are iodine (18), potassium permanganate, potassium persulphate, potassium chlorate (19), nitric acid (6), and cerium(IV) (14,21).

Audrieth and Ogg (1) have reviewed the different oxidative measurements for hydrazine in aqueous media, including an indirect cerium method. Higginson and Sutton (10) have stated that the products of the oxidation

of hydrazine and the stoichiometry depend on the nature of the oxidizing agent i.e., whether it can be classified as a one-electron or a two-electron transfer reagent. In a subsequent report (11) they have stated that the reaction between cerium(IV) and hydrazine was not stoichiometric, although consistant results could be obtained if a standard procedure was used. They report a stoichiometry of 1.05 - 1.5 equivalents of cerium(IV) per mole of hydrazine, and that under carefully controlled conditions 1.06 Ce(IV) $\equiv N_2H_4$. Cahn and Powell (5) have also investigated the mechanism of the oxidation using various oxidizing agents.

Since cerium(IV) is known to be an effective reagent for the oxidation of azides in aqueous media and because of its questionable application to hydrazine in this media, these oxidations were to be investigated in glacial acetic acid. The ultimate objective was the development of an analytical method for these compounds. It was also hoped that some further elucidation of the mechanism of the oxidation of hydrazine by cerium(IV) would result.

II. EXPERIMENTAL

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A. Chemicals

Baker's "Analyzed" and duPont "Reagent Grade" glacial acetic acid were both used as solvents without further purification. A typical Karl Fisher water analysis of the acid showed a water content of 0.16 per cent. Eastman Kodak Company "White Label" acetic anhydride was used in the preparation of diacethydrazide. The 70 per cent perchloric acid used was Mallinckrodt "AR" grade.

The ammonium hexanitratocerate was obtained from the G. Fredrick Smith Chemical Company. Merk "Reagent" primary standard sodium oxalate was used. Anhydrous ethyl acetate from Matheson, Coleman and Bell was used in the preparation of acethydrazide. The hydrazine hydrate used was Eastman Kodak "Yellow Label" 64 per cent practical. This was analyzed by the indirect iodate method of Bray and Cuy (4) before use. Technical grade sodium azide was obtained from the Explosives Division, E. I. duPont de Nemours and Company. All solutions of sodium azide were analyzed by the indirect cerium method of Martin (14) to serve as a reference analysis for the cerium(IV) oxidations in acetic acid.

The hydrazine acetate used was prepared by adding acetic acid to a quantity of hydrazine hydrate until there was no evolution of heat upon further addition. Upon cooling to room temperature the mixture became very viscous, and with spot cooling on dry ice the hydrazine acetate crystallized. The crude material was collected on a filter and washed with ether. The material was then recrystallized from a 1:1 chloroform-ethanol mixture, filtered, and again washed with ether. The resulting material had a melting point of 96-97°C. and an acid-base equivalent weight of 92 ± 0.4. The theoretical equivalent weight is 92.11.

The acethydrazide was prepared by a modification of the procedure used by Curtius and Hofmann (8). To seventy-five grams of hydrazine hydrate in a 250 ml. iodine flask was added slowly one hundred and ten grams of anhydrous ethyl acetate. The flask was then fitted with a reflux condenser and placed in a water bath at approximately 97°C. for two days. At this time the mixture was cooled and the volume reduced about one third by vacuum distillation of part of the water-ethanol solution left after reaction. Cooling of the remaining solution on dry ice for a short time induced precipitation of the acethydrazide. The crude material was then dissolved in hot chloroform and reprecipitated with ethyl ether. The precipitate was collected on a filter, washed

with ethyl ether and allowed to air dry. This procedure resulted in a material having a melting point of 66-67°C. and an equivalent weight, by titration with perchloric acid in glacial acetic acid, of 74.2 ± 0.5. This compared to a melting point of 67°, as reported by Curtius and Hofmann, and a formula weight of 74.11.

Symmetrical diacethydrazide was prepared according to the procedure of Stolle (22). Hydrazine hydrate and acetic anhydride were mixed in a mole ratio of one to three. Care must be taken to keep the ratio at this level since higher ratios lead to the production of the tri- and tetraacethydrazides. The heat of mixing was sufficient to cause the reaction to proceed. Upon cooling, the material was precipitated by diluting with ethanol. The crude material was collected on a filter and then recrystallized from a 1:1 chloroform-ethanol mixture, filtered, washed with ethyl ether and allowed to air dry. The final product had a melting point of 138-40°C. as compared to reported values of 138° (22) and 140°C. (17). A Kjeldahl nitrogen determination produced 24.05 per cent nitrogen compared to 24.15 per cent theoretical. The symmetrical diacethydrazide exhibited neither acidic nor basic properties.

B. Apparatus

A Sargent Model III Manual Polarograph equipped with a Beckman Number 19031 twin inlay platinum electrode was

used for the detection of equivalence points in the amperometric titrations.

The light sensitivity of the cerium(IV) reagent, as reported by Hinsvark (12), made necessary the use of amber burets for titrations with this reagent.

Gas measurements were made using a Lunge nitrometer tube of 50 ml. capacity. The gas identification was carried out on a Perkin Elmer Model 154 Vapor Fractometer. The instrument was equipped with a Cenco coiled aluminum tubing assembly containing Linde Molecular Sieves Type 13X. The aluminum coil was approximately 3.5 inches in diameter with ten and one-half turns of one-quarter inch O. D. tubing. Helium was used to sweep the gas samples through the packed tubing. A Fisher Recordall was used to record the instrument response and determine retention times.

A Perkin-Elmer Model 21 Recording Infra-Red Spectrophotometer equipped with a one meter gas cell was used to determine whether or not the gas had an infrared spectrum.

C. Oxidation Procedures

All the oxidations using cerium(IV) in glacial acetic acid were carried out by an excess method. In addition to this method it was found that the analysis of sodium

azide could be accomplished by means of a direct titration with the cerium(IV) reagent.

1. Excess Methods

All the nitrogen compounds were oxidized by a method using an excess of the cerium(IV) reagent. This excess was subsequently determined by titrating with a standard sodium oxalate solution.

In each case the sample to be oxidized was dissolved in glacial acetic acid and thoroughly mixed. Aliquots of the solution were added to 50 ml. of glacial acetic acid in a 250 ml. iodine flask. To this was added a volume of cerium(IV) reagent calculated to be in excess of the amount needed for oxidation of the sample. The iodine flask was then stoppered, sealed with acetic acid, and placed in the dark in a desk drawer. At the end of the specified period of time the flask was removed from the drawer and the contents transferred to a 180 ml. tall-form beaker for titration of the excess cerium(IV). The sodium oxalate solution used for titration of the excess cerium(IV) was prepared by weighing out a portion of dried, reagent grade sodium oxalate and dissolving it in glacial acetic acid. Sufficient perchloric acid was added so that after dilution to a definite volume with glacial acetic acid the resulting solution would be one normal with respect to perchloric acid.

Hinsvark (12), in his work with cerium(IV) in glacial acetic acid, found that the end point in the oxidation-reduction titrations could be detected by an amperometric method with two active electrodes. This method was applied to the present investigation using a twin inlay platinum electrode. A Sargent Model III Manual Polarograph was used as the source of potential applied across the two platinum leads of the electrode. The potential applied was set at 275 mv.

As the sodium oxalate solution is added to the solution containing the excess cerium(IV), the current increases slightly and then falls off as the end point is approached. The end point is indicated when the current falls to a steady value. The approach of the end point can also be detected visually. The solution containing the excess cerium(IV) is orange in color, and as the titration proceeds this color fades to lighter and lighter shades of yellow. After considerable experience and in the presence of the proper lighting, it is possible to detect the end point visually by watching for the last change from pale yellow to white or clear. The amperometric end point, however, is much more reliable and the author believes that the titration should not be attempted as a visual method in accurate work. It is not necessary to plot the data in order to locate the end

point, provided additions of titrant are sufficiently small in the vicinity of the end point.

Standardization of the cerium(IV) reagent was accomplished in a like manner. An aliquot of the reagent, usually 25 ml., was added to 50 ml. of glacial acetic acid in a 150 ml. beaker. This solution was then titrated with the sodium oxalate in the manner just described.

2. Direct Titration

Sodium azide samples, dissolved in glacial acetic acid which was one normal with respect to perchloric acid content, could be analyzed by a direct titration with the cerium(IV) reagent. The sodium azide was dried at 110°C. for a minimum of two hours, weighed, and dissolved in glacial acetic acid. Aliquots were then added to 50 ml. of glacial acetic acid which was at least one normal in perchloric acid. To the resulting solution, in a 150 ml. beaker, was added the cerium(IV) reagent. There was no flow of current when the twin inlay platinum electrode was immersed in the solution. The current remained unchanged until the end point was reached, at which point the galvanometer deflected rapidly in the positive direction. There was considerable "foaming" in the beaker due to the evolution of nitrogen.

In this titration also it was possible to detect the end point visually. The color change in this case was

just the opposite of that previously described, i.e., from colorless to light yellow. The visual end point was much easier to see than before, but the instrumental detection was always used.

An investigation was made to determine if the titration could be done using nitro-ferroin as the indicator. This was found to be unacceptable in that the indicator changed color before the end point was reached. The potentiometric end point, as detected by a saturated calomel-platinum electrode system, coincides with the amperometric end point.

D. Colorimetric Determination of Hydrazine

While studying the reaction of hydrazine with glacial acetic acid, as described in a later section, it became necessary to devise a method for determining hydrazine in the presence of acethydrazide. Several methods were attempted before it was found that a colorimetric method might be feasible.

