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COMPLEXES OF NICKEL WITH VIC-DIOXIMES IN THE PRESENCE OF AN OXIDIZING AGENT IN ALKALINE MEDIA

by

Anton Burchard Carlson

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

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In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

Iowa State College
1952

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I. INTRODUCTION

It was in 1924 that Feigl (20) first reported an oxidized complex of nickel with a vicinal-dioxime,[1] 2,3-butanedionedioxime. His experimental evidence led him to propose that two vic-dioxime molecules were bound to a nickel(IV) ion as in the nickel(II) compound. The two remaining nickel valencies were used to bond an oxygen atom. Very nearly all of the papers appearing since that time have retained the oxidized connotation.

In 1926, Rollet (69) devised a spectrophotometric method for the determination of nickel based on the work of Feigl. He recommended the use of bromine in ammoniacal solution as oxidant. By noting that the color changed from orange-red to red-brown with time, he indirectly pointed out that two complexes were formed. This is now known as the change of Complex A into Complex B. The experimental procedure of Feigl was such that only one complex was observable. Since then, most investigators have indiscriminately applied the term "nickelic" to both complexes.

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[1] These compounds are also known as α-dioximes, ortho-dioximes and 1,2-dioximes. A paper, concerned with the structure of the vic-dioxime-nickel(II) compounds, has appeared recently (81).

Most of this confusion arose because the colors of the two complexes are so nearly alike. In the past ten years, spectrophotometric data have provided concrete evidence for two complexes. This development encouraged a few workers to investigate, at least briefly, the nature of the reactions involved. It was during this time that the original work of Feigl was questioned.

Only two papers, by the same authors, have appeared that report comprehensive results of a theoretical study of these complexes. However, these investigators did not study the complexes in solution, but were concerned with an isolated solid.

The present investigation was instigated in an attempt to resolve the conflicting data and arrive at suitable structures for these rather unusual complexes. It is believed that, within the limits of present day knowledge of complex ions, this objective was attained in the case of the more stable complex. A structure that is consistent with the known facts is hypothesized for the unstable complex.

The study reported below was carried out as part of a general investigation in progress in this laboratory concerning the chemistry of the vic-dioxime-nickel compounds and complexes. The oxidized complexes are of more than academic interest because their colors are the bases of the principal methods used for the spectrophotometric determination of nickel.

II. REVIEW OF LITERATURE

A. Nature of the Reaction

In 1924, Feigl (20) first reported the formation of an oxidized complex of nickel with 2,3-butanedionedioxime. While investigating nitrate ion interference in the gravimetric determination of nickel with this vic-dioxime, he tested other oxidants for possible interference. He found that a number of other oxidizing agents prevented precipitation of nickel in alkaline solution. Feigl prepared deep, red-brown colored solutions by the addition of lead dioxide to alkaline mixtures of nickel(II) and 2,3-butanedionedioxime. He isolated a red compound from these solutions by cautious neutralization with mineral acid. Analysis of the red compound indicated it to contain a ratio of vic-dioxime to nickel of 2:1. Careful neutralization of the red-brown solution in the presence of iodide ion followed by titration of the iodine with thiosulfate ion led Feigl to conclude the nickel(II) ion had been oxidized to the tetravalent state. The following structure for the red solid was proposed.[1]

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[1] Throughout this study the symbol DH_2 will represent (Footnote continued on next page)

$(DH)_2NiO$

Feigl, of course, devised a spot test for nickel(II) ion using the above reaction which was about 50 times more sensitive than the usual test utilizing the reaction of nickel(II) with 2,3-butanedionedioxime.

Just two years later, Rollet (69) introduced a colorimetric method for the determination of nickel using this reaction. He tested a number of oxidants and recommended bromine as being the best of the group. He observed that the first formed color was orange-red, and this color became red-brown on standing.

Since 1926, a large number of papers have appeared (1,11,16,21,22,31,35,54,59,71,77) dealing with the spectrophotometric determination of nickel, most of them based on the original work of Rollet. Upon examining these papers, it becomes immediately evident that the reactions are poorly understood. Workers disagree among themselves as to the order of addition of reagents, preferred oxidants and factors affecting the stability of the complexes. The majority of papers are concerned with the older, 2,3-butanedionedioxime. However, a number of recent papers have presented

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(continued) any vic-dioxime. The symbols DH^- and $D^=$ will be used to designate the singly charged and doubly charged anions respectively, formed by removal of the oxime hydrogens.

information on the use of other vic-dioximes. Mitchell (58) found 1,2-bis(2-furyl)ethanedionedioxime (α-furildioxime) gave a very unstable nickel complex (Complex A) in the presence of bromine. Both 1,2-cyclohexanedionedioxime (21,42) and 1,2-cycloheptanedionedioxime (22) yield oxidized complexes similar to 2,3-butanedionedioxime.

A total of nine articles, which may be considered of theoretical nature, have appeared. The first of these, by Wulff and Lundberg (83), appeared in 1944 and was entirely qualitative in scope. These workers claimed, without substantiation, that they prepared nickel(III) ion by treatment with bromine. This aqueous solution of "oxidized" nickel ion failed to produce the soluble complex when a vic-dioxime was added. Their second experiment involved treating the vic-dioxime with a limited quantity of bromine, followed by nickel(II) ion. This procedure yielded the orange-red color. From these two experiments, they concluded that the nickel(II) ion reacted with some oxidized product of the vic-dioxime. This was the first refutation of the original work of Feigl.

Furman and McDuffie (24) published spectrophotometric curves which illustrate the difference between the colors reported by Rollet. They devised procedures, which permit each color to be used as the basis of a colorimetric method for the determination of nickel. These workers described the colors as complexes A and B as given in Figure 1. The color of Complex A begins to change in about an hour, while Complex B, prepared with peroxydisulfate ion as oxidant, forms in about an hour and the color fades after about 12 hours.

Babko (6) reported that Complex A contained a nickel to vic-dioxime ratio of 1:2 and Complex B was a 1:3 complex. This worker claimed that the vic-dioxime rather than the nickel(II) ion was oxidized. Only an abstract of this article was available and his experimental procedures are unknown.

Hooreman (36) reported some semi-quantitative results, which indicated the ratio of nickel to vic-dioxime to be 1:2 in Complex A and 1:4 in Complex B. He claimed, or perhaps accepted, the tetravalency of the nickel ion in each complex. However, he reported that it took much less reducing agent to destroy Complex A than Complex B. The limited nature of this study prevents extensive consideration of the results.

Edelman (18) has recently reported the preparation of stable nickel(III) compounds of 1,2-bis(phenyl)ethanedionedioxime (α-benzildioxime). Analyses indicated the following compounds had been prepared.

Bis(α-benzildioximo)nickel(III) bromide

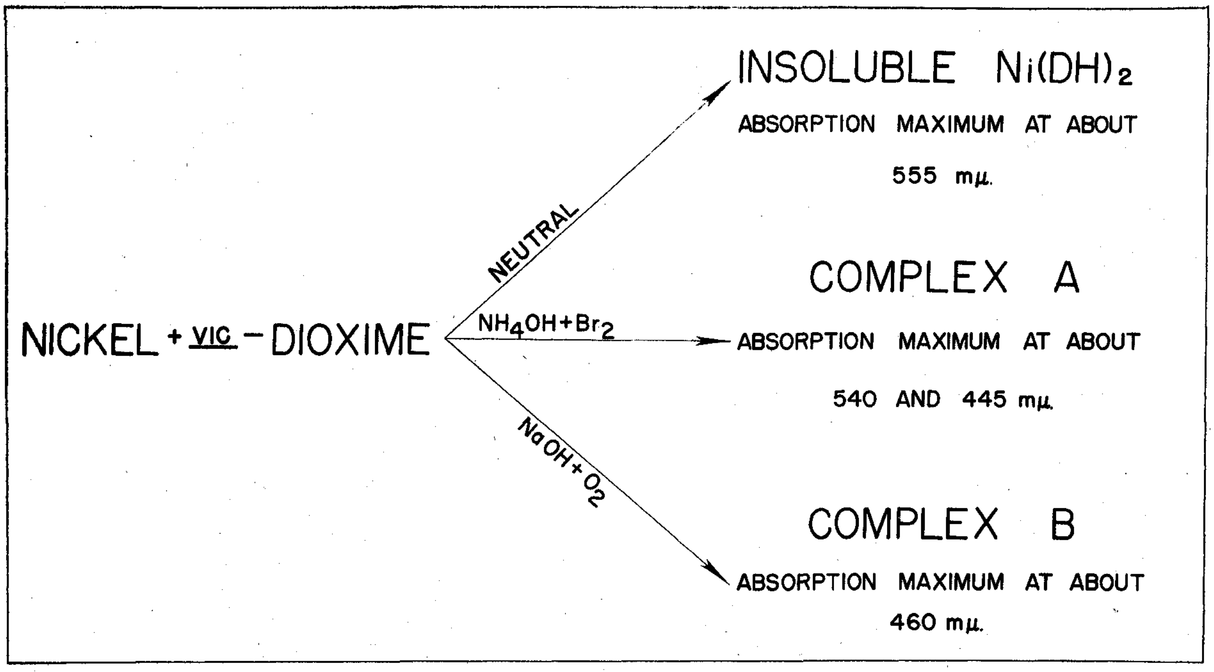


FIG. I – SCHEMATIC OUTLINE OF THE REACTION BETWEEN NICKEL AND *vic* – DIOXIMES.

Bis(α-benzildioximo)nickel(III) iodide

The bromide was prepared by mixing bromine with a carbon tetrachloride solution of 1,2-bis(α-benzildioximo-N,N')-nickel(II). The product separated on standing. The iodide was prepared in a similar fashion using benzyl alcohol as solvent and iodine as oxidant, except the mixture was heated to produce the reaction. The corresponding bis(2,3-butanedionedioximo)nickel(III) bromide derivative was unstable. An attempt to prepare the 1,2-cyclohexanedionedioxime compound resulted in decomposition of the nickel(II) derivative by the bromine.

A recent report (48) claims the following compounds were prepared by the action of bromine on the metal-2,3-butanedionedioxime complexes in alkaline solution.

$$C_8H_{14}O_5N_4Cu$$
$$C_8H_{14}O_6N_4Cu$$
$$C_{12}H_{21}O_9N_6Fe(III)$$

These compounds were stated to be nitroximes. Since only an abstract was available, it is impossible to discuss this paper in a critical manner. An earlier paper by the same workers (47) is believed to be similar to that above except nickel(II) ion was the metal used. This abstract was very uninformative.

The most illuminating papers on this subject appeared in 1948 (62,63). These workers attempted to repeat the original work of Feigl and were only partially successful. The red solids they isolated using Feigl's procedure always contained chloride, lead and sodium ions in varying proportions. They substantiated the claim of Feigl concerning the oxidizing power of the red-brown solutions. However, resolution of the isolated compound in alkali yielded a solution having only weak oxidizing power. Furthermore, analyses of the red solid indicated only half as much nitrogen as Feigl reported, while the nickel values were similar.

Their second paper reported results obtained utilizing their own experimental procedures. Microscopic examination of the red solid obtained by Feigl's method indicated a mixture of white crystals and a red, amorphous solid was present. They identified the white crystals as being the disodium salt of 2,3-butanedionedioxime. They were also able to prepare the pure red solid without using lead dioxide, provided the reaction was performed in about 10 per cent sodium hydroxide solution. This pure red solid separated when the mixture was allowed to stand. The solid showed no oxidizing power and analyses indicated the formula to be DNaNiOH. These workers infer that the red solid is responsible for the color of the solution, but fail to account for the experimentally confirmed oxidizing power of the original solution and lack of oxidizing power of the isolated solid. Their qualitative experiments with the furoxan derivative of 2,3-butanedionedioxime (see Part V.A.3.) lead them to the conclusion that the vic-dioxime was oxidized to some intermediate stage between dioxime and furoxan. They dealt with solutions as much as 1000 times as concentrated as those used in the colorimetric procedures. It seems likely that the results and conclusions presented are valid when applied to the red solid. However, they present no evidence which permits extension of their ideas concerning the solid to the nature of the complex producing the red-brown color in dilute solutions.

It is obvious from the above summary that very little is known about the chemistry of the formation of these oxidized complexes.

B. Oxidation States of Nickel

Latimer (51, p. 187) accepts evidence for the +1, +2, +4, +6 and +8 oxidation numbers of nickel. He claims the oxide, Ni_2O_3, is probably a nickel(II,IV) oxide. The following compounds having higher oxidation states are mentioned: NiO_2, K_2NiO_4 and K_2NiO_5. These compounds are all unstable in acid solution.

The formation of nickel tetracarbonyl during decomposition of organic thio salts has been reported (37). A number of recent papers (29,49,50) report data substantiating the occurrence of nickel(III) and nickel(IV) oxides. The preparation of vic-dioxime-nickel(III) compounds was discussed above.

An excellent paper by Nyholm (60) describes the formation of a nickel(III) complex. Many di(tertiary arsines) react with nickel(II) ions to form compounds of the type, $Ni(diarsine)_2Cl_2$. Using $o\text{-}C_6H_4[As(CH_3)_2]_2$, Nyholm prepared the nickel(II) compound, which is red. Upon refluxing this compound in dilute hydrochloric acid, the solution turned green. He isolated a green compound and found it to be $[Ni(diarsine)_2Cl_2]Cl$. Magnetic susceptibility measurements indicated the compound was paramagnetic to the extent of one unpaired electron. He tested the action of the compound on an ammoniacal solution of 2,3-butanedionedioxime and found a dark, purple-red color was slowly formed on standing. Unfortunately, the color specification does not provide sufficient information for deciding if Complex A or Complex B was formed. However, in ammoniacal solution Complex A would be expected to form more easily.

A more recent paper by Nyholm (61) reports the preparation of a similar nickel(IV) compound, $[NiCl_2(diarsine)_2]\text{-}[ClO_4]_2$, which is deep-blue colored and is diamagnetic.

Jensen and Nygaard (39) reported a nickel(III) compound prepared from anhydrous nickel(II) bromide and triethylphosphine, which they formulated as $NiBr_3[(C_2H_5)_3P]_2$.

The compound has one unpaired electron as expected.

The above evidence indicates that both nickel(III) and nickel(IV) are possible; particularly when they can be stabilized through complex formation.

C. Aqueous Chemistry of Nickel

The studies of complex ions of nickel have been extensive. Most of the papers have been concerned only with the determination of the ratio of the ligand to the central atom. Even though these papers are not of direct interest to this problem, a few will be included for future reference. All of the papers listed below deal with nickel(II) complexes.

A number of papers (9,13,38,73) discuss complexes of nickel(II) with organic acids. The cyanide complexes have also received study (10,12,70). A few papers deal with some phosphate complexes (45,68) and certain ammine complexes (2,3,14,19,28,30,34,43,44,67,79). It should be pointed out that the magnetochemistry of nickel(II) complexes has received considerable emphasis (23,55,56,82).

The cyanide complexes have been studied by radiochemical techniques (53). An attempt has been made to correlate isotopic exchange with bond type in an extensive series of nickel(II) complexes (32,41). The paramagnetic complexes studied readily exchanged, but most of the diamagnetic complexes failed to show exchange. Experiments of this type will undoubtedly be extended.