The reaction of hydrazine acetate with salicyaldehyde (9) to yield the corresponding Schiff's base results in a yellow precipitate or a yellow colored solution, depending on the concentration of the hydrazine acetate. The same reaction with acethydrazide yields a colorless solution or a white precipitate. The possibility of a colorimetric method thus presented itself.

In the development of the colorimetric method a concentration range of 0.2-1.2 mg. of hydrazine acetate per ml. was used. The hydrazine acetate was prepared as stated previously in the chemicals section. The practical grade salicyaldehyde was distilled and the fraction boiling at 194.5°C. and above was collected for use. This single distillation resulted in a material having a very slight tinge of yellow. Because of this slight color in the salicyaldehyde it was necessary to add some to the glacial acetic acid of the reference blank.

A solution of hydrazine acetate in glacial acetic acid was prepared to contain four mg. per ml. Various aliquots of this solution were then placed in 10 ml. glass stoppered volumetric flasks such that the resulting concentrations upon dilution to volume would be 0.2, 0.4, 0.6, 0.8, and 1.2 mg. hydrazine acetate per ml. To these flasks was added 5 ml. of the salicyaldehyde and the flasks brought to volume with acetic acid. A reference solution was prepared by mixing salicyaldehyde and glacial acetic acid in a 1:1 ratio. All preliminary semi-quantitative work was done on the Beckman Model DK-2 Recording Spectrophotometer. The visible spectrum of the disalicylalhydrazine is shown in Figure 1. As can be seen, it is extremely simple with the absorbance

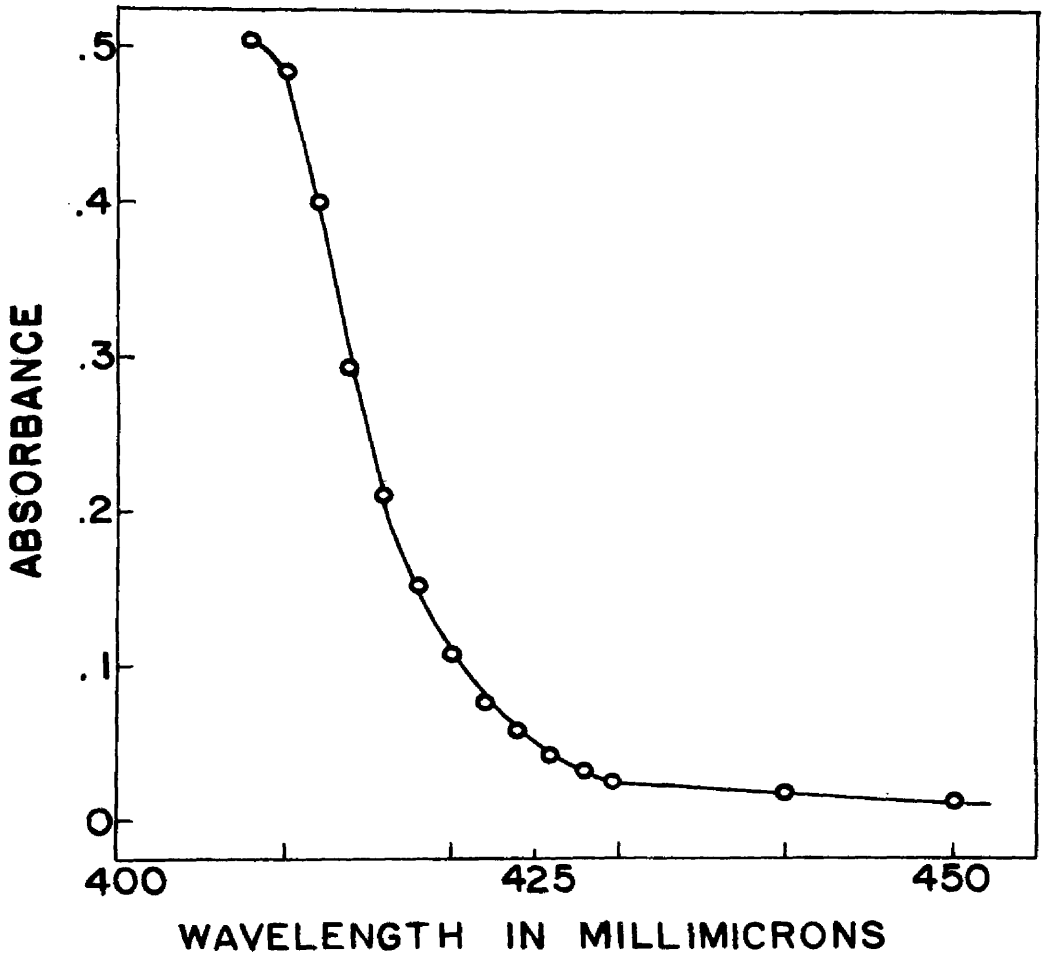


FIG. 1

VISIBLE SPECTRUM FOR DISALICYLALHYDRAZINE

increasing rapidly from about 450mμ to 410mμ, but showing no maximum.

It was found that by using a blank of 50 per cent salicylaldehyde in acetic acid, a Beer's Law plot of concentration versus absorbance yielded a straight line for a variety of wavelengths. Table 1 shows the consistancy of the absorbance versus concentration ratio at 418mμ.

TABLE 1
ABSORBANCE VS. CONCENTRATION OF HYDRAZINE ACETATE

$N_2H_4 \cdot HOAc$ Conc. mg./ml.	As. (418mμ)	As./mg./ml.
0.2	0.157	0.78
0.4	0.318	0.79
0.6	0.469	0.78
0.8	0.611	0.76
1.2	0.930	0.77

Since the blank gave an infinite absorption at wavelengths below 410mμ, it was necessary to choose a wavelength above this which would give good accuracy and sensitivity. As the wavelength is increased from 416 to 428mμ and beyond, the sensitivity, i.e., change in absorbance per change in concentration, decreased. At 416mμ this change was so great that the precision and corresponding accuracy suffered. As a consequence 418mμ,

which offered the next best sensitivity and good accuracy and precision, was selected as the wavelength for all colorimetric measurements. These measurements were made on a Beckman Model DU Spectrophotometer using one cm. Corex cells.

The effect of acethydrazide, symmetrical diacethydrazide, and water on the accuracy of the colorimetric measurements was then determined. This was done by adding varying amounts of each of the three materials to the hydrazine acetate solutions. The relative amounts of each were changed so that measurements were made in which each of these materials was present in amounts both larger and smaller than the amount of hydrazine acetate.

Table 2 shows the absorbancy values obtained with these materials present and absent. The greatest interference occurs in the presence of acethydrazide alone. This, it is felt, is a result of the disproportionation of the acethydrazide to hydrazine and symmetrical diacethydrazide and is not directly attributable to the acethydrazide itself.

TABLE 2
EFFECT OF OTHER CONSTITUTENTS ON ABSORBANCY VALUES FOR HYDRAZINE ACETATE

Absorbance Values			
$N_2H_4 \cdot HOAc$(I) Alone	I with 5.4 Mm. $AcNHNH_2$	I with 5.4 Mm. $AcNHNH_2$ and 5.2 Mm. AcNHNHAc	I with 1% H_2O
.318*	.305	.314	.316
.612**	.618	.610	.611

* conc. $N_2H_4 \cdot HOAc$ 0.4 mg./ml. (4.35 Mm.)
** conc. $N_2H_4 \cdot HOAc$ 0.8 mg./ml. (8.7 Mm.)

E. Gas Collection and Identification

The oxidations of sodium azide, hydrazine acetate, and symmetrical diacethydrazide produced a gas as one of the products. This gas, shown to be nitrogen, was collected over 50 per cent potassium hydroxide in a Lunge nitrometer tube.

The sample to be oxidized was placed in a 150 ml. electrolytic beaker, which had been covered with black tape to exclude light during oxidation by the cerium(IV) reagent. These samples were aliquots of solutions of the various materials in glacial acetic acid. The reaction vessel was fitted with a three-hole rubber stopper. Through one hole was passed a glass tube which was connected, by means of rubber tubing, to the outlet of a Dewar flask containing dry ice as a source of carbon dioxide. This tube extended nearly to the bottom

of the reaction vessel so that the flow of carbon dioxide would bubble through and mix the reaction medium. The sample of material to be oxidized was introduced through a second hole. Through the third hole was passed a glass tube which was in turn connected to a washing tower containing water. The washing tower was connected to a U shaped tube which was inserted in an ice bath in order to remove any low boiling gases and low melting liquids. This tube was then connected to the lower end of the nitrometer tube, which was filled with 50 per cent potassium hydroxide.

Once the apparatus was assembled the entire system was swept with carbon dioxide to remove all air. The nitrometer tube was then filled with the potassium hydroxide, and 50 ml. of solvent and 50 ml. of reagent were added to the reaction vessel. This solution was swept with carbon dioxide for a period of one hour, and the resulting volume of gas collected was recorded as the blank. When determined in this manner, the blank was quite reproducible for a given amount of solvent and reagent on a given day. After measurement of the blank the reaction vessel was disconnected from the apparatus, emptied, and reconnected. The entire system was again swept free of air with carbon dioxide. Then solvent, sample, and reagent were placed in the reaction vessel. The system was swept for one hour, as before,

and the resulting gas collected. The resulting volume of gas was corrected for the blank and then reduced to standard temperature and pressure by use of the nitrogen reduction tables as given on pages 301-310 in Organic Quantitative Microanalysis by Niederl and Niederl.

After collection of the gas produced during the oxidations it was deemed necessary to make a qualitative identification of the material obtained. To do this a Perkin Elmer Model 154 Vapor Fractometer was equipped with a Cenco coiled aluminum tubing assembly containing Linde Molecular Sieves Type 13X. The aluminum coil was approximately 3.5 inches in diameter with ten and one-half turns of one-quarter inch O. D. tubing.

Using this packing for the tube, a sample of air was separated to give two response peaks, presumably due to oxygen and nitrogen. A 0.5 ml. sample of the gas collected as a blank gave these same two peaks. Samples of the gases collected from oxidation of each of the materials under study were injected into the instrument. All samples were 0.5 ml. in size. Helium was used to sweep them through the tube containing the molecular sieves. A pressure of approximately 15 p.s.i. was used to effect the separation. These samples produced the same two peaks as the blank and air. The second peak in each case was greatly increased in height over that of the blank, indicating an increase in the amount of nitrogen present.

A sample of pure nitrogen was then passed through the instrument to produce a single peak.

Table 3 shows the retention time of the two peaks for the various samples tested.

TABLE 3
RETENTION TIMES FOR GAS SAMPLES

Sample	Peak 1		Peak 2	
	Trial 1* (seconds)	Trial 2**	Trial 1* (seconds)	Trial 2**
Air	61	56	75	67.5
Oxidation Blank		56		67.5
Azide Gas	61		75	
$N_2H_4 \cdot$ HOAc Gas		56		67.5
Diacethydrazide Gas	61		75	
Pure Nitrogen	none	none	75	67.5
Pure Oxygen	61		none	
1:1 O_2-N_2 Mixture	61		75	

* cell temperature 37°, pressure 11 p.s.i., flow rate 10
**cell temperature 38°, pressure 15 p.s.i., flow rate 11

It was concluded from these data that the product of the oxidation is a gas which behaves as nitrogen with respect to the molecular sieves used for this examination.

In order to further cement the contention that the gaseous product of the oxidation was nitrogen, a gas sample was collected and an infrared spectrum was taken.

The sample showed no absorption and thus must consist of molecules containing identical atoms. In light of the fact that the retention time of the second peak for all samples matched that of nitrogen, it is concluded that the gas must truly be nitrogen.

III. RESULTS OF OXIDATIONS

III. RESULTS OF OXIDATIONS

A. Sodium Azide

Sodium azide, being about the simplest of nitrogen compounds, was chosen as a starting point in the study of cerium(IV) oxidations of nitrogen compounds in glacial acetic acid. The oxidation of hydrazoic acid and various alkali azides in aqueous solution has been done with a number of oxidizing agents. Among those reported to give quantitative evolution of nitrogen are iodine (18), potassium permanganate (19), and cerium(IV) salts (14,21).

The oxidation with cerium(IV) requires one equivalent of cerium per mole of azide according to the equation

$$2\ NaN_3 + 2\ Ce(IV) \longrightarrow 3\ N_2 + 2\ Na^+ + 2\ Ce(III)$$

For oxidation by cerium(IV) in glacial acetic acid, the sodium azide was dried at 110°C. for a minimum of two hours. A quantity was then weighed and dissolved in acetic acid and made up to a volume such that the final concentration was approximately one molar. Prior to doing any cerium(IV) oxidations in glacial acetic acid the azide solution was analyzed via the indirect cerium method of Martin (14) to determine the actual azide content.

The first attempts to oxidize sodium azide in acetic acid as a direct titration with the cerium(IV) reagent were unsuccessful. The reaction proceeds very rapidly at first and then becomes rather sluggish as the equivalence point is approached. It appears as though the explanation for this behavior lies in the similarity of the ionization constants of acetic and hydrazoic acids.

All oxidative methods for the determination of azide in aqueous media call for the presence of strong acid, so that the azide is present essentially as hydrazoic acid. In the acetic acid medium, however, the ionization constants being 1.8×10^{-5} and 2.6×10^{-5} for acetic and hydrazoic acids respectively, it seems quite possible that the sodium azide would not be completely converted to the acid instantaneously. On this basis it would appear that in order to achieve a quantitative oxidation by means of a direct titration, the active species must be hydrazoic acid. This is not necessarily true, however, if one uses an excess of oxidizing agent and then determines the excess.

Oxidation of azide by the use of excess cerium(IV) and subsequent determination of the excess by titration with oxalate, has been found to be applicable in glacial acetic acid. From a solution approximately one molar in sodium azide, a series of one ml. aliquots were withdrawn

and oxidized in the manner previously described. As the data in Table 4 show, the oxidation is complete after thirty minutes under these conditions. The oxidation is quantitative and consumes one equivalent of cerium(IV) per mole of sodium azide, as is shown in Table 5.

TABLE 4
SODIUM AZIDE BY EXCESS CERIUM

Mg. NaN_3 taken	Reaction Time, Min.	Mg. NaN_3 Found		Mg. NaN_3 Ave.	Percent Error
62.16	15	61.73	61.77	61.75	.66
	30	62.23	62.08	62.16	.12
	45	62.19	62.08	62.14	.10
	60	62.15	62.15	62.15	.02
	90	62.19	62.19	62.19	.05

TABLE 5
SODIUM AZIDE STOICHIOMETRY

Mmol. NaN_3 taken	Meq. Ce(IV) used	Meq. Ce(IV) / Mmol. NaN_3
0.9560	.9570	1.001
	.9564	1.0004
	.9558	.9998
0.9000	.8975	.9996
	.8937	.9931
	.8964	.9961

The oxidation produces a gas as evidenced by the build-up of pressure in the stoppered iodine flask. The gas was later shown to be nitrogen. It was necessary to proceed with some caution when removing the stopper lest some of the acetic acid used for the seal be blown out by the gas escaping from the flask. The gas produced by the oxidation of a 0.5 ml. sample, as delivered from a 500 λ micropipet, was collected and measured according to the procedure as given in the section on gas collection and identification. Table 6 shows the results of the gas measurements. It can be seen from these data that a quantitative evolution of nitrogen is achieved.

TABLE 6
GAS MEASUREMENTS FOR SODIUM AZIDE

Mmol. NaN_3 taken	Vol. N_2 Collected	Mmol. N_2 Collected	$\frac{\text{Mmol. } N_2}{\text{Mmol. } NaN_3}$
.48	16.18	.722	1.502
	16.46	.735	1.53
.45	14.89	.665	1.48
	14.95	.668	1.482

Since it is always more desirable to have a direct method of determination rather than an indirect one, attention was focused on making the oxidation of the azide in acetic acid instantaneous and thereby workable

as a direct titration. As was stated previously, it appeared that in order to get a rapid oxidation it was necessary for the azide to be present in the form of hydrazoic acid. It was found that if the acetic acid used as the solvent for the oxidation of the azide samples was made approximately one normal in perchloric acid, the oxidation could be carried out as a direct titration using cerium(IV) in glacial acetic acid. An excess of only one drop caused a considerable galvanometer deflection and thus the end point was readily detectable. That this is a quantitative oxidation can be seen in the results as shown in Table 7.

TABLE 7
DIRECT TITRATION OF SODIUM AZIDE

Mg. NaN_3 taken	Ml. of Ce(IV)	Ce(IV) Normality	Mg. NaN_3 found	Per cent error
58.50	16.52	0.0543	58.36	-.24
	16.50		58.29	-.36
	19.68	0.0456	58.41	-.15
	19.73		58.56	+.10
	19.69		58.45	-.08

In light of the stoichiometry achieved in the oxidation and the amount of nitrogen collected it may be concluded that the oxidation of sodium azide with

cerium(IV) in glacial acetic acid proceeds according to the equation:

$$NaN_3 + Ce(IV) \longrightarrow 1.5\ N_2 + Ce(III) + Na^+$$

B. Hydrazine

Because of its somewhat peculiar behavior towards oxidizing agents in aqueous media, hydrazine was chosen as the next nitrogen compound to be subjected to oxidation by cerium(IV) in glacial acetic acid. The samples were aliquots of a hydrazine hydrate-acetic acid mixture. The hydrazine was obtained as a 64 per cent solution in water corresponding to 100 per cent hydrazine hydrate. It was analyzed independently by the indirect iodate method of Bray and Cuy (4). A solution of hydrazine hydrate in glacial acetic acid was prepared by adding a known weight of the analyzed hydrazine hydrate to a volume of acetic acid. The water of the hydrate was not removed. Aliquots of this solution were then treated with the cerium(IV) reagent.

The reaction with cerium(IV) was much too slow to be used as a direct titration. All attempts to increase the rate of oxidation of the hydrazine and its derivatives by the addition of perchloric acid were unsuccessful. Samples were then allowed to react with the cerium(IV) reagent in the dark for various lengths of time. In this manner it was found that the reaction

was "complete" after four hours in that the number of milliequivalents of cerium(IV) used was essentially constant for a reaction time of four to ten hours. Thus all subsequent samples of hydrazine were allowed to react for four hours.

As Table 8 shows, the oxidation consumed three equivalents of cerium(IV) per mole of hydrazine. This stoichiometry was also found when samples of hydrazine acetate were allowed to stand in acetic acid for a long period of time before oxidation. This odd stoichiometry was highly unexpected, and therefore an attempt was made to determine what the end products of the oxidation might be. It was evident from the build-up of pressure within the iodine flask that at least one product was a gas, which was shown to be nitrogen. All attempts to isolate a second product, presumably one in which the nitrogen would be present in an oxidation state of minus one, were unsuccessful. Assuming the pressure build-up to be the result of the production of nitrogen, gas measurements were made to determine just how much gas was being produced. The results, as shown in Table 9, indicated that as a first approximation one-half of a mole of nitrogen was being produced per mole of hydrazine. This seemed to indicate even more strongly that another product with nitrogen in the minus one state must be produced.