The hydrolytic equilibria of nickel(II) in both acidic and basic media have been investigated by Gayer and Garrett (25) and by Gayer and Woontner (26).

III. MATERIALS AND APPARATUS

In general, the best available reagent-grade chemicals, as indicated by the manufacturers' labels, were used. A selected lot of sodium hydroxide having a particularly low iron content was used throughout this study. All solutions were prepared with deionized, distilled water.

Nickel metal. Mond nickel from the International Nickel Company. This metal was specified to contain no more than 0.008% cobalt, 0.008% copper and 0.045% iron. A stock solution was prepared by dissolving about 5.9 g. in _aqua regia_. The resulting solution was treated with perchloric acid, evaporated to dense fumes three times and finally diluted to a liter. A gravimetric analysis of this solution by the electrolytic method indicated the nickel(II) ion concentration to be 0.0996 ± 0.0001 M. A spot test for chloride ion with silver nitrate was negative. Dilute solutions for the experimental work were prepared by diluting measured volumes of this standard solution.

Vic-dioximes. Reagent-grade 2,3-butanedionedioxime (dimethylglyoxime) from a commercial source was used. Both the 1,2-cyclohexanedionedioxime (nioxime) and 1,2-cycloheptanedionedioxime (heptoxime) were prepared in these laboratories (66,78). Stock solutions of each _vic_-dioxime were standardized by adding an excess of nickel(II) chloride solution to ammonium acetate buffered aliquots of the various vic-dioxime solutions and weighing the precipitates obtained in the usual manner. It was found that 2,3-butanedione-dioxime has a water solubility about twice, or 0.8 g. per liter, that given by Diehl (15, p. 20) and by Babko and Mikhelson (7). This solubility was checked by analyzing for nickel in the above precipitates by the "heptoxime" method (80). No attempt was made to ensure the solubility measured was maximal. The solution was prepared by adding an excess of solid vic-dioxime to water and allowing the mixture to stand several days with occasional shaking. The solution was filtered just prior to standardization.

"Normax" brand glassware was used throughout this study except in a few cases where the measured volumes did not require such accuracy. All of the solutions of the complexes and vic-dioximes prepared for spectrophotometric examination were contained in 200 ml. "Normax" volumetric flasks.

A Cary, Model 12, recording spectrophotometer was used to obtain all of the absorption curves reported below. The instrument was operated as recommended by the manufacturer and with a Slit Control setting of 10. A Beckman, Model DU, spectrophotometer was used to obtain the absorbancy measurements of solutions employed in the study of the formation constant of Complex B. Matched sets of 2.000-cm. and

5.000-cm. cuvettes were used for all solutions and blanks. Corrections for slight differences in the transmittancies of the cuvettes were made whenever necessary.

All pH measurements were made with a Beckman, Model G, pH meter equipped with a Type E glass electrode. The instrument was standardized against commercial buffers in the usual manner.

The potentiometric titrations were carried out with the Model G pH meter by substituting a platinum electrode for the glass electrode. The end points in the iodometric titrations were determined by means of a Fisher Titrimeter.

A Sargent, Model XXI, polarograph equipped with an H-type electrolysis vessel was used to investigate the polarographic behavior of the oxidized complexes.

IV. EXPERIMENTAL PROCEDURES

The less common experimental procedures employed in this study are described in this section. The symbology used in the various equations was standardized as much as possible. The terminology of spectrophotometry recommended by Gibson (27) has been followed.

A_s = Absorbancy = log $1/T_s$ (Optical Density)

a_M = Molar Absorbancy Index (Extinction Coefficient)

b = Depth of solution traversed by the light beam

Other terms of interest herein conform to the following system.

( ) = Equilibrium activity of the species indicated

[ ] = Equilibrium molar concentration of the species indicated

C_x = Analytical or total molar concentration of x

μ = Ionic strength

γ_x = Molar activity coefficient of x

K' = Molar equilibrium constant

K = Thermodynamic equilibrium constant

log = Logarithm to base 10

A. Determination of Acidic Dissociation Constants

Stenström and Goldsmith (74) devised a method for determining the dissociation constants of acids and bases from spectrophotometric data. The method may be applied only in instances where it is possible to infer at least a part of the absorption spectra of the acid or base and its salt. An experimentally demonstrated isosbestic point would fulfill this requirement. The value of pK' can be calculated using the equation developed below. These workers did not treat cases where further ionization can occur.

Let the following terminology apply.

C = Molar concentration of acid (or base) added

X = Fraction of ionized molecules

$1-X$ = Fraction of unionized molecules

a_M = Molar absorbancy index for a mixture of the two absorbing species

a'_M = Molar absorbancy index for unionized molecules

a''_M = Molar absorbancy index for ionized molecules

Then

$$a_M = a'_M \{1-X\} + a''_M \{X\} .$$

From the law of mass action

$$\frac{[H^+][A^-]}{[HA]} = K',$$

$$\frac{[H^+][CX]}{C\{1-X\}} = K',$$

$$X = \frac{K'}{K' + [H^+]} .$$

Combining

$$a_M = a_M' \frac{[H^+]}{[H^+] + K'} + a_M'' \frac{K'}{[H^+] + K'} .$$

Rearranging

$$K' = \frac{a_M - a_M'}{a_M'' - a_M} [H^+].$$

Provided the concentration, C, and cell length, b, remain constant, the absorbancy may be substituted for the molar absorbancy index thus simplifying the calculations. The prime designations retain their original connotation.

$$K' = \frac{A_s - A_s'}{A_s'' - A_s} [H^+].$$

The experimental procedure to be followed involves a determination of the absorption spectra of the unionized molecule, the ion and a mixture of ionic and nonionic forms having a pH near the pK' value. The pH of the solution containing this mixture, together with absorbancy measurements of the three solutions are used to calculate K'. An average value is obtained by calculating K' from data taken at several wavelengths.

A similar equation can be derived for the case where further ionization is possible. When the second dissociation constant is sufficiently different from the first, no particular difficulty should arise. However, when K_2' is less than about 1000 K_1', it may become impossible to obtain the true absorption spectrum of the intermediate ion. In this case K_1' and K_2' cannot be accurately determined.

The thermodynamic ionization constant can be estimated by application of the Debye and Hückel theory (8). The equilibrium equation may be written as

$$pK = pH + \log \frac{[HA]}{[A^-]} + \log \gamma_{HA} - \log \gamma_{A^-} .$$

The activity coefficient of a 1:1 electrolyte is given by

$$-\log \gamma = \frac{A\mu^{1/2}}{1 + B\mu^{1/2}} + C\mu$$

and for an unionized molecule by

$$-\log \gamma = C'\mu .$$

The terms A, B, C and C' are characteristic constants which depend on type of solvent, etc. Substitution of these terms into the equilibrium equation gives

$$pK = pH + \log \frac{[HA]}{[A^-]} - C\mu + C'\mu + \frac{A\mu^{1/2}}{1 + B\mu^{1/2}} .$$

Since the values for the constants C and C' are usually small (about 0.02) for weak organic acids, these terms can be eliminated because $C'\mu - C\mu$ becomes negligibly small. The value of A for water as solvent at 25° C. is 0.509 and the value of B can be taken as unity. The final equation becomes

$$pK = pH + \log \frac{[HA]}{[A^-]} + \frac{0.509\mu^{1/2}}{1 + \mu^{1/2}} .$$

This correction term, which must be added to the pK_1' values, is 0.12 for $\mu = 0.1$ and 0.21 for $\mu = 0.5$.

A similar treatment may be applied to determine pK_2 from pK_2'.

$$pK = pH + \log \frac{[HA^-]}{[A^=]} + \log \gamma_{HA^-} - \log \gamma_{A^=} .$$

The activity coefficient terms may be calculated by

$$-\log \gamma_{HA^-} = \frac{A\mu^{1/2}}{1 + B\mu^{1/2}} + C\mu ,$$

$$-\log \gamma_{A^=} = \frac{2A\mu^{1/2}}{1 + B\mu^{1/2}} + C'\mu .$$

The factor of two in the coefficient for $A^=$ is the valency correction factor for a 2:1 electrolyte. Combination of the above equations and elimination of the C and C' terms as before gives

$$pK = pH + \log \frac{[HA^-]}{[A^=]} + \frac{0.509\mu^{1/2}}{1 + \mu^{1/2}} .$$

Thus the activity coefficient factor is the same as that for the first ionization step.

B. Determination of Ratio of Ligand to Central Atom

1. Job's method

The method of continuous variations, first proposed by Job in 1928 (40) and reviewed by Vosburgh and Cooper in 1941 (79), is probably the method most used for the determination of the formula of a complex ion in solution. Its application has become so common that it is unnecessary to discuss the method here.

2. Slope ratio method

Recently, a new method was reported by Harvey and

Manning (33). These workers developed the slope ratio method and presented it along with a review of a number of methods that had been proposed before. The derivation of this new method is presented here.

The reaction for the formation of a complex ion may be written as

$$mA + nB = A_mB_n \ .$$

If the concentration of B is constant and in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex ion will be proportional to the analytical concentration of A added in the reaction; so

$$[A_mB_n] = \frac{C_A}{m} \ . \qquad (1)$$

Assuming the unreacted molecules of A and B do not absorb or are compensated for, the Bouguer-Beer relation becomes

$$A_s = a_M b [A_mB_n] \ . \qquad (2)$$

Substituting the value of the complex from (1) into (2) gives

$$A_s = a_M b C_A / m \ . \qquad (3)$$

The absorbancy is plotted against different analytical concentrations of A, keeping the concentration of B constant and in excess. Over the straight line portion of the curve, equation (3) is valid and this straight line will have a slope given by

$$\text{Slope}_1 = a_M b/m \ . \tag{4}$$

Similarly, if A is the component in constant excess and the concentration of B is varied

$$[A_m B_n] = C_B/n \tag{5}$$

and if A_s is plotted against C_B, the slope of the straight line portion of the curve will be

$$\text{Slope}_2 = a_M b/n \ . \tag{6}$$

The ratio of n to m in the complex may be found by taking the ratio of the two slopes

$$\text{Slope}_1 / \text{Slope}_2 = n/m \ . \tag{7}$$

When this method is applied to complex ions in aqueous solution, it is generally possible to assume m to be unity and thus determine n.

C. Determination of Electron Change by Potentiometric Titration

The data obtained in a potentiometric titration can be used to determine the electron change of the material being titrated. The method is based on a simple mathematical treatment of the Nernst equation.

$$\text{oxidized} + n\ e^- = \text{reduced}$$

$$E = E^o + \frac{RT}{nF} \log \frac{(\text{oxid})}{(\text{red})}$$

A straight line should be obtained when the potential E is plotted against log (oxid)/(red). This line will have a slope equal to RT/nF. As a first approximation, the terms (oxid) and (red) can be obtained from the volume of titrant added at any point and the total volume required to reach the stoichiometric end point.

(red) = volume added
(oxid) = equivalence volume - volume added at E

Since the constants R, T and F are known, the value of n can be found from the value of the slope.

V. RESULTS

A. _Vic_-Dioxime Chemistry

The _vic_-dioximes are stable compounds in neutral aqueous solution, but hydrolysis of the oxime groups is to be expected in acid or alkaline solution. Strong oxidizing agents should attack the dioximes bringing about more rapid decomposition. These aspects of _vic_-dioxime chemistry were investigated together with the determination of the acidic ionization constants and are discussed below. Finally, some information concerning the furoxan derivative of 2,3-butanedionedioxime is presented.

1. Stability

The stability of the _vic_-dioximes was investigated only under conditions of interest to this study.

a. _Alkaline solutions_. The decomposition of the _vic_-dioximes in alkaline solution was followed by means of the spectrophotometer. Absorption curves were obtained at intervals of 24-48 hours and representative curves appear in Figure 2. The solutions were scanned in 2.0-cm. cuvettes against a 0.5 M sodium hydroxide solution: curve 1, after five minutes; curve 2, after 142 hours; curve 3, after 435

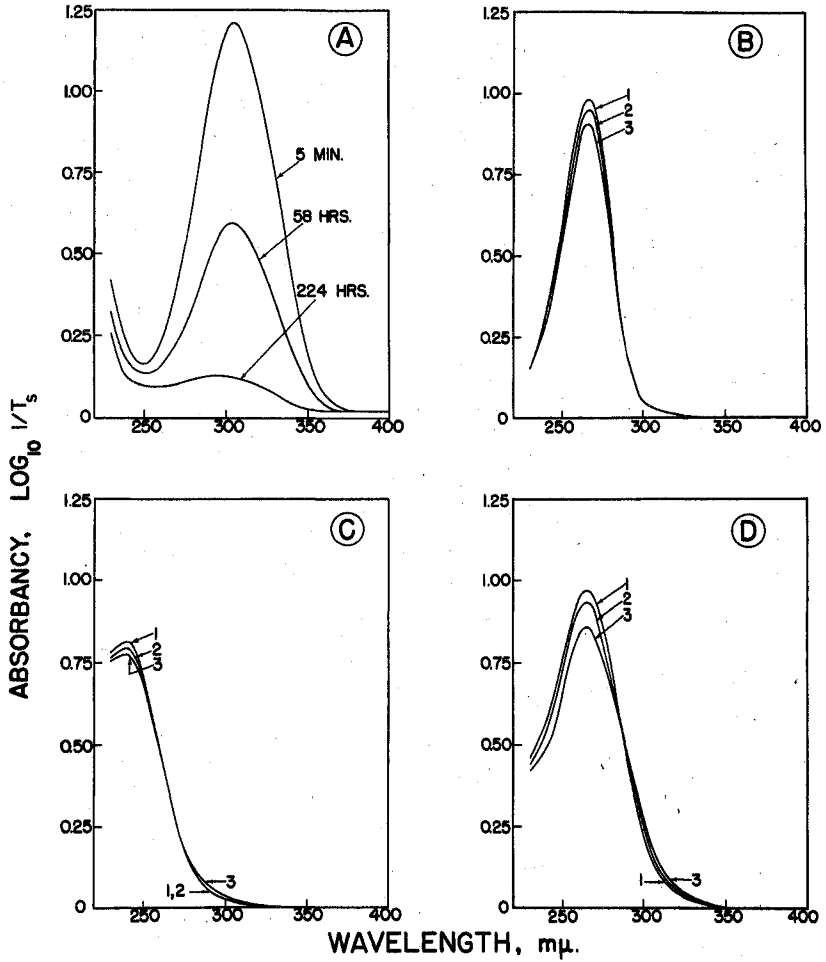


FIG. 2 – DIONE AND DIOXIME STABILITY IN 0.5 M SODIUM HYDROXIDE SOLUTION.