TABLE 8
PRELIMINARY HYDRAZINE - CERIUM STOICHIOMETRY

Mmol. N_2H_4 taken	Meq. Ce(IV) Used		$\frac{\text{Meq. Ce(IV)}}{\text{Mmol. } N_2H_4}$
0.07	0.1969		2.82
	0.2153		3.07
	0.2150		3.07
		Ave.	2.95
0.12	0.3544		2.95
	0.3752		3.12
	0.3302		2.75
		Ave.	2.94
0.20	0.6110		3.05
	0.6359		3.18
	0.5698		2.85
		Ave.	3.02
0.30	0.8534		2.84
	0.9213		3.07
	0.9680		3.22
		Ave.	3.04
		Combined Ave.	2.99

TABLE 9
PRELIMINARY GAS MEASUREMENT

Mmol. N_2H_4 taken	Ml. N_2 STP	Mmol. N_2 STP	$\frac{\text{Mmol. } N_2}{\text{Mmol. } N_2H_4}$
0.3	4.09	0.18	0.60
0.3	4.06	0.18	0.60
0.3	3.60	0.16	0.53

In order to re-establish the identity of the starting material a portion of the solution of hydrazine hydrate in acetic acid was diluted ten-fold with ethyl ether. Treatment in this manner produced a massive white precipitate which was neutral to both perchloric acid in glacial acetic acid and sodium methoxide in benzene-methanol solvent. After reprecipitation from a 1:1 chloroform-ethanol solution the material had a melting point of 138-140°C. This corresponds to literature values of 138°C. (22) and 140°C. (17) reported for symmetrical diacethydrazide.

The obvious conclusion to be drawn from this observation is that a solution of hydrazine in glacial acetic acid is not stable. As will be shown in a later section, hydrazine hydrate in glacial acetic acid is present as the salt, hydrazine acetate, after standing only two hours. A solution of the salt is also instable. This instability of the solution made it necessary to prepare

and purify hydrazine acetate, acethydrazide, and the symmetrical diacethydrazide and treat each separately with the cerium(IV) reagent. The procedures used for the preparation of these materials are given in the preceeding section dealing with chemicals.

Subsequent studies with acethydrazide in acetic acid showed that it disproportionates to hydrazine and symmetrical diacethydrazide very rapidly. Due to the necessary time of oxidation i.e., four hours, compared to the rate of disproportionation, it was deemed unprofitable to continue any further oxidative studies with the acethydrazide. Attention was then turned to the oxidation of the hydrazine acetate and symmetrical diacethydrazide.

1. Hydrazine Acetate Oxidation

Solutions of hydrazine acetate, containing four milligrams per ml., in acetic acid were prepared and subjected to oxidation with the cerium(IV) reagent. These solutions were prepared fresh each day that they were to be used, and all samples were removed from the stock solutions within four hours after preparation. This was done in order to insure that the material would be in its original form for the oxidation. Table 10 shows the stoichiometry achieved in the oxidation of the hydrazine acetate. On the basis of visual

observation there appeared to be no gas evolved from this oxidation. In order to prove or disprove this observation a sample was placed in the reaction vessel connected to the nitrometer tube, and the oxidation was carried out while sweeping with carbon dioxide. In this manner it was found that a gas, subsequently shown to be nitrogen, was being produced at the rate of 0.5 moles of gas per mole of hydrazine oxidized, as can be seen in Table 11.

TABLE 10
HYDRAZINE ACETATE - CERIUM STOICHIOMETRY

Trial	Mmol. Salt Taken	Meq. Ce(IV) Used	Meq. Ce(IV) / Mmol. Salt
1	0.215*	0.416	1.93
2		0.474	2.20
3		0.498	2.30
4		0.480	2.22
5		0.491	2.27
6		0.462	2.14
7		0.456	2.11
8		0.490	2.26
		Ave.	2.18

*20 mg.

TABLE 11
HYDRAZINE ACETATE GAS MEASUREMENTS

Mmol. $N_2H_4 \cdot HOAc$ Taken	Vol. N_2 Collected STP	Mmol. N_2 STP	Mmol. N_2 * / Mmol. N_2H_4
0.215	2.56	0.114	0.521
	2.50	0.112	0.520
	2.48	0.110	0.512
	2.77	0.129	0.567
	2.51	0.112	0.520

*value calculated on basis of Ce(IV) consumption= 0.545

The oxidation of hydrazine in aqueous solution has been dealt with by a number of investigators (10,11,5) with the result that several mechanisms have been proposed. These mechanisms are based on oxidations performed with iron(III) rather than cerium(IV). Both are classified as one electron transfer agents, however, and thus would be expected to react in the same manner. Included among these are

$$2\ N_2H_4 \xrightarrow{2\ eq} 2\ N_2H_3$$

$$2\ N_2H_3 \longrightarrow NH_2\text{-}NH\text{-}NH\text{-}NH_2$$

$$NH_2\text{-}NH\text{-}NH\text{-}NH_2 \longrightarrow NH_3 + HN{=}N\text{-}NH_2$$

$$HN{=}N\text{-}NH_2 \rightleftharpoons NH_2N{=}NH \longrightarrow NH_3 + N_2$$

A $\quad 2\ N_2H_4 \xrightarrow{2\ eq} 2\ NH_3 + N_2$

$$N_2H_4 \xrightarrow{1\ eq} N_2H_3$$

$$N_2H_3 \xrightarrow{1\ eq} N_2H_2$$

$$N_2H_2 \xrightarrow{2\ eq} N_2$$

B $\quad N_2H_4 \xrightarrow{4\ eq} N_2$

$$2\ N_2H_4 \xrightarrow{2\ eq} 2\ N_2H_3$$

$$2\ N_2H_3 \longrightarrow N_2H_2 + N_2H_4$$

$$N_2H_2 \xrightarrow{2\ eq} N_2$$

C $\quad N_2H_4 \xrightarrow{4\ eq} N_2$

Mechanism A requires one equivalent per mole while both B and C require four equivalents per mole. The following mechanism is also included in the review of Cahn and Powell (5).

$$2\ N_2H_4 \xrightarrow{4\ eq} 2\ NH{=}NH$$

$$2\ NH{=}NH \longrightarrow NH{=}N{-}NH{-}NH_2$$

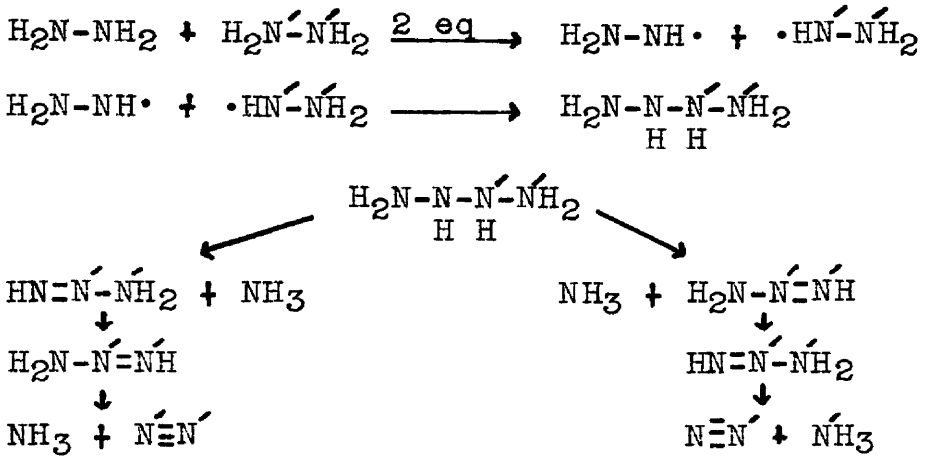
$$NH{=}N{-}NH{-}NH_2 \longrightarrow HN_3 + NH_3$$

If this were the path the reaction takes it would not stop at this point. It has already been shown the cerium(IV) in glacial acetic acid oxidizes hydrazoic acid quantitatively to nitrogen. Thus in the above mechanism a fourth step would be required.

$$HN_3 \xrightarrow{1\ eq} 1.5\ N_2$$

This would result in a stoichiometry of 2.5 equivalents of cerium(IV) per mole of hydrazine.

The studies of Higginson and Sutton (10) and Cahn and Powell (5) were carried out by use of radioactive N^{15} labeled hydrazine. By this means it was found that half of the nitrogen evolved was formed from two hydrazine molecules and half from one hydrazine molecule. This would suggest that reaction A above would actually be:



The stoichiometry achieved in the oxidation of hydrazine acetate by cerium(IV) in glacial acetic acid is 2.21 ± .09 equivalents of cerium(IV) per mole of hydrazine acetate. A combination of the foregoing proposed mechanisms can be devised which will yield such a stoichiometry. Such a combination fails, however, when the resulting amount of nitrogen produced is compared to the amount actually collected. It will be noted that oxidation of hydrazine acetate to give one mole of nitrogen as the only product, by either reaction B or C above, requires four equivalents of oxidizing agent

per mole of hydrazine. If it is assumed that nitrogen is the only product of the oxidation and the stoichiometry is a result of incomplete reaction, then the theoretical amount of nitrogen to be collected becomes 0.545 millimoles per millimole of hydrazine acetate used. A comparison of the values obtained experimentally with the theoretical yield shows that the evolution of nitrogen is very nearly quantitative.