(A) ABOUT 10^{-4} M 1,2- CYCLOHEXANEDIONE
(B) 2.30×10^{-5} M 2,3- BUTANEDIONEDIOXIME
(C) 4.80×10^{-5} M 1,2- CYCLOHEPTANEDIONEDIOXIME
(D) 5.00×10^{-5} M 1,2- CYCLOHEXANEDIONEDIOXIME

hours. The curves indicate that the dione is much less stable than the vic-dioximes tested. Absorption by carbonate ion prevented extending the curves to shorter wavelengths. The absorbancy of the absorption maxima decreased in 435 hours as follows:

1,2-Cyclohexanedionedioxime	13%
2,3-Butanedionedioxime	7%
1,2-Cycloheptanedionedioxime	5%

No attempt was made to identify the decomposition products of the vic-dioximes. The formation of dione is to be expected and the absorption curves show an absorbancy increase in the region of dione absorption. Decomposition of the dione does not appear to lead to appreciable quantities of compounds which absorb light in the region studied.

b. Alkaline solutions containing peroxydisulfate. This study was performed in the same manner as that in the previous section. Representative absorption curves are presented in Figure 3. The solutions were scanned in 2.0-cm. cuvettes against a 0.05 M sodium hydroxide solution: curve 1, after five minutes; curve 2, after 77-1/2 hours; curve 3, after 247 hours. The absorbancy of the absorption maxima decreased in 435 hours as follows:

2,3-Butanedionedioxime	83%
1,2-Cyclohexanedionedioxime	73%

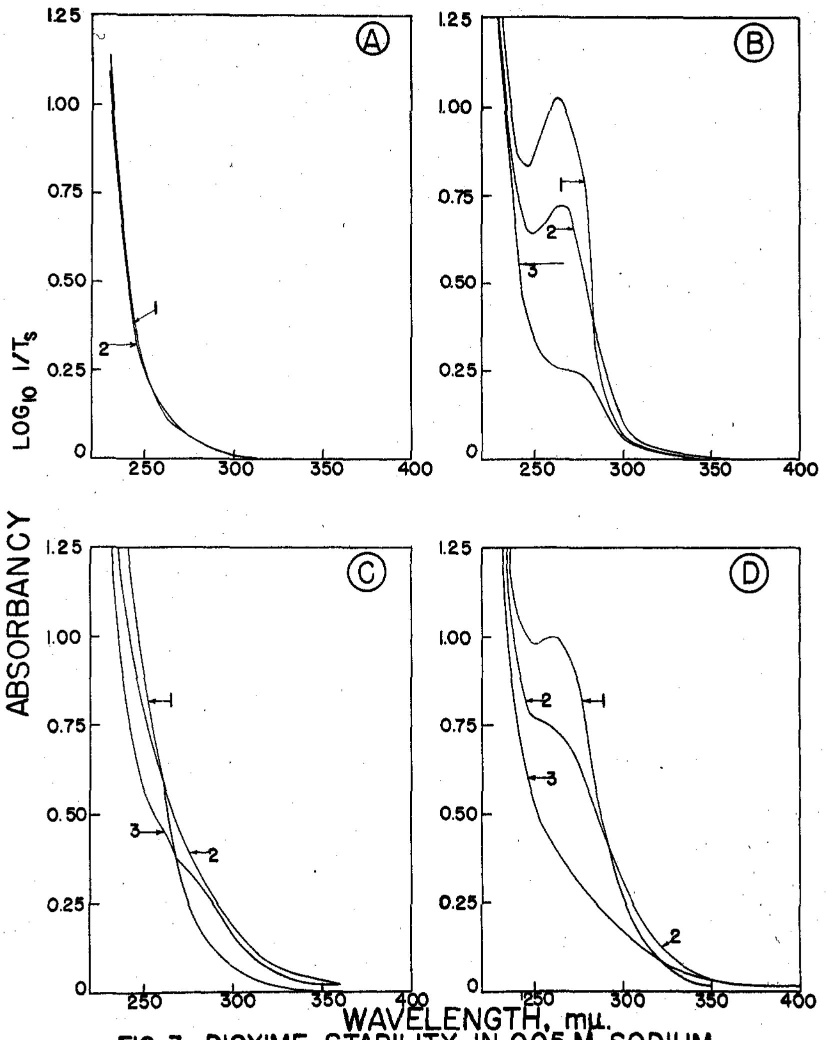


FIG. 3–DIOXIME STABILITY IN 0.05 M SODIUM HYDROXIDE SOLUTION CONTAINING 5×10^{-3} M POTASSIUM PEROXYDISULFATE.

(A) 5×10^{-3} M POTASSIUM PEROXYDISULFATE ALONE
(B) 2.30×10^{-5} M 2,3-BUTANEDIONEDIOXIME
(C) 4.80×10^{-5} M 1,2-CYCLOHEPTANEDIONEDIOXIME
(D) 5.00×10^{-5} M 1,2-CYCLOHEXANEDIONEDIOXIME

1,2-Cycloheptanedionedioxime 57%

No new maxima appear above 250 mμ. The slight increase in absorbancy in the region of 300 mμ. is probably due to dione absorption.

c. Ammoniacal solutions containing bromine. An attempt was made to obtain ultraviolet absorption curves showing the decomposition of vic-dioxime by bromine. However, the absorption curve of the vic-dioxime was completely obscured by absorption due to hypobromite ion. Qualitative tests with nickel(II) ion indicated complete destruction of the vic-dioxime by bromine in a matter of minutes, depending on the ratio of bromine to vic-dioxime. These results partially explain the known instability of the color of Complex A.

2. Determination of the acidic dissociation constants

Most oximes are weak acids and this acidic nature of the vic-dioximes was of particular interest in the study of the complexes with nickel ion. Other workers have reported studies of the acidity of 2,3-butanedionedioxime (7,75,76). Preliminary tests indicated that the ultraviolet absorption maxima of the vic-dioximes under consideration are shifted to longer wavelengths with an increase in pH. Consequently, this physical property was used to determine the ionization constants. It is assumed that this change in absorption spectra represents removal of the protons from the oxime groups.

Solutions of the vic-dioximes for these studies were prepared in the following manner. The pH of each solution was adjusted to an approximate value by the addition of a measured volume of sodium hydroxide solution. Sodium chloride solution was added, when necessary, to maintain constant ionic strength and the mixture diluted to nearly 200 ml. The solutions were then allowed to equilibrate at room temperature ($23 \pm 2^{\circ}$ C.). The vic-dioxime was added just prior (5-10 minutes) to scanning the solution against a blank of similar composition and pH with the Cary spectrophotometer. Some of the absorption curves for solutions listed in the tables were omitted from the figures to avoid confusion.

a. 2,3-Butanedionedioxime. Upon examination of Figure 4, curve 6 was chosen as representing the absorption spectrum of the singly charged anion. Using this curve together with curves 1 and 3, a calculation of pK'_1 was made by the method of Stenström and Goldsmith (see Part IV). The average value obtained for nine wavelengths was 10.61 ± 0.04. The curve for singly charged anion probably lies between curves 5 and 6. The calculated pK'_1 value obtained using curve 5 is about 10.5. The activity coefficient correction for this case is 0.1; therefore, the best value for pK_1 is concluded to be 10.65 ± 0.05.

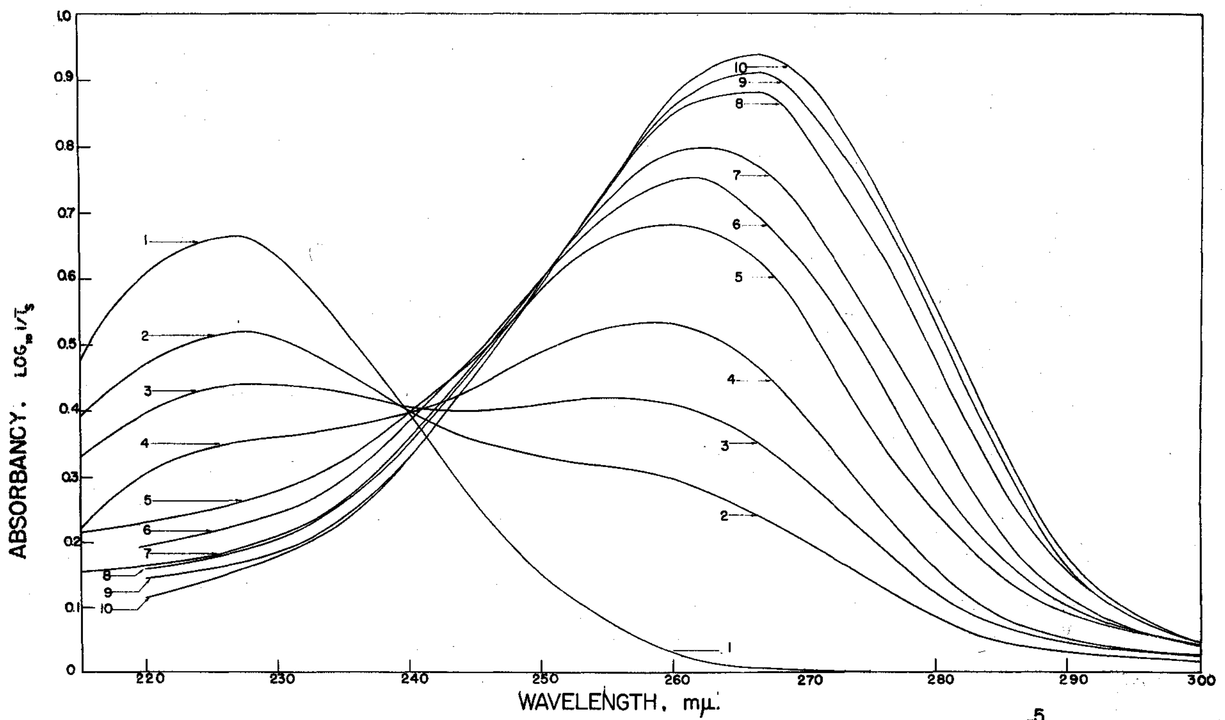


FIG. 4–ABSORPTION CURVES ILLUSTRATING EFFECT OF VARYING pH OF 2.30×10^{-5} M SOLUTIONS OF 2,3-BUTANEDIONEDIOXIME AT IONIC STRENGTH OF 0.1.

NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLE I. SCANNED IN 2.0-cm. CUVETTES vs. APPROPRIATE BLANKS.

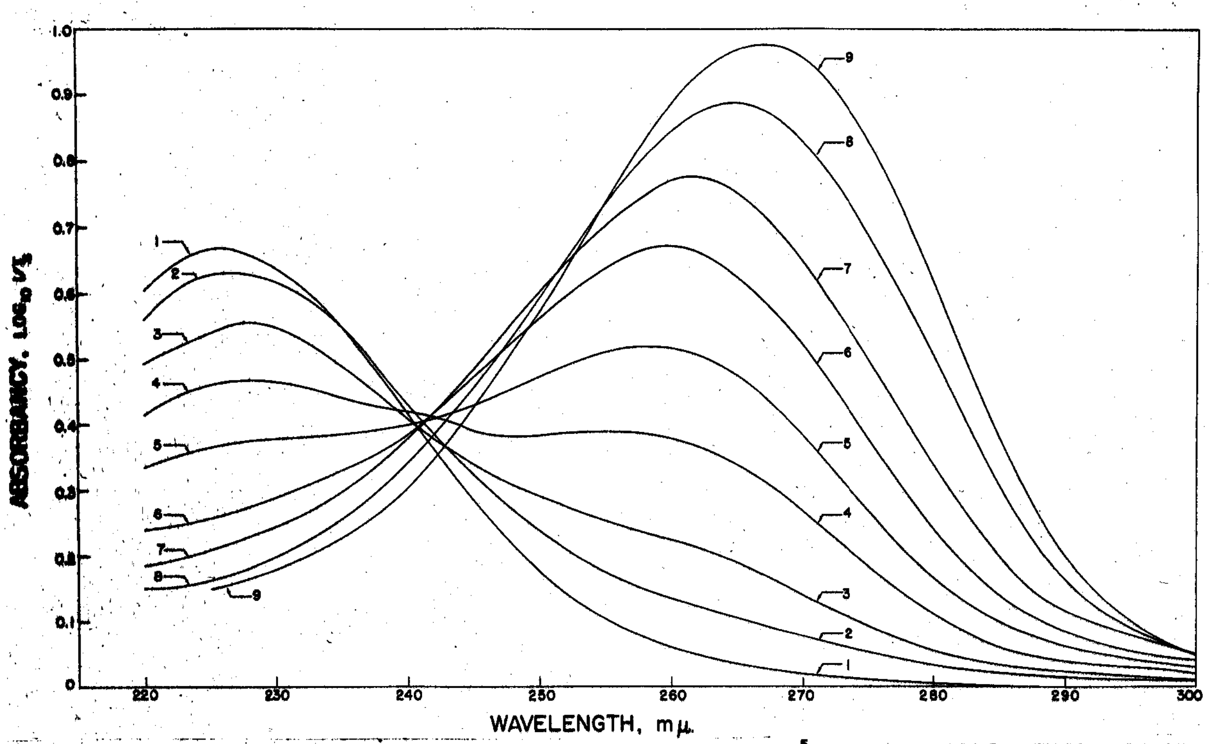


FIG. 5- ABSORPTION CURVES ILLUSTRATING EFFECT OF VARYING pH OF 2.30x10^{-5}M SOLUTIONS OF 2,3-BUTANEDIONEDIOXIME AT IONIC STRENGTH OF 0.5.
NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLE II.
SCANNED IN 2.0-cm. CUVETTES vs. APPROPRIATE BLANKS.

Using curves 1, 4 and 6 from Figure 5, pK_1' was calculated to be 10.30 ± 0.02. If curve 7 is substituted for curve 6, pK_1' is found to be about 10.4. The activity coefficient correction for this case is 0.2 and the best value for pK_1 becomes 10.55 ± 0.05.

Examination of Figures 4 and 5 indicates a new species of absorbing ion is being formed at high pH. There is a further shift in the absorption maximum as well as a departure from the isosbestic point. It is assumed that these changes occur due to formation of the doubly charged anion by removal of the second oxime hydrogen.

The data in Table I are presented in Figure 6. For an ideal case, the midpoint of the break in the curve would correspond to the point at which the pH became identical with the pK.

$$pK = pH - \log (A^-)/(HA)$$

At this point the solution would contain an equal amount of unionized and ionized molecules.

The lines fitting the data plotted in Figure 6 were drawn in a somewhat arbitrary fashion. In order to obtain a graphical pK_1' value corresponding to the calculated value, it is necessary to assume there is a break in the vertical portion of the curves. The midpoints of the breaks yield the following pK' values:

TABLE I

Solutions used for the Determination of the Ionization Constants of 2,3-Butanedionedioxime with $\mu = 0.1$

Solution No.	pH	A_s^{227}	A_s^{260}
1	5.95	0.665	0.025
1a	9.33	0.645	0.110
2	10.31	0.520	0.295
3	10.60	0.440	0.415
4	11.00	0.345	0.530
5	11.43	0.260	0.595
6	11.76	0.215	0.750
7	12.07	0.180	0.795
8	12.49	0.175	0.855
9	12.77	0.160	0.870
10	13.04	0.155	0.885

TABLE II

Solutions used for the Determination of the Ionization Constant of 2,3-Butanedionedioxime with $\mu = 0.5$

Solution No.	pH
1	6.51
1a	7.49
1b	8.98
2	9.31
3	9.96
4	10.32
5	10.70
6	11.20
7	11.61
7a	12.01
8	12.10
8a	13.18
9	13.48

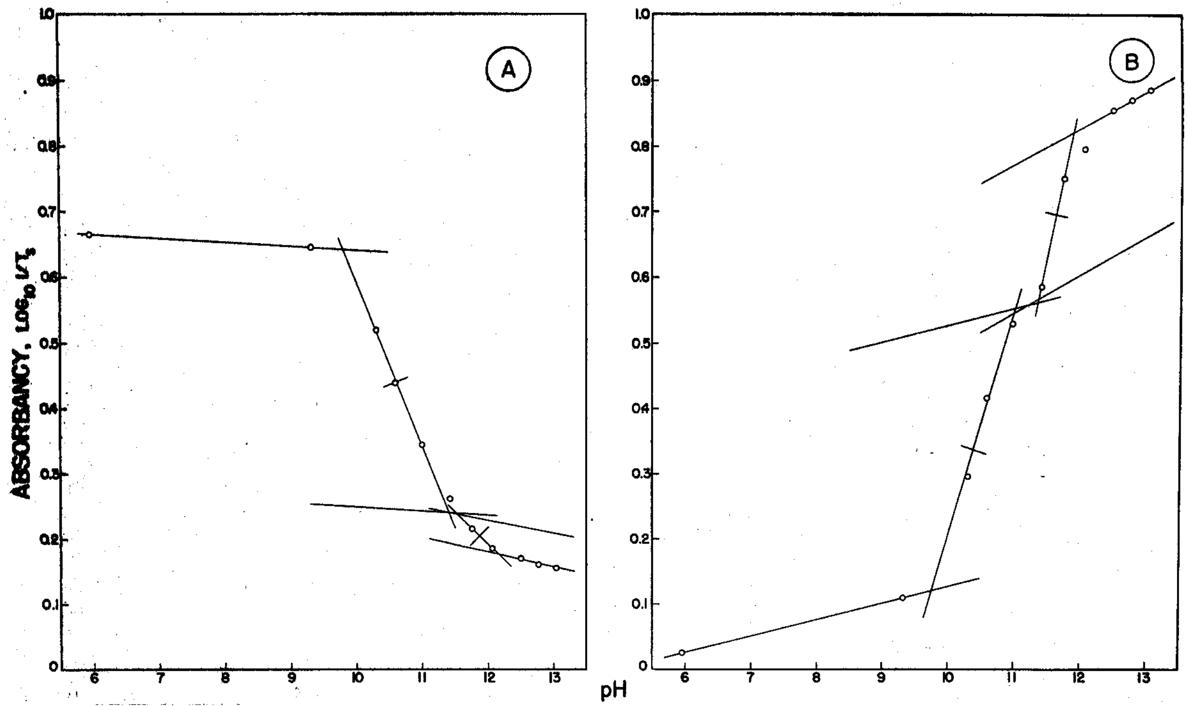


FIG. 6- GRAPHICAL DETERMINATION OF IONIZATION CONSTANTS OF 2,3- BUTANEDIONEDIOXIME FROM DATA IN TABLE I.
(A) 227 mμ.
(B) 260 mμ.

	227 mμ	260 mμ
pK'_1	10.61	10.40
pK'_2	11.87	11.64

If pK'_1 is taken to be 10.50, the pK'_2 values become 11.73 and 11.77 respectively, when calculated by direct proportion. The pK_2 value becomes 11.85

An absorbancy vs. pH plot for the data obtained at an ionic strength of 0.5 was used to obtain further pK'_2 values. At 226 mμ. pK'_2 was found to be 12.2, while at 260 mμ. the value obtained was 11.7.

A consideration of the data above leads to the following values for these constants:

pK_1	10.6 ± 0.1
pK_2	11.9 ± 0.3

The paper by Babko and Mikhelson (7) was not available, but the abstract listed a pK'_1 value of 11.1. The fact that this value lies between the pK_1 and pK_2 values listed above indicates these workers failed to isolate their pK'_1 data from the effects of removal of the second proton.

b. 1,2-Cyclohexanedionedioxime. This vic-dioxime was treated experimentally as in Part a above. The data for the solutions used are presented in Table III and representative absorption curves are reproduced in Figure 7.

TABLE III

Solutions used for the Determination of the Ionization Constants of 1,2-Cyclohexanedionedioxime with $\mu = 0.5$

Solution No.	pH	$A_s^{232.5}$	A_s^{265}
1	6.53	0.665	0.220
1a	8.70	0.660	0.250
2	9.78	0.615	0.335
3	10.43	0.530	0.515
4	10.82	0.475	0.630
5	11.28	0.430	0.755
6	11.60	0.435	0.825
7	12.85	0.510	1.060
8	13.58	0.525	1.095

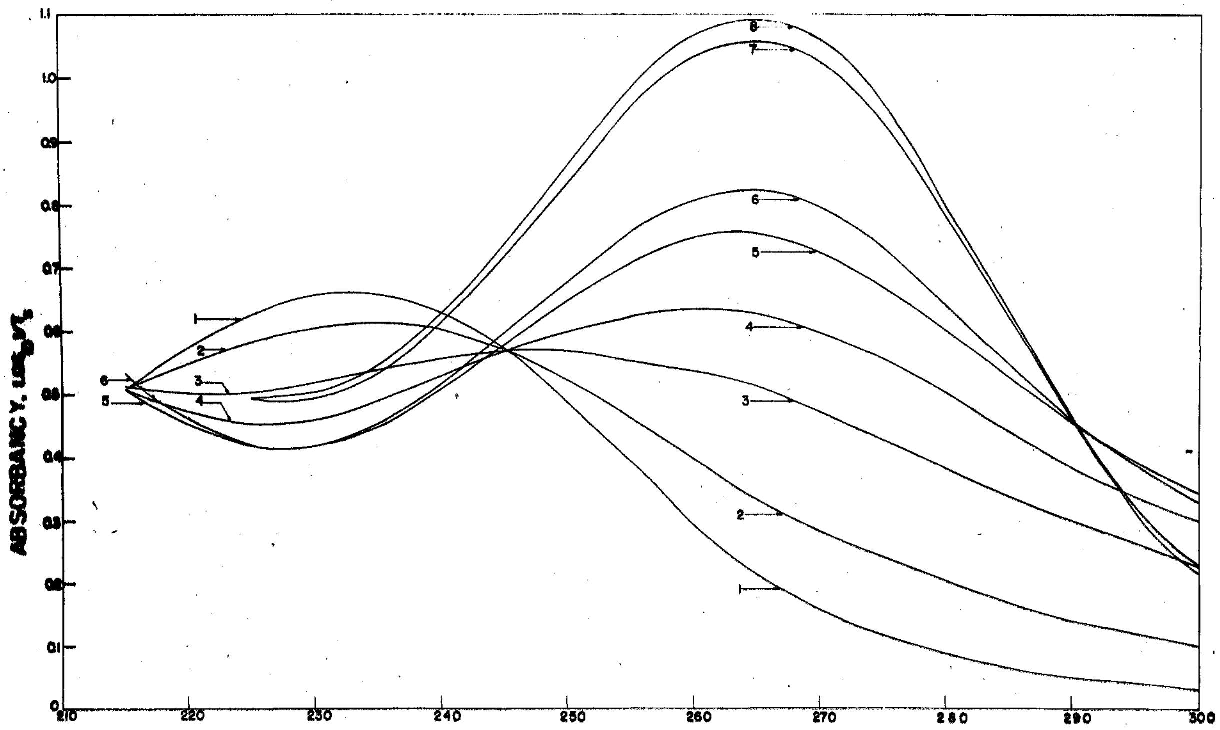


FIG. 7-ABSORPTION CURVES ILLUSTRATING EFFECT OF VARYING pH OF 5.00 x 10^{-5} M SOLUTIONS OF 1,2-CYCLOHEXANEDIONEDIOXIME AT IONIC STRENGTH OF 0.5.

NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLE III.
SCANNED IN 2.0-cm. CUVETTES vs. APPROPRIATE BLANKS.

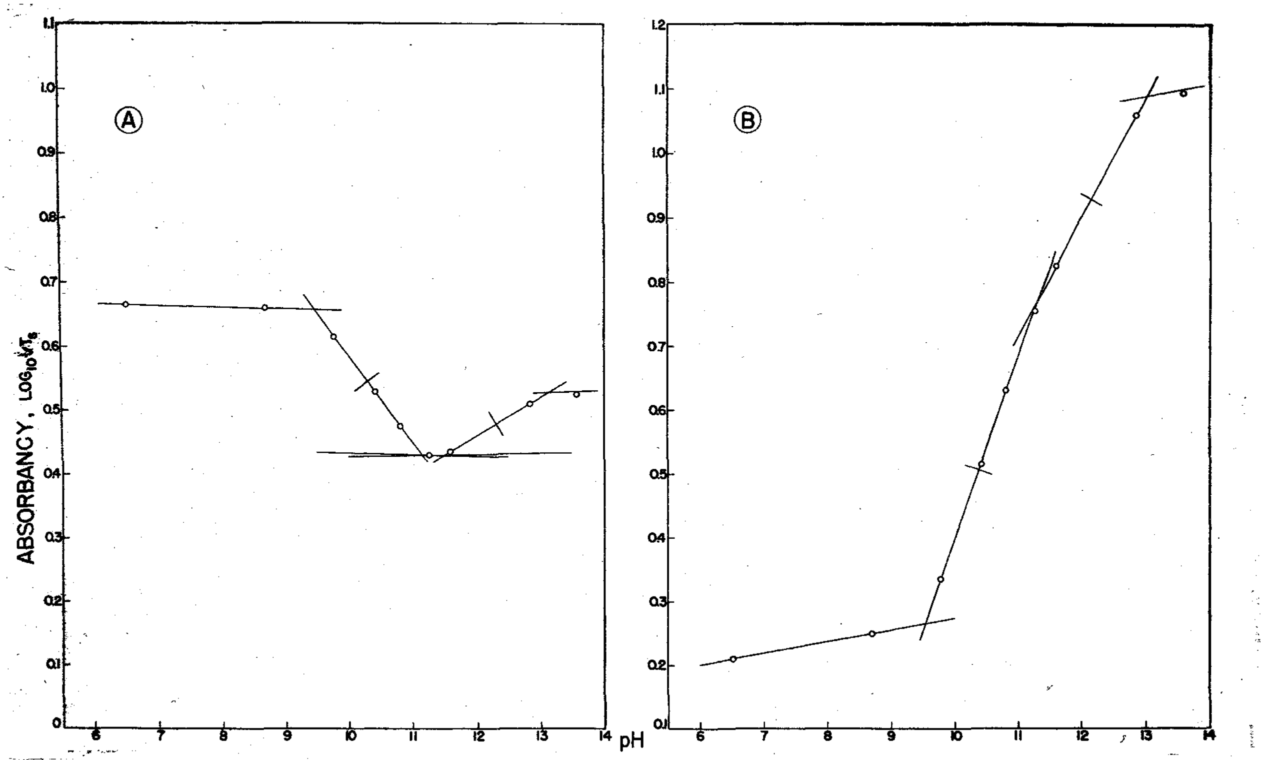


FIG. 8 – GRAPHICAL DETERMINATION OF IONIZATION CONSTANTS OF 1,2-CYCLOHEXANEDIONEDIOXIME FROM DATA IN TABLE III.
(A) 232.5 mμ.
(B) 265 mμ.

Solutions numbered 1, 3 and 5 were used to calculate pK_1'. The average value obtained for nine wavelengths was 10.33 ± 0.04. The pK' values were estimated from Figure 8. The points of inflection were found by inspection and the midpoints indicate the following values for the constants:

	232.5 mμ.	265 mμ.
pK_1'	10.31	10.39
pK_2'	12.33	12.16

The activity coefficient correction for this case is 0.2. Consideration of the above data leads to the following best values for these dissociation constants:

pK_1	$10.5_5 \pm 0.1$
pK_2	12.4 ± 0.5

c. <u>1,2-Cycloheptanedionedioxime</u>. The experimental procedure used with this <u>vic</u>-dioxime was the same as that described above. Table IV contains the data for the solutions employed and representative curves are presented in Figure 9. Unfortunately the absorption maxima related to this <u>vic</u>-dioxime occur at such short wavelengths that carbonate ion absorption obscures critical portions of the curves for solutions at high pH. The region of 290 mμ. might be of value provided higher <u>vic</u>-dioxime concentrations were used. Since very little work with this <u>vic</u>-dioxime was planned, this alternative was not pursued.

TABLE IV

Solutions used for the Determination of the Ionization Constants of 1,2-Cycloheptanedionedioxime with $\mu = 0.5$

Solution No.	pH	A_s^{240}	A_s^{290}
1	6.53	0.235	0.000
1a	6.86	0.230	0.005
1b	8.98	0.255	0.020
1c	9.97	0.320	0.030
2	10.28	0.365	0.045
3	10.61	0.445	0.080
4	11.10	0.545	0.105
4a	11.51	0.605	0.110
5	11.76	0.655	0.095
5a	12.12	0.700	0.100
5b	12.43	0.740	0.080
6	12.50	0.735	0.050
6a	12.92	0.800	0.065
6b	13.14	0.805	0.055
6c	13.33	0.805	0.055
7	13.44	0.805	0.050

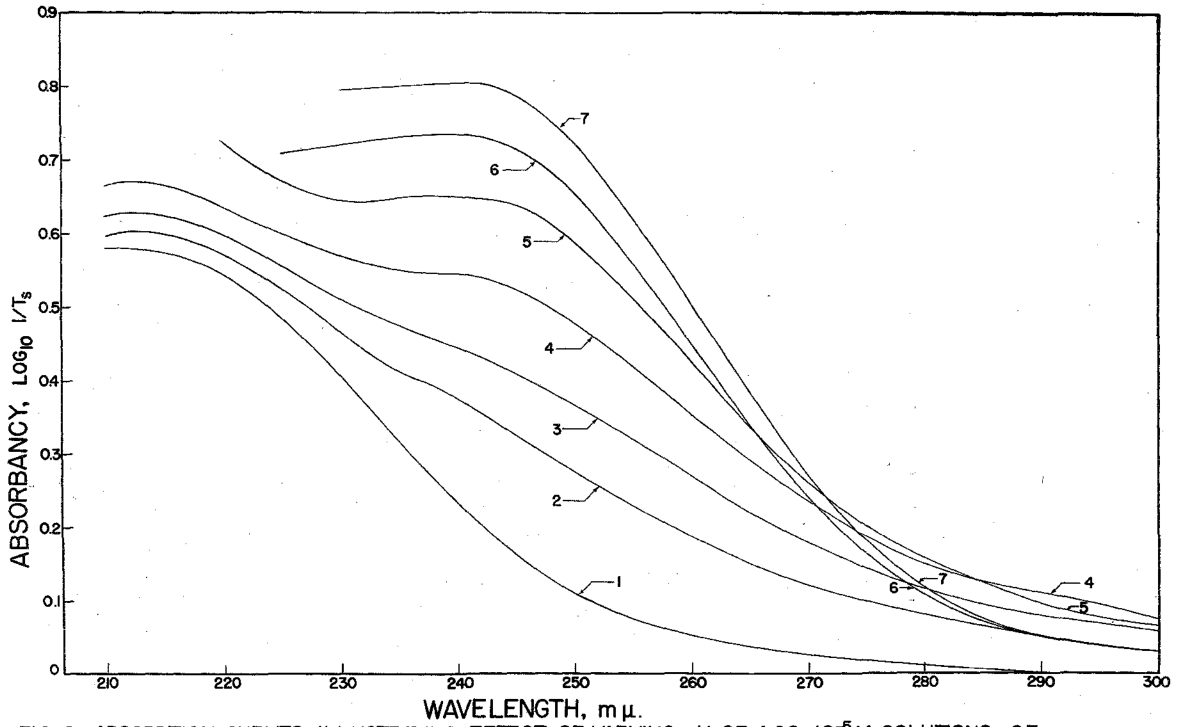


FIG. 9—ABSORPTION CURVES ILLUSTRATING EFFECT OF VARYING pH OF 4.80x10^{-5}M SOLUTIONS OF 1, 2-CYCLOHEPTANEDIONEDIOXIME.

NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLE IV.
SCANNED IN 2.0-cm. CUVETTES vs. APPROPRIATE BLANKS.

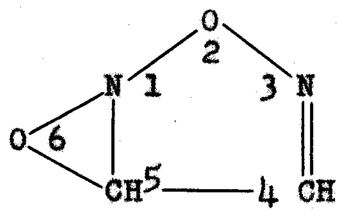
Figure 10 permits an estimation of the pK' values. The curve at 290 mμ. indicates a pK_1' value of 10.49. When this value is used to determine the point of inflection in the curve at 240 mμ., pK_2' is found to be 12.08. Here again the activity coefficient correction is 0.2. A consideration of these results, together with the assumption that this vic-dioxime should behave similarly to those above, leads to the following estimates for the constants:

pK_1	10.7 ± 0.2
pK_2	12.3 ± 0.5

3. Furoxan derivative of 2,3-butanedionedioxime

This derivative was prepared by the method of Scholl (72). The procedure was followed as described except commercial, tank dinitrogen tetroxide was employed. A 50 per cent yield was obtained. The compound is a yellow oil, which distills under 14 mm. of mercury at about 108° C.

The Ring Index (64, p. 84) describes the furoxan ring as 2,6-dioxa-1,3-diazabicyclo[3.1.0]-hexane.



K. v. Auwers (4,5) proposed the following equilibria based

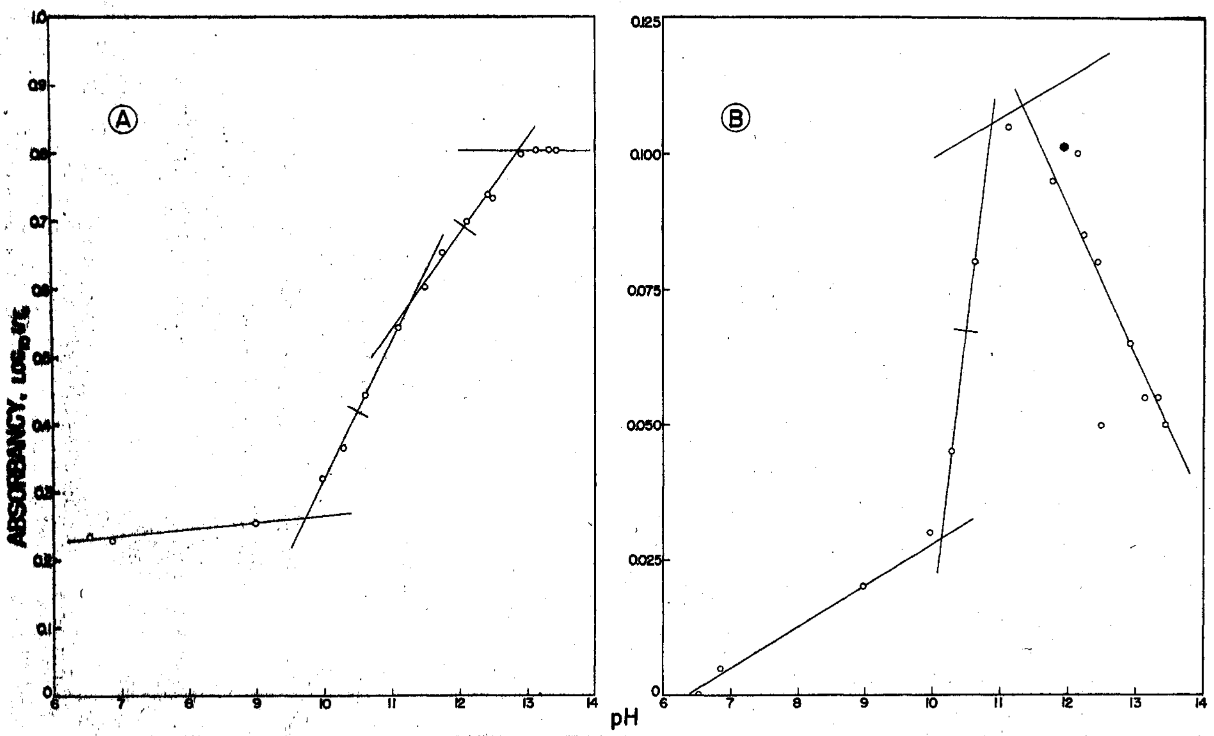
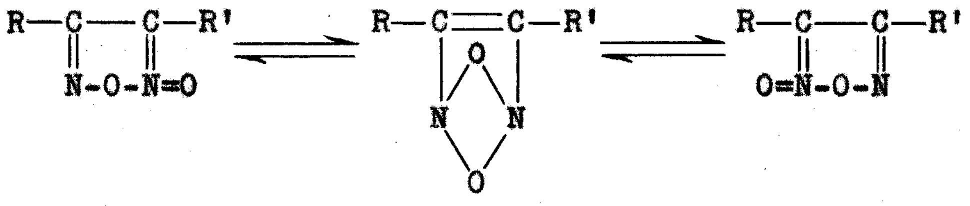


FIG. 10–GRAPHICAL DETERMINATION OF IONIZATION CONSTANTS OF 1,2-CYCLOHEPTANEDIONEDIOXIME FROM DATA IN TABLE IV.

(A) 240 mμ.
(B) 290 mμ.

on valency and refraction experiments.



(1) (2) (3)

Kinney and Harwood (46) used ozonolysis reactions to confirm the presence of structure 2. The isolation of isomers of structures 1 and 3 has not been reported. Further information concerning the furoxans and related compounds can be found in the extensive dioxime work of Ponzio and coworkers (57,65).

Spectrophotometric curves of the furoxan are reproduced in Figure 11. Decomposition of the furoxan in hot alkaline solution is apparent. After this curve was obtained, nickel(II) ion was added to the solution: no color developed on standing up to 24 hours. This would indicate that very little vic-dioxime had formed from the furoxan.

A few of the qualitative experiments reported by Okáč and Polster (62) were repeated. It immediately became apparent that these workers were dealing with a compound whose structure was unrelated to that of Complex B. Experiments reported below (Part B) indicate Complex B does not form with 2,3-butanedionedioxime at the high sodium hydroxide concentrations used by these workers. The results of their

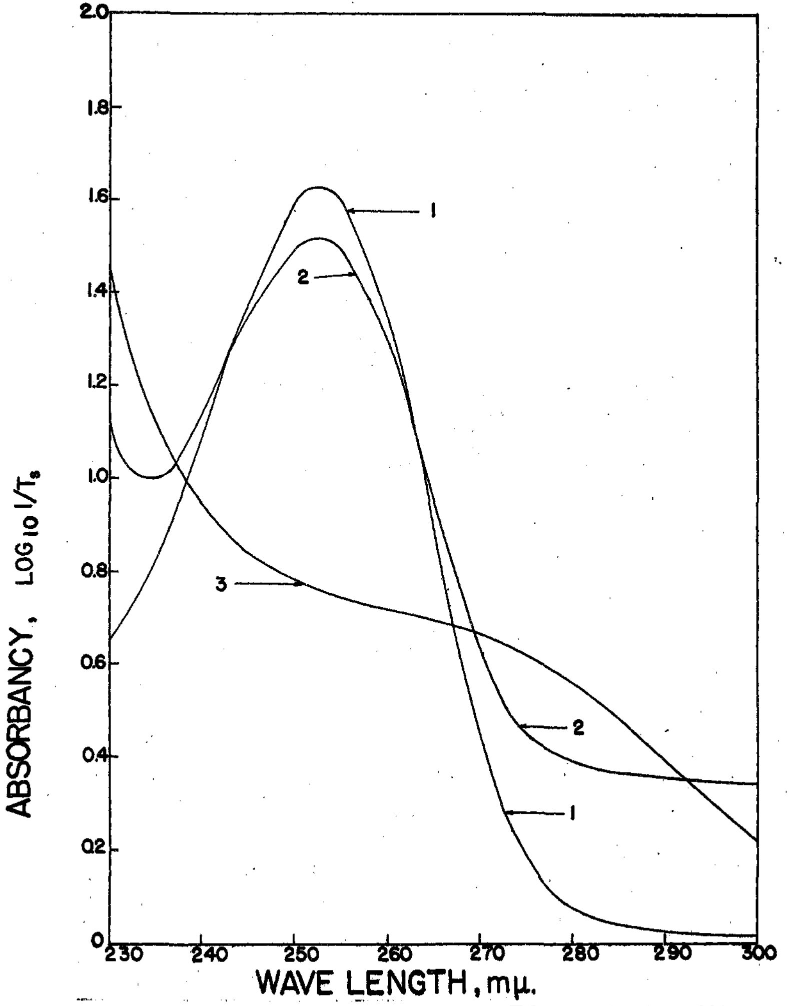


FIG. 11-ABSORPTION CURVES OF FUROXAN DERIVATIVE OF 2,3-BUTANEDIONEDIOXIME.
SCANNED IN 5.0-cm. CUVETTES vs. DISTILLED WATER.
CURVE 1: NEUTRAL
CURVE 2: 0.5 M SODIUM HYDROXIDE
CURVE 3: 0.5 M SODIUM HYDROXIDE
SCANNED AFTER HEATING 1½ HOURS.

work, while of general interest, probably have very little bearing on the structures of Complex A and Complex B.

B. Stable Complex (Complex B)

1. Effect of pH and time

The visible color of Complex B is characterized by a broad absorption maximum in the region of 460 mμ. and a minimum near 410 mμ. The actual values of these points is dependent upon the *vic*-dioxime used. Absorption curves of Complex B, Complex A and the stabilized nickel(II) compound[1] are presented in Figure 12 for comparison. The spectrum of Complex A lies intermediate between that for Complex B and that for the nickel(II) compound. This figure will be referred to again in a later section.

a. *Visible spectrum.* The effect of both time and pH were investigated in the region of 350-600 mμ. Absorption curves were obtained at intervals of about 72 hours. The data obtained at the large absorption maxima are plotted in Figure 13. The absorbancy measurements are less accurate than might be expected due to the presence in the solutions of suspended sodium carbonate.

Only part of the time curve for 0.05 M sodium hydroxide

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[1] Taken from the original data of Ferguson and Banks (21).

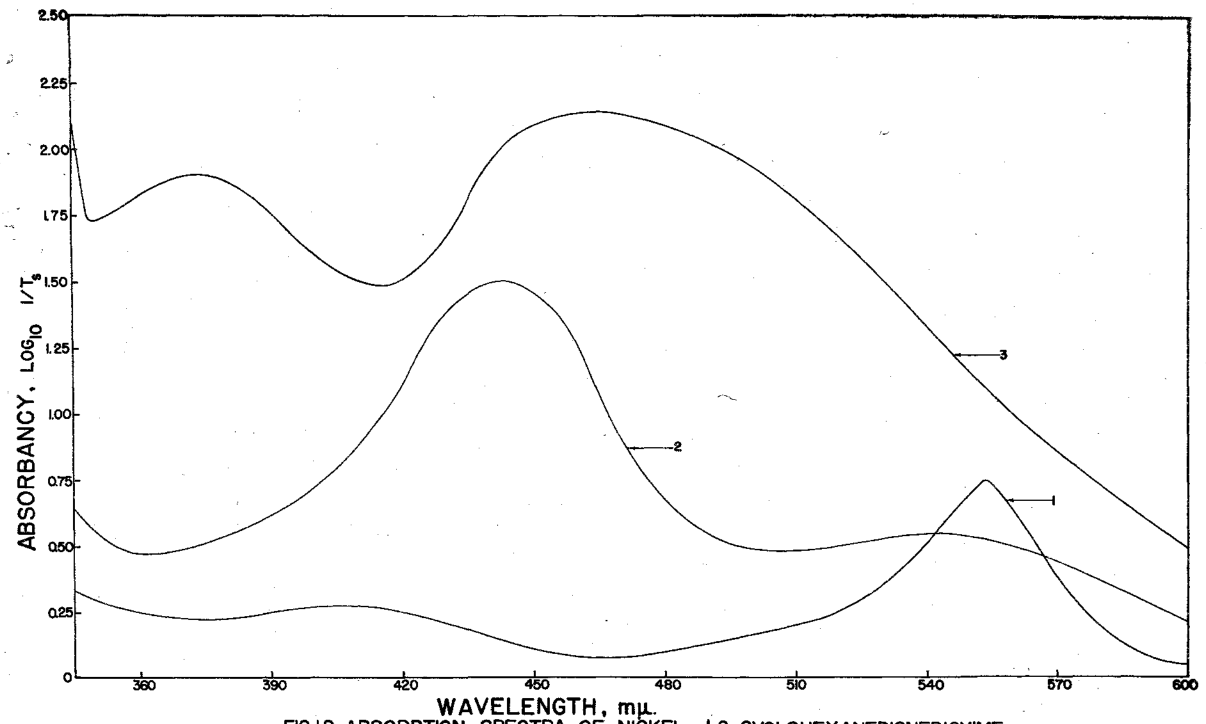

FIG.12-ABSORPTION SPECTRA OF NICKEL- 1,2-CYCLOHEXANEDIONEDIOXIME SOLUTIONS.