2. Symmetrical Diacethydrazide Oxidation

In a like manner solutions of symmetrical diacethydrazide in acetic acid were prepared and allowed to react with the cerium(IV) reagent. The oxidations did not consume the expected number of milliequivalents of cerium(IV) as can be seen from the data in Table 12; however, the results were quite reproducible. It was evident from the gas escaping upon opening the reaction vessels that a pressure was developed in these oxidations. Subsequently, gas measurements were made on the oxidation of symmetrical diacethydrazide. The data for these gas measurements is shown in Table 13. As can be seen from the data, the volume of gas which was shown to be nitrogen, is about three-fourths the amount necessary for a quantitative yield. If, however, the volume of nitrogen collected is compared with the number of milliequivalents of cerium(IV) consumed by the oxidation, a quantitative yield results. The logical conclusion to

be derived from these data is that the oxidation is incomplete. The proposed route of the oxidation is

$$AcNHNHAc + 2\ Ce^{+4} \longrightarrow AcN{=}NAc + 2\ Ce^{+3} + 2\ H^{+}$$

$$AcN{=}NAc \longrightarrow CH_3COCOCH_3 + N_2$$

$$CH_3COCOCH_3 + 2\ Ce^{+4} + 2\ OH^{-} \longrightarrow CH_3COOH + 2\ Ce^{+3}$$

This produces a stoichiometry of four equivalents of cerium(IV) consumed per mole of symmetrical diacethydrazide, and one mole of nitrogen produced. The amount of water present in the glacial acetic acid is sufficient to provide the hydroxyl ion.

TABLE 12
DIACETHYDRAZIDE - CERIUM STOICHIOMETRY

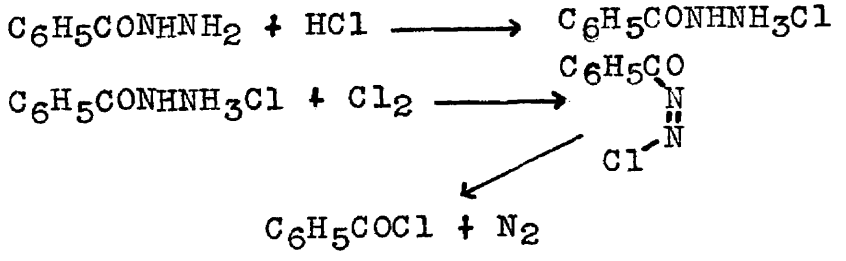
Mmol. Sample	Meq. Ce(IV) Used	Meq. Ce(IV) / Mmol. Sample
0.172	0.581	3.38
	0.574	3.34
	0.578	3.36
	0.586	3.41
	0.578	3.36
	0.580	3.37
	0.581	3.38
	Ave.	3.37

TABLE 13
GAS DATA FOR DIACETHYDRAZIDE

Mmol. Sample Taken	Vol. N_2 STP	Mmol. N_2 STP	Mmol. N_2* / Meq. Ce(IV)
0.344	6.46	0.288	0.855
	6.31	0.282	0.840
	6.34	0.283	0.842
	6.42	0.287	0.853
	6.38	0.285	0.847

*value calculated on basis of Ce(IV) consumption=0.860

This type of reaction in which nitrogen is split from the molecule has been shown by Carpino (7) to take place when acid hydrazides are oxidized with chlorine in the presence of excess hydrogen chloride. The products of such a reaction are the acid chloride and nitrogen. An example of his work is the oxidation of benzhydrazide to benzoyl chloride in the following manner:



A Kries color test (16) for diacetyl, using 1 per cent phloroglucinol in ethyl ether, was positive if an insufficient amount of cerium(IV) was added to the sample.

Attempts to prepare a solid derivative were unsuccessful, however. Treatment of both the acetic acid used as solvent and the cerium(IV) reagent with the Kries reagent produced negative results. The failure to secure a solid derivative for the diacetyl, however, does not necessarily mean that it is not present. Under the operating conditions being used diacetyl is very rapidly oxidized by cerium(IV) as was determined experimentally. The oxidation requires approximately two equivalents of cerium(IV) per mole. Therefore, either reaction 1 or 2 above must be the limiting reaction. In either case the amount of diacetyl present at any time, even when an insufficient quantity of cerium(IV) is used, will be very small. Thus the preparation of a derivative would be quite difficult and failure to do so can not be considered a negative result.

IV. HYDRAZINE-ACETIC ACID REACTION

IV. HYDRAZINE-ACETIC ACID REACTION

As previously noted, a solution of hydrazine in glacial acetic acid is not stable. Because of this it was considered necessary to study the reaction between hydrazine and acetic acid. All such reactions reported between hydrazine and acetic acid or acetic anhydride have been carried out at elevated temperatures. Stolle (22) has prepared di-, tri-, and tetraacethydrazide by the reaction of hydrazine hydrate and acetic anhydride at elevated temperatures. There was no record found of any study being made at room temperature, nor any evidence that such a reaction would proceed at room temperature.

Earlier experiments showed that the end product of the reaction was symmetrical diacethydrazide. This material is neutral to acid and base and its production necessarily results in a decrease in total basicity of the solution. Since both hydrazine acetate and acethydrazide can be titrated by perchloric acid in glacial acetic acid, it was considered practical to follow the reaction by means of such a titration.

A solution, approximately two molar with respect to hydrazine in glacial acetic acid, was prepared. At various time intervals a one ml. sample was withdrawn

and titrated with perchloric acid in glacial acetic acid. Simultaneously a second sample of 0.15 ml. was allowed to react with cerium(IV). There was no apparent change in the hydrazine content for the first twenty-four hours or so, and then the acid titer began to fall off at a regular rate.

At various times twenty-five ml. samples were removed and diluted ten-fold with ethyl ether in an effort to isolate some of the material present in the solution at that particular time. With the early samples this treatment left about five to ten ml. of oil. By cooling on dry ice, it was possible to obtain a precipitate from this oil which, after recrystallization from a 1:1 chloroform-ethanol mixture, had a melting point of 96-97°C. A search of the literature failed to yield a value close to this; however, Semishin (20) had reported a melting point of 87.5° for hydrazine acetate.

A titration of the recrystallized material with perchloric acid in glacial acetic acid to the blue-green color of crystal violet yielded an equivalent weight of 91.54, and a titration with sodium hydroxide in water gave an equivalent weight of 92.62. In connection with the latter titration it was necessary to continue titrating until no further change in color of the phenolphthalein indicator could be observed. The average equivalent weight, 92.07, corresponds to the mono salt,

$N_2H_4 \cdot HOAc$, and the previously reported melting point is therefore assumed to be in error.

After twelve days the samples treated with ether gave a precipitate of symmetrical diacethydrazide as evidenced by a melting point of 138-40°C. after recrystallization from 1:1 chloroform-ethanol. The quantity of this precipitate increased with time during the remainder of the study. At no time during the study was there any indication of the presence of the logical intermediate i.e., acethydrazide. Since this compound is also titratable with perchloric acid, the acid titer could conceivably have been a combined one.

In order to gain a clearer insight into the reaction, it was obviously necessary to devise some method for distinguishing between hydrazine acetate and acethydrazide. It was thought that there might be a distinguishing difference in their reactivity toward various oxidizing agents. Several were tried, including sodium permanganate, iodine, chromic oxide, and ferric perchlorate, without success.

The next step involved treating the two compounds with salicylaldehyde to form the corresponding Schiff's base and then titrating with perchloric acid in glacial acetic acid to a potentiometric end point. This was done in hope of finding a useable difference in basicity between the two compounds. This method was unsuccessful

in itself but did point the way to the final solution.

It was observed that the reaction of hydrazine acetate with salicylaldehyde imparted a light yellow color to the solution. The agitation resulting from transfer to the titrating vessel, for the perchloric acid titration, caused a precipitate to form. In a like manner a precipitate formed in the solution containing the acethydrazide and salicylaldehyde; however, in this case there was no color imparted to the solution. Upon collection and drying, the precipitates gave melting points of 212-14°C. and 196-98°C. respectively. These compare to values of 213-14°C., and 201°C. as reported in the literature for disalicylaldhydrazine (3) and acetic acid salicylidenehydrazide (9) respectively. A colorimetric method, described previously, for the determination of hydrazine in the presence of acethydrazide was based on this reaction.

Once the colorimetric procedure had been developed the time study was repeated in duplicate. Hydrazine hydrate was used for one and hydrazine acetate for the other. Both were made approximately two molar with respect to hydrazine in acetic acid, placed in glass-stoppered flasks, and immersed in a water bath at 25 $\pm$ 0.5°C. By using the two different materials the effect of water on the reaction could be observed and also its effect on the cerium(IV) oxidations would be

indicated. For the colorimetric measurements dilutions were made in such a manner that the final solution for measurement had a concentration of approximately 0.4 milligram hydrazine acetate per ml.

As can be seen from Figure 2B, the reaction between hydrazine acetate and acetic acid follows first order kinetics. Figure 2A shows that there is some production of acethydrazide during the reaction but its concentration is never large enough to allow it to be isolated by the procedure being used. Similar plots for the reaction with hydrazine hydrate are essentially the same, with the exception that the slope of the log concentration versus time is slightly less. This shows that the water slows the rate somewhat but does not change the kinetics of the reaction.

A second set of duplicate time studies was then prepared, using acethydrazide as prepared according to the previously mentioned procedure of Curtius (8). One solution was made two molar in water, corresponding to the amount of water produced by a two molar solution of hydrazine acetate reacting to yield acethydrazide and water. The second solution was made four molar in water to correspond, in the same manner, to the previous trial in which hydrazine hydrate was used.