CURVE 1: NICKELOUS COMPOUND STABILIZED WITH GUM ARABIC
CURVE 2: COMPLEX A
CURVE 3: COMPLEX B

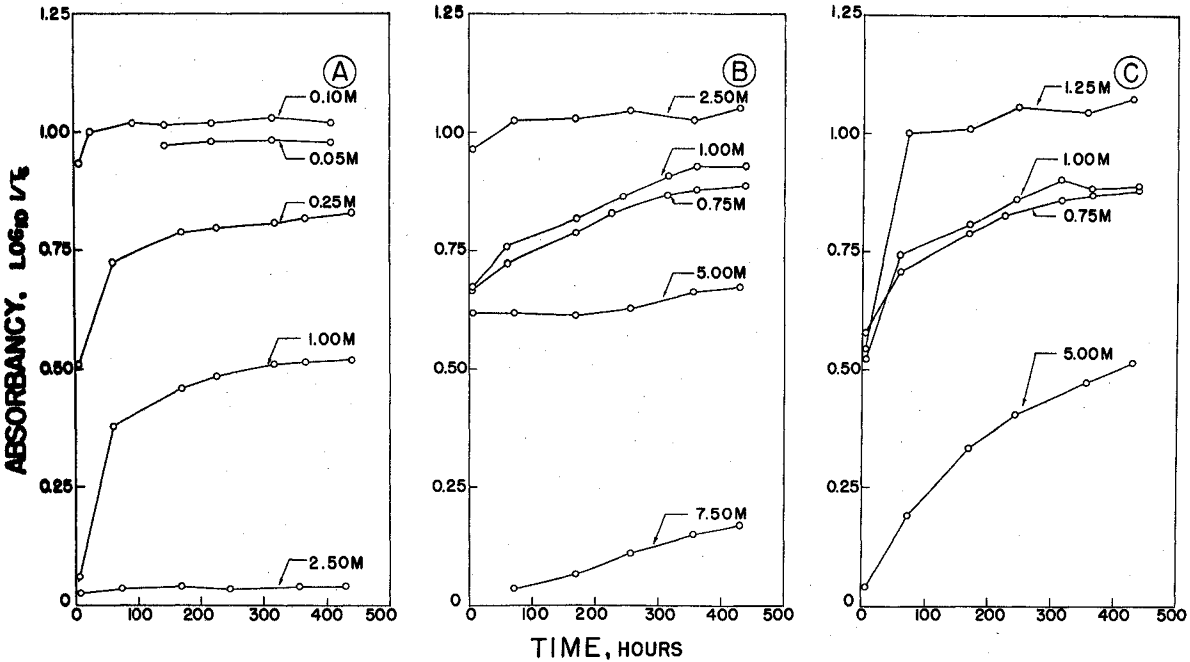

FIG. 13- EFFECT OF TIME AND pH ON THE STABILITY OF COMPLEX B.
NUMBERS REPRESENT CONCENTRATION OF SODIUM HYDROXIDE.
ALL SOLUTIONS WERE 1.50×10^{-5}M NICKEL AND 4.60×10^{-4} M DIOXIME.
(A) 2,3-BUTANEDIONEDIOXIME
(B) 1, 2-CYCLOHEXANEDIONEDIOXIME
(C) 1, 2-CYCLOHEPTANEDIONEDIOXIME

solution is shown in part A of Figure 13 because the solution originally contained the insoluble nickel(II) compound. Table V presents the significant results of this study.

The results presented in Figure 13 and Table V illustrate the striking differences in the reactivities of these three vic-dioximes. These differences are also apparent in the insoluble vic-dioxime-nickel(II) compounds: the 1,2-cyclohexanedionedioxime derivative appears to be much more insoluble than the other two; the 1,2-cycloheptanedionedioxime derivative is yellow while the other two are red; and the lower pH limit for complete precipitation varies between all three. Reasons for this somewhat anomalous behavior cannot be given at present.

b. Ultraviolet spectrum. A few studies were made to investigate the ultraviolet absorption spectrum of Complex B. This region is not readily accessible due to the strong absorption by the vic-dioxime. Representative data are presented in Figure 14.

Part A of Figure 14 shows a strong increase in absorption at the vic-dioxime maximum immediately after adding nickel(II) ion. As the visible color reached its maximum, the 270 mμ. absorption peak shifted to longer wavelengths accompanied by a decrease in absorption. The solution was yellow for the first few hours. This may be due to the presence of appreciable quantities of lower complexes, since the metal ion was in excess over the vic-dioxime.

TABLE V

Résumé of Study of Effect of Time and pH on Stability of Complex B

1.50×10^{-5} M Nickel ion

4.60×10^{-4} M *Vic*-dioxime

Vic-dioxime	Optimum concentration of sodium hydroxide	Concentration of sodium hydroxide where precipitation occurred
2,3-Butanedionedioxime	0.01 M	0.05 M
1,2-Cyclohexanedionedioxime	2.50	0.10
1,2-Cycloheptanedionedioxime	1.25	0.25

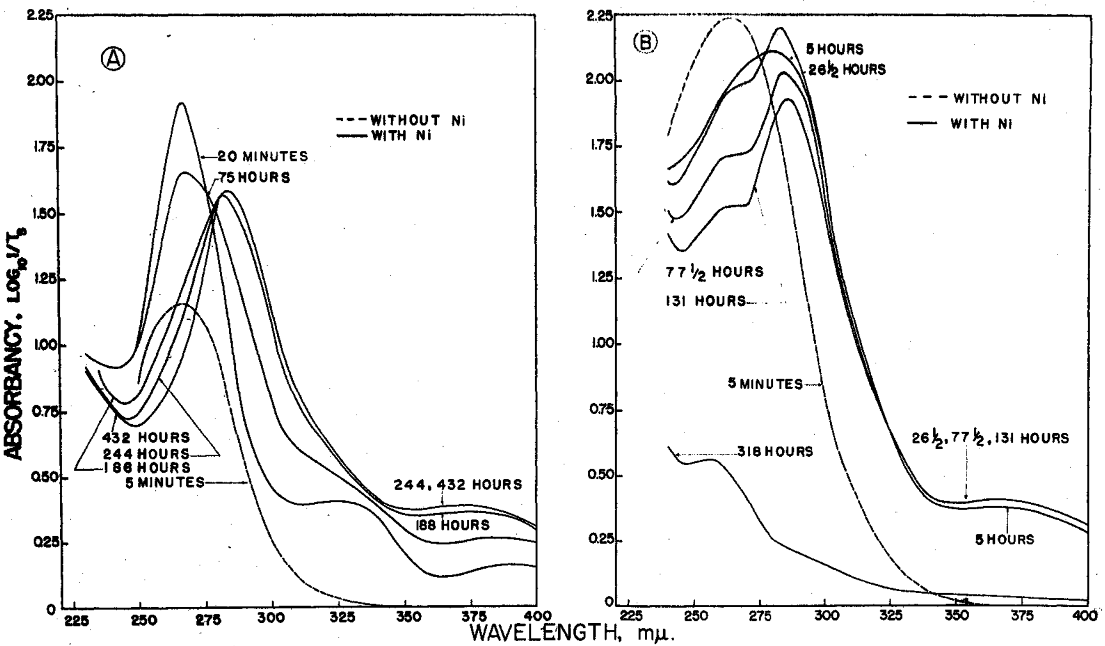

FIG. 14–ULTRAVIOLET ABSORPTION SPECTRA OF COMPLEX B PREPARED WITH 1,2-CYCLOHEXANEDIONEDIOXIME.
SCANNED vs. SODIUM HYDROXIDE BLANKS.
(A) 0.5M SODIUM HYDROXIDE, 2.50×10^{-5} M DIOXIME AND 3.00×10^{-5} M NICKEL; 5.0-cm. CUVETTES.
(B) 0.05M SODIUM HYDROXIDE, 2.5×10^{-5} M POTASSIUM PEROXYDISULFATE, 1.50×10^{-4} M DIOXIME AND 1.50×10^{-5} M NICKEL; 2.0-cm. CUVETTES.

Part B of Figure 14 illustrates that peroxydisulfate ion only causes Complex B to form more rapidly. Since there was an excess of vic-dioxime over nickel(II) ion, lower complexes probably were not present to any extent. No increase in absorption was observed at the vic-dioxime maximum.

Lifschitz, et al. (52) pointed out that most diamagnetic nickel(II) complexes are bright red through red-brown to yellow in color. The work of Mellor and coworkers (55,56) indicates that the ultraviolet spectrum of a nickel(II) complex forms a more reliable basis for prediction of magnetic type. These workers present the following conclusions. In paramagnetic complexes of nickel(II), there is very little difference between the absorption spectrum of the metal complex and that of the chelate molecule from which it is derived. However, the diamagnetic complexes of nickel(II) usually show a broad band between 385 and 415 mμ. and a bathochromic shift in the bands of the chelating group.

The evidence presented thus far would lead to the prediction that Complex B is a diamagnetic nickel complex. Experimental evidence concerning this prediction is presented below.

2. Oxidizing agents

As mentioned previously, many oxidizing agents have been used to form these "oxidized" complexes. All of those reported, except peroxydisulfate ion, first form Complex A. It has been found that, when Complex A is formed with 1,2-cyclohexanedionedioxime in the usual manner, the spectrum of Complex B does not appear.

When the color of Complex B has been used as the basis of an analytical method for nickel ion, the recommended oxidant has been peroxydisulfate ion. Using a standardized procedure, this oxidant will yield satisfactory results (24). Since this study was directed toward an understanding of the complexes, peroxydisulfate ion was only used in a few experiments.

A simple test proved that formation of Complex B was brought about by air oxidation. Oxygen-free nitrogen was bubbled through an alkaline solution of 1,2-cyclohexanedione dioxime. After 0.5 hour, a small quantity of a nickel perchlorate solution was added. The nickel(II) compound precipitated leaving a colorless solution.

An attempt was made to increase the rate of color development by bubbling oxygen into solutions of Complex B. Absorbancy measurements failed to indicate a more rapid formation of the complex. This would indicate that, under normal conditions, the concentration of dissolved oxygen remains sufficiently high to prevent the oxygen from being rate determining.

3. Ratio of ligand to central atom

The formula of Complex B was determined by Job's method (40). The results obtained using 1,2-cyclohexanedionedioxime are presented in the form of absorption curves in Figure 15. The solutions are described in Table VI.

Inspection of Figure 15 indicates that the ratio of vic-dioxime to nickel ion is 3:1 at all wavelengths between 350-600 mμ. This ratio was confirmed by plotting the data as recommended by Vosburgh and Cooper (79). Such a plot at one wavelength is presented in Figure 17.

The ratio of 3:1 did not appear to change when the solutions were allowed to stand (see Figure 15). The positions of the maxima and minimum depend upon the ratio of vic-dioxime to nickel ion. This may be interpreted as being due to the formation of other complexes. However, if this is true, their molar absorbancy indexes must be considerably less than that for the 3:1 complex. The problem is complicated because it is necessary to obtain the data under non-equilibrium conditions.

The data obtained for Complex B prepared with the other vic-dioximes appear in Figure 16. The solutions are described in Tables VII and VIII. All of these solutions were

TABLE VI

Solutions used for the Determination of the Ratio of Nickel to 1,2-Cyclohexanedionedioxime as Complex B by Job's Method

All solutions contained 0.5 M sodium hydroxide with a final volume of 200 ml.

Solution No.	ml. of 3.00×10^{-3} M solution Nickel	 *Vic*-dioxime
1	10.0	0.0
2	8.0	2.0
3	6.0	4.0
4	5.0	5.0
5	4.5	5.5
6	4.0	6.0
7	3.5	6.5
8	3.0	7.0
9	2.5	7.5
10	2.0	8.0
11	1.5	8.5
12	1.0	9.0
13	0.0	10.0

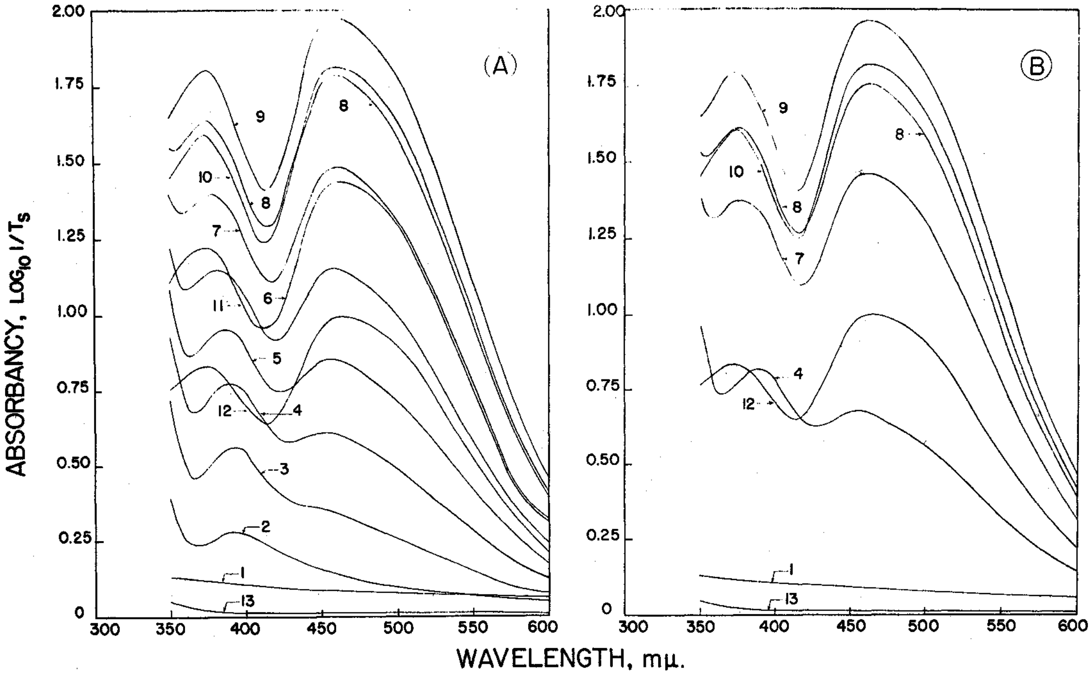

FIG. 15–ABSORPTION CURVES OF JOB'S SOLUTIONS OF COMPLEX B WITH 1,2-CYCLOHEXANEDIONEDIOXIME.
NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLE VI.
SCANNED IN 5.0-cm. CUVETTES vs. DISTILLED WATER.
(A) 14 HOURS AFTER PREPARATION
(B) 24 HOURS AFTER PREPARATION

TABLE VII

Solutions used for the Determination of the Ratio of Nickel to 1,2-Cycloheptanedionedioxime as Complex B by Job's Method.

All solutions contained 1.25 M sodium hydroxide with a final volume of 200 ml.

Solution No.	ml. of 3.00×10^{-3} M solution Nickel	 *Vic*-dioxime
1	8.0	2.0
2	6.0	4.0
3	5.0	5.0
4	4.0	6.0
5	3.0	7.0
6	2.5	7.5
7	2.0	8.0
8	1.0	9.0

TABLE VIII

Solutions used for the Determination of the Ratio of Nickel to 2,3-Butanedionedioxime as Complex B by Job's Method.

All solutions contained 0.25 M sodium hydroxide with a final volume of 200 ml.