In Figure 3B shows, the reaction between acethydrazide and acetic acid follows second order kinetics. In

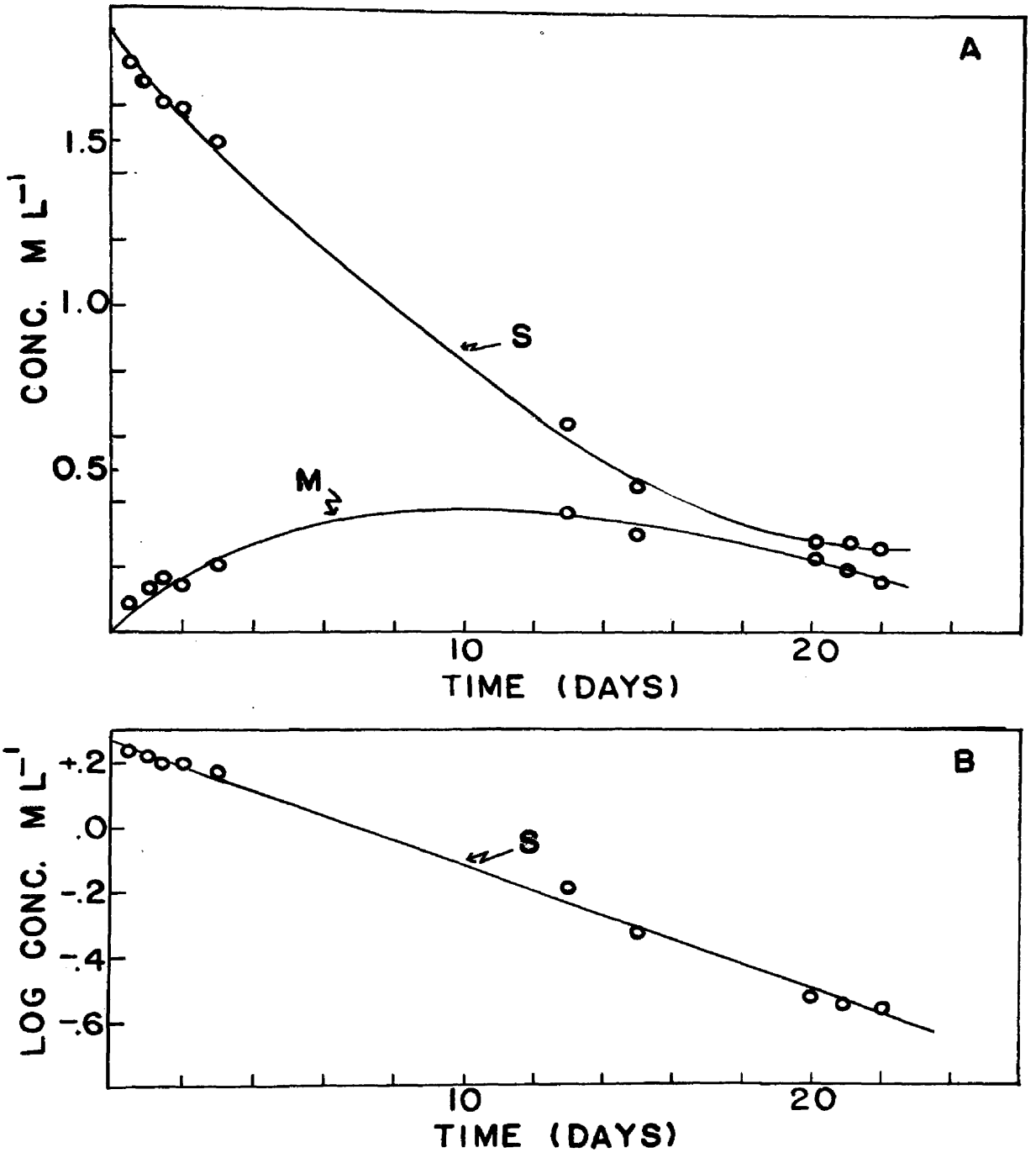


FIG. 2

A. HYDRAZINE-ACETIC ACID REACTION
S - SALT CONCENTRATION
M - ACETHYDRAZIDE CONCENTRATION

B. FIRST ORDER PLOT FOR HYDRAZINE ACETATE

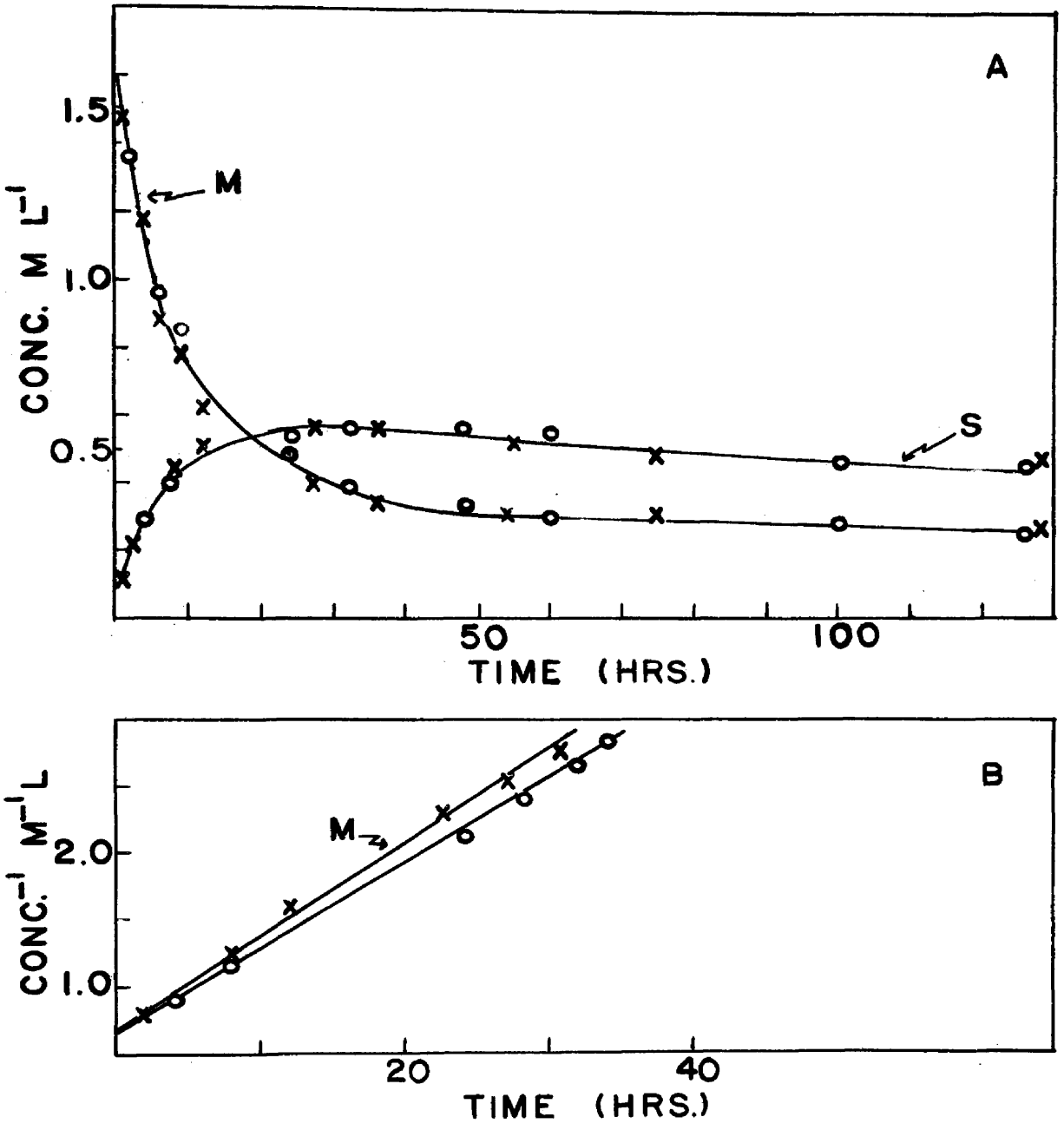


FIG. 3

A. DISPROPORTIONATION OF ACETHYDRAZIDE

M - ACETHYDRAZIDE

S - SALT

x - 2 M H_2O o - 4 M H_2O

B. SECOND ORDER PLOT FOR ACETHYDRAZIDE

this case, as in the previous one, the presence of water slows the reaction to a very slight extent but does not change the over-all kinetics. The complete data for all time studies may be found in the appendix.

As a comparison of Figures 2A and 3A shows, the reaction of hydrazine with acetic acid is very slow in comparison to the reaction rate of the acethydrazide.

The results of the time studies show that the disappearance of the hydrazine is first order, and the disappearance of the acethydrazide is second order. This would suggest that the reaction of hydrazine with acetic acid proceeds according to the following set of equations:

$$N_2H_4 + HOAc \xrightarrow{k_1} N_2H_4 \cdot HOAc$$

$$N_2H_4 \cdot HOAc \xrightarrow{k_2} H_2NNHAc + H_2O$$

$$2H_2NNHAc \xrightarrow{k_3} AcNHNHAc + N_2H_4$$

Since hydrazine acetate could be prepared merely by mixing hydrazine hydrate with acetic acid and cooling, it would be concluded that $k_1 \gg k_2 \ll k_3$. The disproportionation type reaction (equation 3) has been reported by Autenrieth and Spiess (2) as a method for obtaining a symmetrical secondary acid hydrazine from a primary acid hydrazine. Whereas the present study was done at room temperature, all previous reports of such a reaction state that it takes place at elevated temperatures and is usually done near the melting point of the primary acid hydrazine.

V. SUMMARY

V. SUMMARY

Cerium(IV) in glacial acetic acid can be used for the oxidation of some simple nitrogen compounds. Among those which have been treated with this reagent are sodium azide, hydrazine acetate, acethydrazide, and symmetrical diacethydrazide. Of these only the sodium azide is quantitatively oxidized. This oxidation to nitrogen can be done by dissolving the sample in glacial acetic acid alone, adding excess cerium(IV) reagent, allowing to stand for one-half hour and then determining the excess cerium(IV) by using sodium oxalate. It may also be accomplished as a direct titration with the cerium(IV) reagent, provided that the glacial acetic acid used as solvent is made at least one normal in perchloric acid.

As has been shown, the acethydrazide is too unstable in glacial acetic acid to lend any meaning to the values obtained in its oxidation.

Oxidation of both hydrazine acetate and the symmetrical diacethydrazide yielded odd values of stoichiometry. Both stoichiometries were quite reproducible however. As might be expected, the values obtained in the oxidation of the symmetrical diacethydrazide were more consistent than those achieved in the oxidation of the hydrazine

acetate. This would be expected since the symmetrical diacethydrazide, being the end product of the hydrazine-acetic acid reaction, is stable in the glacial acetic acid while the hydrazine acetate does react on standing.

In both cases it appears that the oxidation results in the formation of nitrogen as the only product. The amount of nitrogen produced is not quantitative at first glance. However, if the amount of nitrogen collected is compared to the ratio of milliequivalents of cerium(IV) actually used to that required for oxidation to nitrogen as the only product, the evolution is quantitative.

It can be concluded that under a set of standardized conditions, the stoichiometry achieved in the oxidation of hydrazine acetate is 2.21 ± .09 Ce(IV) = $N_2H_4 \cdot HOAc$. Similarly, the stoichiometry in the oxidation of symmetrical diacethydrazide is 3.37 ± .03 Ce(IV) = $CH_3\overset{\overset{O}{\|}}{C}NHNH\overset{\overset{O}{\|}}{C}CH_3$. For the latter oxidation the following route is proposed:

$$CH_3\overset{\overset{O}{\|}}{C}NHNH\overset{\overset{O}{\|}}{C}CH_3 + 2\ Ce(IV) \longrightarrow CH_3\overset{\overset{O}{\|}}{C}N{=}N\overset{\overset{O}{\|}}{C}CH_3 + 2\ Ce(III) + 2\ H^+$$

$$CH_3\overset{\overset{O}{\|}}{C}N{=}N\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}CCH_3 + N_2$$

$$CH_3\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}CCH_3 + 2\ OH^- + 2\ Ce(IV) \longrightarrow 2\ CH_3COOH + 2\ Ce(III)$$

Hydrazine and acethydrazide can both be titrated with perchloric acid in glacial acetic acid to the blue-green color of crystal violet. Each requires one equivalent of acid per mole.

Hydrazine may also be determined colorimetrically by reaction with salicylaldehyde and measurement of the resulting color at 418mμ. The apparent limit of concentration of hydrazine is determined by the solubility of the reaction product, disalicylalhydrazine.

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APPENDIXES

APPENDIX A

A qualitative study of the effect of the perchloric acid concentration on the rate of decomposition of the cerium(IV) reagent was carried out. In this study a volume of standardized cerium(IV) reagent was added to 50 ml. of glacial acetic acid of varying perchloric acid concentration in an iodine flask much the same as for the oxidations. A series of such samples were prepared and allowed to stand in the dark for varying lengths of time. At the end of a specified length of time the remaining cerium(IV) was determined by titration with sodium oxalate.

Four such series were run varying the perchloric acid concentration from zero to approximately one normal. The following table contains the data from this study. A plot of 1/C vs. time for the concentration of cerium(IV) yields a straight line for each of the four series run. The slopes vary with the concentration of the perchloric acid. A plot of the slope vs. 1/C of the perchloric acid also produced a straight line.

In this manner it was found that the decomposition of the cerium(IV) reagent was second order with respect to the cerium(IV) and also second order with respect to the perchloric acid. There exists, however, the

possibility that this effect may be due to the presence of water from the perchloric acid and not the acid alone. This point will bear further investigation on a more quantitative basis.

CERIUM(IV) DECOMPOSITION DATA

Time (min.)	Meq. Ce(IV) Trial 1 0 $HClO_4$	Trial 2 .25N $HClO_4$	Trial 3 .5N $HClO_4$	Trial 4 1N $HClO_4$
0	1.544	1.558	1.594	1.544
15	1.530	1.484	1.187	1.207
30	1.530	1.457	1.032	0.998
60	1.534	1.341	0.816	0.727
90	1.534	1.287	0.646	0.672
120	1.538	1.260	0.672	0.432

An attempt was also made to find a suitable non-aqueous diluent so as to study the effect of the acetic acid concentration on the decomposition of the reagent. Among the materials used were carbon tetrachloride, acetone, hexane, dioxane, dimethyl formamide, ethyl acetate, chloroform, acetonitrile, and dimethyl ether of ethylene glycol (1,2 dimethoxyethane). Of these the latter was the only one to show any real promise. All of the others either reacted with the cerium(IV) of the reagent themselves, or caused precipitation of the

cerium(IV) salt. At the time of this investigation the supply of 1,2 dimethoxyethane was very limited, there being only enough for one dilution. As mentioned, this one attempt appeared promising but further work was not done.

APPENDIX B

DATA FROM TIME STUDIES OF HYDRAZINE - ACETIC ACID REACTION

ACID SUMMARY
Time Study I - Hydrazine Hydrate
Original Concentration 1.88M.

Sample No.	Elapsed Time	$HClO_4$ Ml.	$HClO_4$ Normality	As	Meq. Total	Meq. Salt	Meq. Mono.
1	0 hr.	14.13	0.1322	0.246	1.87	1.74	0.13
2	1	14.18		0.248	1.87	1.74	0.13
3	2	14.09		0.248	1.86	1.74	0.12
4	4	14.11		0.233	1.87	1.66	0.21
5	6	14.19		0.233	1.87	1.66	0.21
6	8	14.13		0.260	1.87	1.85	0.02
7	12	14.11		0.253	1.87	1.82	0.05
8	24	14.04		0.260	1.85	1.85	0.00
9	27	13.99		0.248	1.85	1.74	0.10
10	30	13.90		0.250	1.84	1.79	0.05
11	36	13.83		0.240	1.83	1.71	0.12
12	47	13.70		0.243	1.81	1.71	0.10
13	50	13.62		0.246	1.80	1.74	0.06

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ACID SUMMARY - Continued

Sample No.	Elapsed Time	$HClO_4$ Ml.	$HClO_4$ Normality	As	Meq. Total	Meq. Salt	Meq. Mono.
14	55 hrs.	13.56		0.248	1.79	1.74	0.05
15	73	13.23		0.236	1.75	1.68	0.07
16	101	12.95		0.228	1.71	1.61	0.10
17	127	12.35		0.223	1.68	1.58	0.10
18	145	12.16		0.196	1.61	1.39	0.22
19	175	15.55	0.1006	0.185	1.56	1.31	0.25
20	194	14.94		0.178	1.49	1.25	0.24
21	17 days	10.68		-	1.07	-	-
22	18	9.05		0.086	0.91	0.60	0.31
23	20	7.05		0.057	0.71	0.41	0.30
24	25	4.85		0.072*	0.49	0.25	0.24
25	26	4.51		0.193**	0.45	0.27	0.18
26	27	4.27		0.193**	0.43	0.27	0.16
27	38	1.64	0.1108	0.061	0.18	0.09	0.09

* dilution factor 1:250
**dilution factor 1:100

CERIUM(IV) SUMMARY
Time Study I - Hydrazine Hydrate

Sample No.	Elapsed Time	Meq. Added	Meq. Left	Meq. Used	Meq. / Mmole.
1	0 hr.	1.2794	0.7073	0.5721	2.02
2	1	1.2747	0.7621	0.5126	1.87
3	2	1.2682	0.6768	0.5914	2.08
4	4	1.2593	0.7003	0.5590	1.92
5	6	1.2452	0.7121	0.5331	1.88
6	8	1.2255	0.6691	0.5564	1.96
7	12	-	-	-	-
8	24	1.2720	0.5757	0.6963	2.45
9	27	1.2225	0.5168	0.7057	2.48
10	30	1.1913	0.6510	0.5403	1.97
11	36	-	-	-	-
12	47	1.2661	0.6881	0.5780	2.03
13	50	1.2144	0.6928	0.5216	1.84

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CERIUM(IV) SUMMARY - Continued

Sample No.	Elapsed Time	Meq. Added	Meq. Left	Meq. Used	Meq./Mmole.
14	55 hrs.	-	-	-	-
15	73	1.6617	1.0575	0.6042	2.12
16	101	1.6466	0.9892	0.6564	2.31
17	127	1.6595	0.9816	0.6779	2.38
18	145	1.4217	0.6992	0.7226	2.54
19	175	1.4640	0.8130	0.6510	2.29
20	194	1.2930	0.5944	0.6986	2.46
21	17 days	-	-	-	-
22	18	1.5430	0.7215	0.8215	2.90
23	20	1.4524	0.6114	0.8410	2.95
24	25	1.0180	0.2530	0.7650	2.70
25	26	1.3640	0.5054	0.8586	3.02
26	27	1.5076	0.6302	0.8774	3.08
27	38	1.3775	0.4924	0.8851	3.11

ACID SUMMARY
Time Study II - Hydrazine Acetate
Original Concentration 1.86M.