Solution No.	ml. of 3.00×10^{-3} M solution Nickel	Vic-dioxime
1	8.0	2.0
2	6.0	4.0
3	5.0	5.0
4	4.0	6.0
5	3.0	7.0
6	2.5	7.5
7	2.0	8.0
8	1.0	9.0

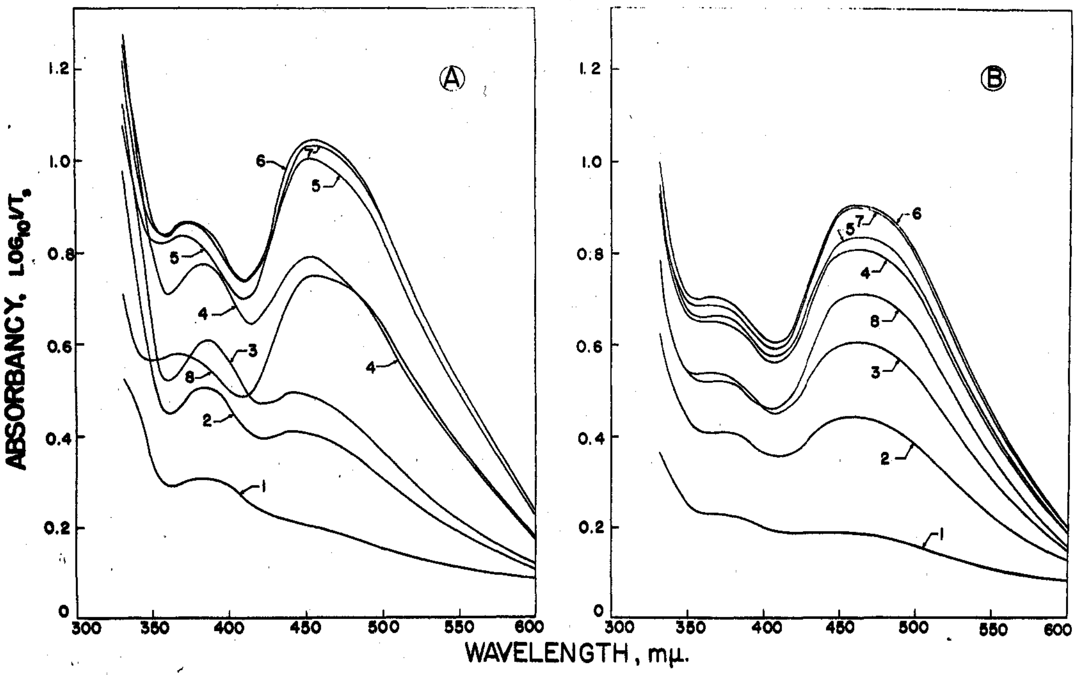

FIG. 16- ABSORPTION CURVES OF JOB'S SOLUTIONS OF COMPLEX B.
NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLES VII AND VIII.
SCANNED IN 5.0-cm. CUVETTES vs. DISTILLED WATER 100 HOURS AFTER PREPARATION.
(A) 1,2-CYCLOHEPTANEDIONEDIOXIME
(B) 2,3-BUTANEDIONEDIOXIME

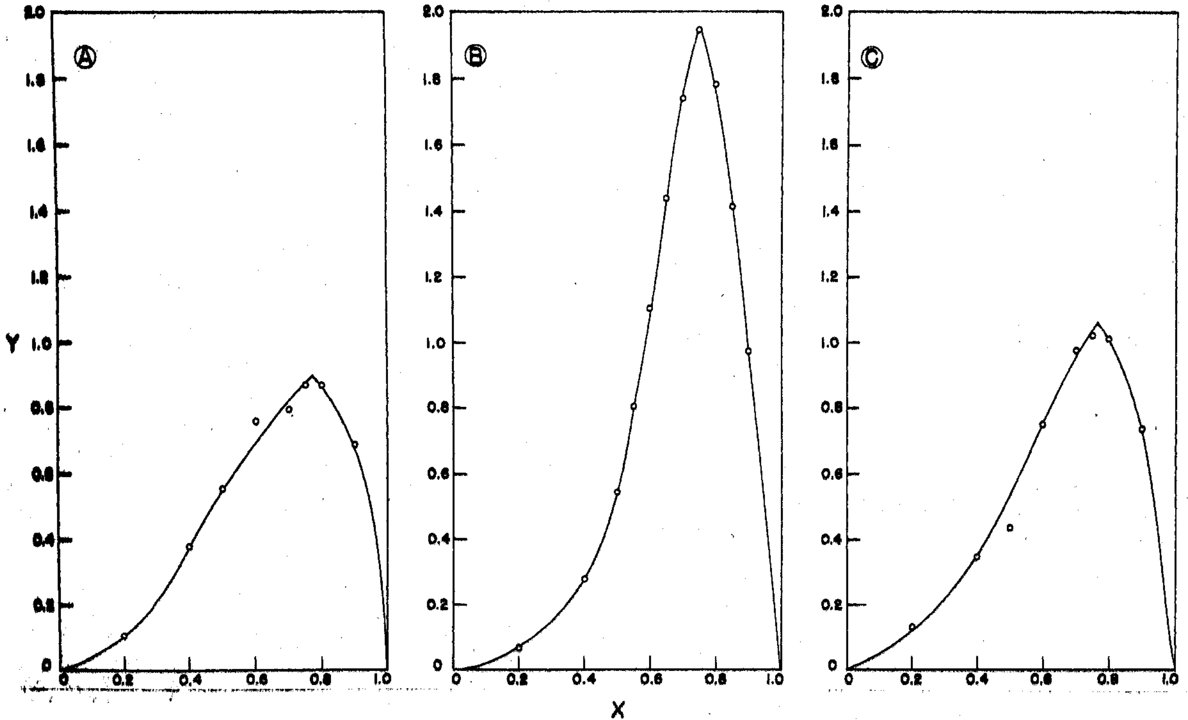

FIG. 17– DETERMINATION OF COMPOSITION MAXIMUM OF COMPLEX B BY JOB'S METHOD.
(A) 2,3-BUTANEDIONEDIOXIME AT 460 mμ.
(B) 1,2-CYCLOHEXANEDIONEDIOXIME AT 463 mμ.
(C) 1,2-CYCLOHEPTANEDIONEDIOXIME AT 455 mμ.

scanned 150 hours after preparation with only minor changes in the absorption curves. The condition of equal molarity of the two reacting species loses its validity after this length of time because of decomposition of the *vic*-dioxime. This may be the cause of the flat maxima obtained for these *vic*-dioximes in Figure 17. Color development was very slow in these solutions and non-equilibrium conditions prevailed.

An attempt was made to obtain more conclusive evidence for the ratio using the slope ratio method (33). This method failed for the complex prepared with 1,2-cycloheptanedionedioxime because the red-brown color failed to develop in the solutions containing excess nickel(II) ion.

It was possible to obtain the red-brown color in solutions of 2,3-butanedionedioxime in which there was a constant excess of nickel(II) ion. However, the ratio of *vic*-dioxime to nickel ion was about 4.4:1. This high ratio can be explained if it is assumed that the solutions containing excess nickel(II) ion do not develop maximum color.

Since the result obtained for Complex B prepared with 1,2-cyclohexanedionedioxime was so conclusive, it will be assumed that the predominate species present in alkaline solutions has a *vic*-dioxime to nickel ion ratio of 3:1.

4. Ionic charge

The sign of the charge on Complex B was determined by simple migration experiments. Several tests were made, but only one will be described. A solution of Complex B was made up to contain 0.5 M sodium hydroxide, 0.5 M lithium nitrate, 4.00×10^{-5} M nickel(II) perchlorate and 1.00×10^{-4} M 1,2-cyclohexanedionedioxime. A U-tube was half filled with the above solution. Portions of 0.5 M sodium hydroxide solution were carefully added to each arm in such a way that the boundary remained distinct. Platinum electrodes were inserted in each arm of the U-tube and connected through a rheostat to a six-volt battery. A current of about five-milliamperes was allowed to pass through the solution for two days. Movement of the boundary was apparent at the end of the first day.

The color of Complex B rose in the arm connected to the positive pole of the battery. From these results, it was concluded that Complex B carries one or more negative charges.

5. Magnetic susceptibility

The magnetic susceptibility of Complex B was determined by the Gouy method. These measurements were made by Mr. R. W. Vander Haar of these laboratories.

It was found difficult to prepare solutions sufficiently concentrated to permit evaluation of the susceptibility. Some of the insoluble vic-dioxime-nickel(II) compound always formed. The following procedure was used: 10 ml. of 0.10 M nickel(II) perchlorate solution were slowly added to about 125 ml. of a solution containing 20 ml. of 10 M sodium hydroxide and 1.5 g. of 1,2-cyclohexanedionedioxime. Oxygen was bubbled through the solution for about three hours. At the end of this time, 0.5 g. more of the vic-dioxime was added and oxygen bubbled through the solution for two hours. The solution was made to a volume of 200 ml., allowed to stand for about 12 hours and then filtered through a medium, sintered-glass filter crucible. A blank solution containing no nickel(II) ion was prepared in a similar manner. Spectrophotometric analysis of the solution containing nickel(II) ion indicated the concentration of complex to be about 1.5×10^{-3} M.

The experimentally observed magnetic susceptibility of the complex was found to be -0.709×10^{-6} c.g.s.u./ml. with an experimental error of less than 0.001×10^{-6} c.g.s.u./ml. The calculated value of the susceptibility for a complex having a magnetic moment of 2.83 Bohr magnetons is -0.703×10^{-6} c.g.s.u./ml. From these measurements, it was concluded that Complex B is a diamagnetic complex of nickel.

6. Electrometric experiments

As mentioned earlier, Feigl determined the oxidation state of the nickel ion in Complex B in an indirect manner. It was hoped that the electrometric work described below would give more direct evidence for the electron change.

a. Polarography. A few attempts were made to apply the polarographic method to the study of Complex B. Very poor polarograms were obtained. An indication of two breaks was observed: one at about -0.95 volt, the other at about -1.2 volts *vs*. S.C.E.

It was impossible to calculate consistent electron change values from the polarograms. The n values obtained for each break ranged from 0.4 - 0.8. This would indicate an electron change of one for each step in the curve. However, it must be emphasized that the data obtained were very poor.

b. Potentiometric titrations. A search for a suitable reducing agent was made after the polarographic method was found unsatisfactory. It was hoped that the complex could be titrated directly. Sodium dithionite, $Na_2S_2O_4$, the only agent that appeared to react rapidly, was used to titrate a solution of Complex B. A nearly normal potentiometric titration curve was obtained when the potential of a platinum *vs*. a saturated calomel electrode was measured. An accurate determination of the normality of the Complex B solution could not be obtained due to the instability of the sodium dithionite solution and the nature of its unknown oxidation product. However, the electron change of the nickel ion can be estimated by use of the Nernst equation. A value of 1.8 was found for the electron change.

Here again the method does not provide uncontestable results. However, the titration provides further evidence to substantiate the claim for an oxidation state of four for the nickel in Complex B.

An iodometric titration was performed to substantiate the results of earlier workers. Solutions of Complex B containing 5.00×10^{-5} M nickel(II) perchlorate, 2.3×10^{-3} M 2,3-butanedionedioxime and 0.1 M sodium hydroxide were prepared. The sodium thiosulfate solution was standardized as described below by addition to a blank solution containing sodium hydroxide and _vic_-dioxime. The solution to be titrated was added to a 600 ml. beaker containing 50 ml. of 10 per cent potassium iodide and 50 ml. of 7 per cent sodium bicarbonate. The solution was magnetically stirred during the slow acidification of the solution by 6 N hydrochloric acid. After acidification, 10 ml. of about 0.003 N sodium thiosulfate solution were added and the excess back-titrated with standard 0.001 N potassium iodate. The end point of the titration was determined potentiometrically. An average value of 1.6 was obtained for the electron change of the nickel from decomposition of Complex B.

Spectrophotometric evidence indicated that nearly all of the nickel ion was present as Complex B. The reason for an electron change of less than two is believed to be due to part of the complex decomposing without reaction with iodide ion. Nickel(IV) would be expected to react with both water and vic-dioxime; the oxidized products might not oxidize iodide ion or, if gaseous, might be swept out of the solution by the carbon dioxide before reaction could occur.

Using more concentrated solutions, Feigl (20) obtained values of 1.8 and 1.9 for the electron change. The values reported in this work are in fair agreement.

7. Formation constant of the complex

The work of Gayer and Garrett (25) indicates that nickel(II) ion is present in alkaline solution as the nickelate ion, $HNiO_2^-$. They calculate the following equilibrium constant to be:

$$Ni(OH)_2 + OH^- = HNiO_2^- + HOH$$
$$K = (6 \pm 5) \times 10^{-5}.$$

The upper limit of their value, 1.1×10^{-4} was chosen for the study reported below, since the median value gave a less precise value for the formation constant of Complex B.

A consideration of all the data at hand indicates that the reaction should be formulated as follows:

$$\mathrm{Ni(II)} = \mathrm{Ni(IV)} + 2\ e^{-} \qquad (1)$$

$$\frac{1}{2}\ O_2 + \mathrm{HOH} + 2\ e^{-} = 2\ \mathrm{OH}^{-}. \qquad (2)$$

Combining equations (1) and (2) together with the addition of <u>vic</u>-dioxime gives:

$$\mathrm{HNiO}_2^{-} + 3\ D^{=} + \frac{1}{2}\ O_2 + 2\ \mathrm{HOH} = \mathrm{NiD}_3^{=} + 5\ \mathrm{OH}^{-}. \qquad (3)$$

The formation constant becomes:

$$K_3 = \frac{(\mathrm{NiD}_3^{=})\ (\mathrm{OH}^{-})^5}{(\mathrm{HNiO}_2^{-})\ (D^{=})^3\ (O_2)^{1/2}\ (\mathrm{HOH})^2}\ .$$

Under conditions of constant ionic strength, the activity coefficients of the ions can be combined with K_3. It will be assumed that the activities of oxygen and water remain constant, if not unity, and thus obtain the following constant:

$$K_3' = \frac{[\mathrm{NiD}_3^{=}]\ (\mathrm{OH}^{-})^5}{[\mathrm{HNiO}_2^{-}]\ [D^{=}]^3}\ .$$

The activity of the hydroxide ion was left in the above expression because variation in the pH was experimentally observed.

The formation constant, K_3', for the complex prepared using 2,3-butanedionedioxime, was calculated by means of the molar absorbancy index. The *vic*-dioxime concentration was corrected to allow for its slow decomposition in alkaline solution. The absorbancies used in the calculations represent the maximum value attained by each solution and appropriate corrections were applied for absorption due to the reacting species. The absorbancy measurements were made with the Beckman spectrophotometer using 5.0-cm. cuvettes.

Data for the calculation of the formation constant were obtained from two experiments. An ionic strength of 0.1 was obtained by the addition of sodium hydroxide solution to give a final pH of 13. The solutions were maintained at 23-25 degrees centigrade.

A series of solutions, described in Table IX, were prepared in which the *vic*-dioxime concentration was varied while the nickel ion concentration was kept constant. A similar series, in which the nickel ion concentration was varied, is described in Table X. The data obtained are plotted in Figure 18: the curves were calculated as described below.

The value of the molar absorbancy index for Complex B was obtained for each series by successive approximations. The minimum deviation in K'_3 was obtained when 14,000 was chosen for the value of a_{M_3} in each series.