Sample No.	Elapsed Time	$HClO_4$ Ml.	$HClO_4$ Normality	As	Meq. Total	Meq. Salt	Meq. Mono.
1	0 hr.	14.03	0.1322	0.258	1.86	1.84	0.02
2	1	14.07		0.253	1.86	1.82	0.04
3	2	14.02		0.248	1.86	1.74	0.12
4	4	13.95		0.260	1.85	1.85	0.00
5	6	13.97		0.255	1.85	1.80	0.05
6	8	13.98		0.260	1.85	1.85	0.00
7	12	13.86		0.246	1.83	1.74	0.09
8	24	13.78		0.236	1.82	1.68	0.14
9	27.5	13.68		0.233	1.81	1.66	0.15
10	31	13.63		0.230	1.80	1.63	0.17
11	36	13.57		0.228	1.79	1.61	0.18
12	48	17.45	0.1006	0.225	1.75	1.60	0.15
13	51.5	17.24		0.223	1.72	1.58	0.14

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ACID SUMMARY - Continued

Sample No.	Elapsed Time	$HClO_4$ Ml.	$HClO_4$ Normality	As	Meq. Total	Meq. Salt	Meq. Mono.
14	55 hr.	17.28		0.217	1.74	1.55	0.19
15	71	17.01		0.212	1.71	1.50	0.21
16	12 days	10.74		-	1.08	-	-
17	13	10.27		0.093	1.03	0.65	0.38
18	15	7.69		0.064	0.77	0.46	0.31
19	20	5.30		0.086*	0.53	0.29	0.24
20	21	4.78		0.196**	0.48	0.28	0.20
21	22	4.27		0.193**	0.43	0.27	0.16
22	33	1.56		0.045**	0.17	0.06	0.11

* dilution factor 1:250
**dilution factor 1:100

CERIUM(IV) SUMMARY
Time Study II - Hydrazine Acetate

Sample No.	Elapsed Time	Meq. Added	Meq. Left	Meq. Used	Meq./Mmole.
1	0 hr.	1.6527	0.9646	0.6881	2.46
2	1	1.6554	1.0016	0.6538	2.34
3	2	1.6572	1.0363	0.6209	2.23
4	4	1.6508	1.0311	0.6197	2.22
5	6	1.6589	1.0287	0.6302	2.26
6	8	1.6595	1.0185	0.6410	2.30
7	12	-	-	-	-
8	24	1.4316	0.7665	0.6651	2.38
9	27.5	1.4116	0.7261	0.6855	2.46
10	31	1.4094	0.7361	0.6733	2.41
11	36	-	-	-	-
12	48	1.2410	0.5590	0.6820	2.46
13	51.5	1.2189	0.5597	0.6592	2.36

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CERIUM(IV) SUMMARY - Continued

Sample No.	Elapsed Time	Meq. Added	Meq. Left	Meq. Used	Meq./Mmole.
14	55 hrs.	1.4502	0.7550	0.6952	2.49
15	71	1.3296	0.6121	0.7175	2.57
16	12 days	-	-	-	-
17	13	1.5419	0.7321	0.8098	2.89
18	15	1.4588	0.6108	0.8480	3.04
19	20	1.0197	0.2660	0.7537	2.70
20	21	1.3704	0.4878	0.8826	3.15
21	22	1.5128	0.5996	0.9132	3.26
22	33	1.3810	0.4878	0.8932	3.19

ACID SUMMARY
Time Study III - Acethydrazide
Original Concentration 1.88M.

Sample No.	Elapsed Time	$HClO_4$ Ml.	$HClO_4$ Normality	As	Meq. Total	Meq. Salt	Meq. Mono.
1	20 min.	17.15	0.1006	0.004*	1.73	0.14	1.59
2	1 hr.	15.95		0.086**	1.61	0.12	1.49
3	2	15.06		0.155	1.51	0.22	1.39
4	4	13.93		0.230	1.40	0.32	1.18
5	6	12.82		0.281	1.29	0.40	0.89
6	8	12.11		0.312	1.22	0.44	0.78
7	12	11.20		0.354	1.13	0.51	0.62
8	22.5	9.82		0.386	0.99	0.55	0.44
9	27	9.65		0.389	0.97	0.56	0.41
10	30.5	9.39		0.394	0.94	0.57	0.37
11	36	8.85		0.386	0.89	0.55	0.34
12	48	8.37		0.375	0.84	0.53	0.31
13	54	8.26		0.365	0.83	0.52	0.31

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ACID SUMMARY - Continued

Sample No.	Elapsed Time	$HClO_4$ Ml.	$HClO_4$ Normality	As	Meq. Total	Meq. Salt	Meq. Mono.
14	60 hr.	8.15		0.358	0.82	0.51	0.31
15	74.5	6.97	0.1108	0.338	0.77	0.48	0.31
16	99	6.63		0.316	0.73	0.45	0.28
17	128	5.97		0.272	0.66	0.39	0.27
18	150	5.48		0.248	0.61	0.36	0.25
19	168	5.04		0.238	0.56	0.34	0.22
20	194	4.75		0.201	0.53	0.29	0.24
21	220	4.47		0.176	0.49	0.25	0.24
22	245	4.18		0.170	0.46	0.23	0.23

* dilution factor 1:250
**dilution factor 1:100

CERIUM(IV) SUMMARY
Time Study III - Acethydrazide

Sample No.	Elapsed Time	Meq. Added	Meq. Left	Meq. Used	Meq. / Mmole.
1	20 min.	1.2453	0.4147	0.8306	2.94
2	1 hr.	-	-	-	-
3	2	1.4265	0.5684	0.8581	3.04
4	4	1.4195	0.5848	0.8347	2.96
5	6	1.4216	0.5943	0.8273	2.93
6	8	1.4163	0.5872	0.8291	2.94
7	12	-	-	-	-
8	22.5	2.1225	1.2904	0.8321	2.95
9	27	1.8547	1.0192	0.8355	2.96
10	30.5	1.8294	1.0044	0.8250	2.92
11	36	-	-	-	-
12	48	1.6209	0.7940	0.8269	2.93
13	54	1.4827	0.6940	0.7887	2.80

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CERIUM(IV) SUMMARY - Continued

Sample No.	Elapsed Time	Meq. Added	Meq. Left	Meq. Used	Meq./Mmole.
14	60 hr.	-	-	-	-
15	74.5	1.3150	0.5070	0.8080	2.86
16	99	1.2216	0.4311	0.7905	2.80
17	128	1.7544	0.8772	0.8772	3.11
18	150	1.1535	0.3839	0.7696	2.73
19	168	1.7549	0.8760	0.8789	3.11
20	194	1.4814	0.6224	0.8590	3.04
21	220	1.3512	0.5017	0.8495	3.01
22	245	-	-	-	-

ACID SUMMARY
Time Study IV - Acethydrazide + Water
Original Concentration 1.88M.

Sample No.	Elapsed Time	$HClO_4$ Ml.	$HClO_4$ Normality	As	Meq. Total	Meq. Salt	Meq. Mono.
1	20 min.	15.92	0.1108	0.025	1.77	0.08	1.65
2	1 hr.	14.78		0.083	1.64	0.11	1.53
3	2	13.90		0.130	1.54	0.18	1.36
4	4	12.76		0.215	1.41	0.30	1.11
5	6	11.92		0.253	1.32	0.36	0.96
6	8	11.39		0.286	1.26	0.41	0.85
7	12	10.23		-	1.18	-	-
8	24	9.15		0.378	1.01	0.54	0.47
9	28	8.77		0.387	0.97	0.55	0.42
10	32	8.49		0.393	0.94	0.56	0.38
11	36	8.31		0.400	0.92	0.57	0.35
12	48	8.00		0.394	0.89	0.56	0.33
13	55	7.77		0.389	0.86	0.55	0.31

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ACID SUMMARY - Continued

Sample No.	Elapsed Time	$HClO_4$ Ml.	$HClO_4$ Normality	As	Meq. Total	Meq. Salt	Meq. Mono.
14	60 hr.	7.65		0.388	0.85	0.55	0.30
15	75	7.18		0.356	0.80	0.51	0.29
16	100	6.70		0.326	0.74	0.46	0.28
17	126	6.23		0.318	0.69	0.45	0.24
18	148	5.97		0.276	0.66	0.39	0.27
19	170	5.60		0.250	0.62	0.35	0.27
20	192	5.38		0.223	0.596	0.32	0.28

CERIUM(IV) SUMMARY
Time Study IV - Acethydrazide + Water

Sample No.	Elapsed Time	Meq. Added	Meq. Left	Meq. Used	Meq./Mmole.
1	20 min.	2.0193	1.1038	0.9155	3.24
2	1 hr.	1.7673	0.8607	0.9066	3.21
3	2	1.7662	0.8795	0.8867	3.14
4	4	2.0111	1.1132	0.8979	3.18
5	6	1.7638	0.8784	0.8854	3.14
6	8	1.7579	0.8675	0.8884	3.15
7	12	-	-	-	-
8	24	1.0367	0.3226	0.7141	2.53
9	28	1.0311	0.3102	0.7209	2.56
10	32	1.1588	0.3881	0.7701	2.73
11	36	-	-	-	-
12	48	1.7496	0.9170	0.8326	2.95
13	55	1.7198	0.8795	0.8403	2.98

Continued next page

CERIUM(IV) SUMMARY - Continued

Sample No.	Elapsed Time	Meq. Added	Meq. Left	Meq. Used	Meq. / Mmole.
14	60 hr.	-	-	-	-
15	75	1.4915	0.6628	0.8287	2.94
16	100	1.3476	0.5285	0.8191	2.90
17	126	1.7662	0.8854	0.8808	3.12
18	148	-	-	-	-
19	170	0.8340	0.1084	0.7256	2.58
20	192	1.6918	0.8104	0.8814	3.12