This value for the molar absorbancy index was used to calculate the concentration of complex ion in each case. The

TABLE IX

Molar Ratio Solutions of Complex B Prepared with 2,3-Butanedionedioxime at a Constant Concentration of Nickel Ion equal to 1.50 x 10^{-5} M

No.	A_s^{460}	Vic-Dioxime Concentration x 10^5	pH
1	0.070	0.99	12.95
2	0.125	1.48	12.95
3	0.175	1.98	12.96
4	0.240	2.53	12.96
5	0.320	3.03	12.96
6	0.385	3.54	13.00
7	0.400	3.95	13.01
8	0.450	4.45	13.01
9	0.515	4.95	13.02
10	0.585	5.45	13.02
11	0.645	5.91	12.98
12	0.680	6.41	13.01
13	0.775	7.21	12.97
14	0.880	9.61	12.97
15	0.960	11.99	13.01
16	0.975	14.40	13.02
17	0.995	16.77	13.02
18	0.980	19.17	13.02
19	1.010	23.97	13.02

TABLE X

Molar Ratio Solutions of Complex B Prepared with 2,3-Butanedionedioxime at a Nearly Constant Concentration of *Vic*-Dioxime equal to 3×10^{-5} M

No.	A_s^{460}	Nickel Concentration $\times 10^5$	*Vic*-Dioxime Concentration $\times 10^5$	pH
1	0.110	0.25	2.90	13.01
2	0.190	0.50	2.94	13.00
3	0.250	0.75	2.90	13.00
4	0.265	1.00	2.96	13.00
5	0.275	1.25	2.96	13.00
6	0.275	1.50	2.96	13.00
7	0.295	1.75	2.96	13.01
8	0.320	2.00	2.90	13.01
9	0.320	2.50	2.88	13.01
10	0.365	3.00	2.88	13.01
11	0.375	3.50	2.88	13.02
12	0.375	4.00	2.88	13.02
13	0.395	4.50	2.88	13.02
14	0.390	5.00	2.88	13.02

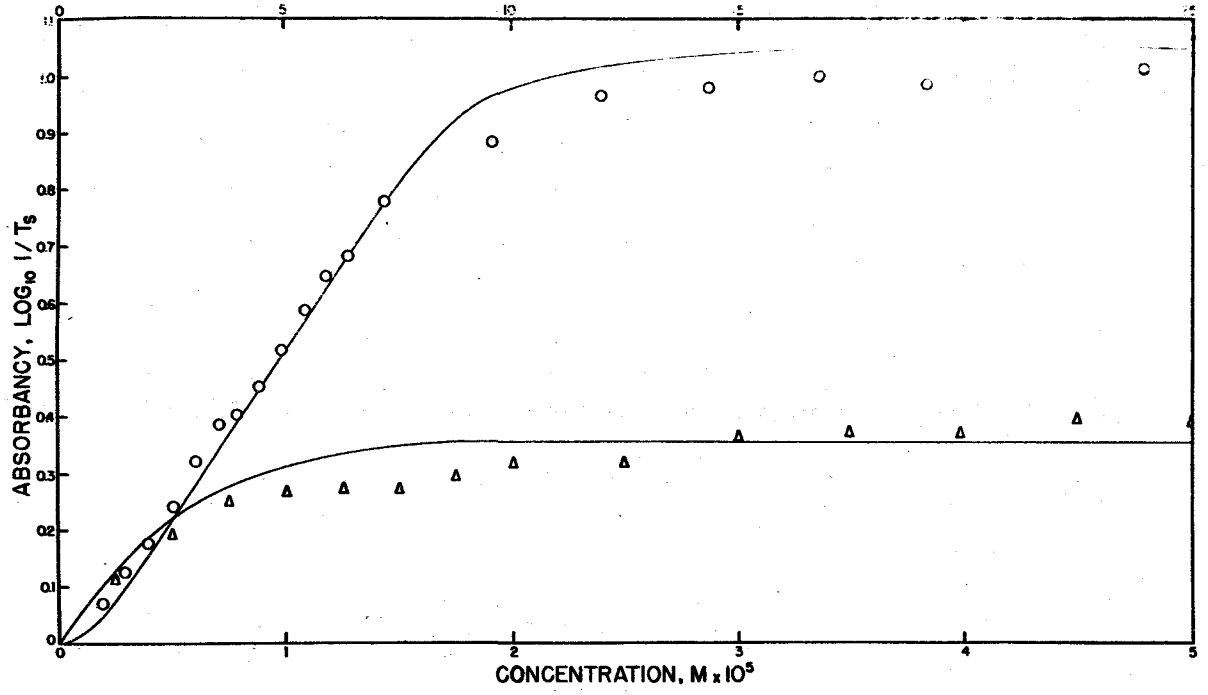

FIG. 18- MOLAR RATIO CURVES FOR COMPLEX B PREPARE WITH 2,3-BUTANEDIONEDIOXIME.

DATA FROM TABLES IX AND X.
O-VARYING DIOXIME: UPPER ABSCISSA
Δ-VARYING NICKEL: LOWER ABSCISSA

formation constant was then calculated. A sample calculation follows:

$$A_s = 0.385 \qquad \text{pH} = 13.00$$

$$C_{Ni} = 1.50 \times 10^{-5}\ M \qquad (OH^-) = 0.100$$

$$C_D = 3.54 \times 10^{-5}\ M$$

$$NiD_3^{=} = \frac{0.385}{5 \times 14{,}000} = 0.55 \times 10^{-5},$$

$$K'_3 = \frac{[0.55 \times 10^{-5}]\,[0.100]^5}{[(1.50 - 0.55) \times 10^{-5}]\,[(3.54 - 1.65) \times 10^{-5}]^3},$$

$$K'_3 = 0.64 \times 10^9.$$

The results obtained by such calculations are presented in Tables XI and XII.

The curves presented in Figure 18 were calculated by assuming the average value for K'_3 for each series was the true value of the constant. The value of the absorbancy for each solution was then calculated assuming the molar absorbancy index value was 14,000. Thus, Figure 18 illustrates the "goodness of fit" of the final value of K'_3 for each series to the experimental data.

A grand average of all the K'_3 values yields $(1.1 \pm 0.6) \times 10^9$. The accuracy to which the formation constant is known leaves much to be desired. No reason for the difference in average K'_3 values between the two series can be given.

TABLE XI

Calculation of Formation Constant of Complex B Using the Data in Table IX

$a_{M_3} = 14{,}000$

No.	$K'_3 \times 10^{-9}$
1	1.60
2	1.10
3	0.77
4	0.57
5	0.58
6	0.74
7	0.52
8	0.41
9	0.41
10	0.63
11	0.40
12	0.48
13	0.34
14	0.19
15	0.24
16	0.15
17	0.11
18	0.05
19	0.04
	Ave. $(0.5 \pm 0.3) \times 10^9$

TABLE XII

Calculation of Formation Constant of Complex B Using the Data in Table X

No.	$K_3' \times 10^{-9}$
1	1.32
2	1.22
3	1.52
4	1.01
5	0.80
6	0.62
7	0.88
8	1.33
9	1.38
10	2.31
11	3.06
12	3.06
13	3.73
14	3.92
	Ave. $(2 \pm 1) \times 10^9$

One source of error lies in the measurement of pH of each solution. An error of 0.02 pH unit introduces a variation of about 0.3×10^9 in the value of the constant. The measurement of pH in the region of 13 is probably less accurate than ± 0.02 unit. An error of 0.01 in the absorbancy measurement results in a similar error in K_3'. The presence of suspended sodium carbonate in these solutions could cause an error of as much as 0.01 absorbancy unit. An additional error arises due to the uncertainties in the equilibrium concentration of vic-dioxime, which is a cubic term in the equilibrium expression.

Perhaps a large portion of the errors present have their origin in the chemistry of the reaction. For a case such as this, there is reason to doubt the existence of a true thermodynamic equilibrium. If this is true, the application of the Bouguer-Beer relationship above is probably invalidated.

The presence of complexes other than the 3:1 species cannot be completely ruled out. However, it is unlikely that appreciable quantities of these complexes can be present. The presence of a 1:1 nickel(II) complex is unlikely since the 2:1 nickel(II) compound is insoluble at pH 13. The presence of 1:1 and 2:1 nickel(III) and nickel(IV) complexes are not expected. The formation of a 4:1 complex also appears unlikely.

A consideration of the above results and discussion indicates that Complex B is a 3:1 complex containing nickel(IV) ion and its formation constant has a value of about 1 x 10^9.

C. Unstable Complex (Complex A)

1. Factors affecting stability

Furman and McDuffie (24) have presented a good discussion of this complex from the viewpoint of the analyst. Their general method was used in most of the work described below.

Complex A is characterized by its very rapid formation and short period of stability. Decomposition is indicated by complete loss of color when the complex is prepared with 1,2-cyclohexanedionedioxime. Conversion to Complex B occurs when Complex A is prepared with 2,3-butanedionedioxime and 1,2-cycloheptanedionedioxime. High ammonium ion concentration tends to stabilize the complex prepared with each of the *vic*-dioximes and bromine water appears to be the preferred oxidant.

The time required for complete decomposition of the color of Complex A varies with the conditions of preparation, but appears to be complete in 12 hours in all cases. This ultimate loss of color is due to the decomposition of the *vic*-dioxime by the bromine.

A strong, rapid oxidant is required in order to obtain Complex A without forming a precipitate of the insoluble 1,2-bis(*vic*-dioximo-*N*,*N'*)nickel(II). Once the precipitate forms, it only slowly redissolves to form the complex.

These considerations make a theoretical study of Complex A very difficult.

2. Ratio of ligand to central atom

Considerable difficulty was encountered while attempting to determine the ratio of *vic*-dioxime to nickel in Complex A. It was learned that the time elapsed between addition of bromine-water and *vic*-dioxime was an important factor governing the amount of complex formed. A standardized procedure was devised which permitted reasonable data to be obtained in most cases.

All Complex A solutions were prepared as follows: 20 ml. of 7.5 M ammonium nitrate, 4 ml. of 1 M trisodium citrate, 10 ml. of 28 per cent ammonium hydroxide and the appropriate quantity of nickel(II) perchlorate solutions were added to a 200 ml. volumetric flask containing about 130 ml. of water. To this solution were added 10 ml. of saturated (25° C.) bromine-water. The mixture was then made homogeneous. Exactly 0.5 minute after the start of addition of the bromine-water, the addition of *vic*-dioxime solution was started. The solution was finally diluted to the mark and thoroughly mixed. Absorption curves were obtained at measured intervals after the start of addition of the vic-dioxime solution.

Complex A solutions prepared with 1,2-cyclohexanedione-dioxime were studied by Job's method (40). Absorption curves, for solutions described in Table XIII, are reproduced in Figure 19. The ratio of vic-dioxime to nickel ion is quite clearly 3:1 over the wavelength region studied. The data for several wavelengths were plotted as recommended by Vosburgh and Cooper (79) with confirming results.

Complex A prepared with the other vic-dioximes was studied by the slope ratio method (33). The solutions were prepared as described in Tables XIV and XV. Figure 20 presents the results in the form of a time study. The difference in stability between solutions having excess nickel ion and those having excess vic-dioxime is striking. An extrapolation to zero time was made to determine the maximum absorbancy for solutions in which the nickel ion was in excess.

The data obtained from Figure 20 are shown in Figure 21, where the absorbancy is plotted against the concentration of varying species. The straight lines through the plotted points were obtained by the method of least squares.

The results obtained by this method for Complex A prepared with 2,3-butanedionedioxime were satisfactory. A ratio

TABLE XIII

Solutions used for the Determination of the Ratio of Nickel to 1,2-Cyclohexanedionedioxime in Complex A by Job's Method

Solution No.	ml. of 3.00×10^{-3} M solution Nickel	 *Vic*-dioxime
1	4.0	6.0
2	3.5	6.5
3	3.0	7.0
4	2.5	7.5
5	2.0	8.0
6	1.5	8.5
7	1.0	9.0

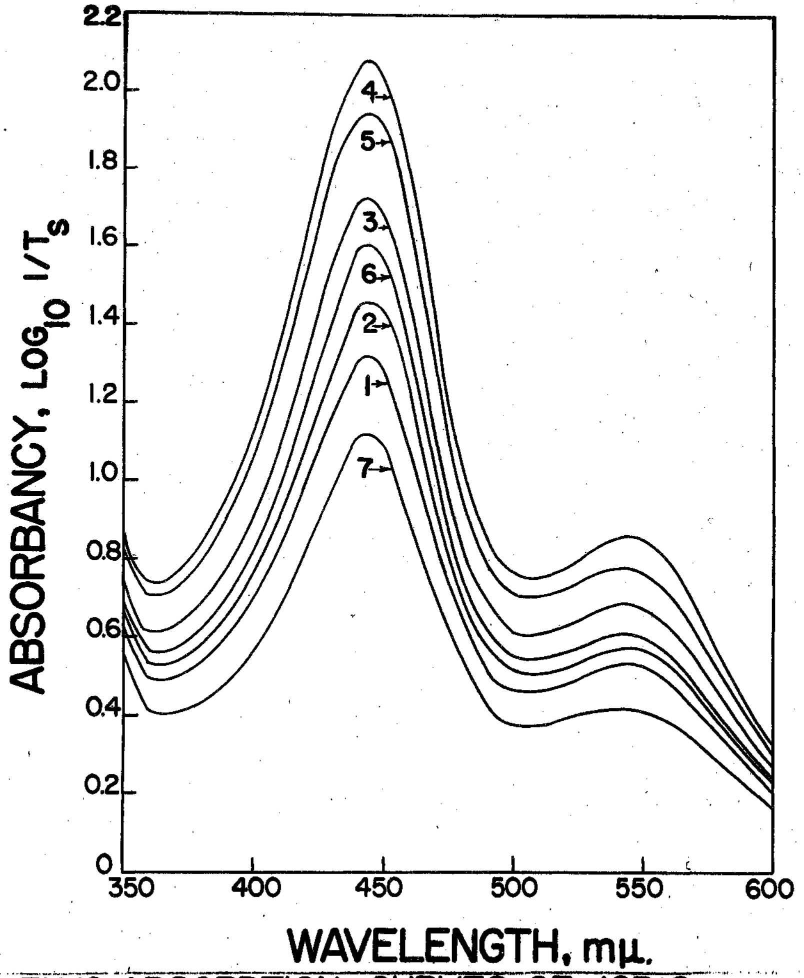

FIG.19-ABSORPTION CURVES OF JOB'S SOLUTIONS OF COMPLEX A WITH 1,2-CYCLOHEXANEDIONEDIOXIME.

NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLE XIII. SCANNED IN 5.0-cm. CUVETTES vs. DISTILLED WATER 5 MINUTES AFTER PREPARATION.

TABLE XIV

Solutions used for the Determination of the Ratio of Nickel to 1,2-Cycloheptanedionedioxime in Complex A by the Slope Ratio Method

Solution No.	ml. of 3.00×10^{-3} M solution Nickel	Vic-Dioxime
1	0.5	(5×10^{-4} M)
2	1.0	(")
3	1.5	(")
4	2.0	(")
5	2.5	(")
6	(5×10^{-4} M)	1.0
7	(")	2.0
8	(")	3.0
9	(")	4.0
10	(")	6.0
11	(")	8.0

TABLE XV

Solutions used for the Determination of the Ratio of Nickel to 2,3-Butanedionedioxime in Complex A by the Slope Ratio Method

Solution No.	ml. of 3.00×10^{-3} M solution	
	Nickel	Vic-Dioxime
1	0.5	(5×10^{-4} M)
2	1.0	(")
3	1.5	(")
4	2.0	(")
5	2.5	(")
6	(5×10^{-4} M)	1.0
7	(")	2.0
8	(")	3.0
9	(")	4.0
10	(")	6.0
11	(")	8.0

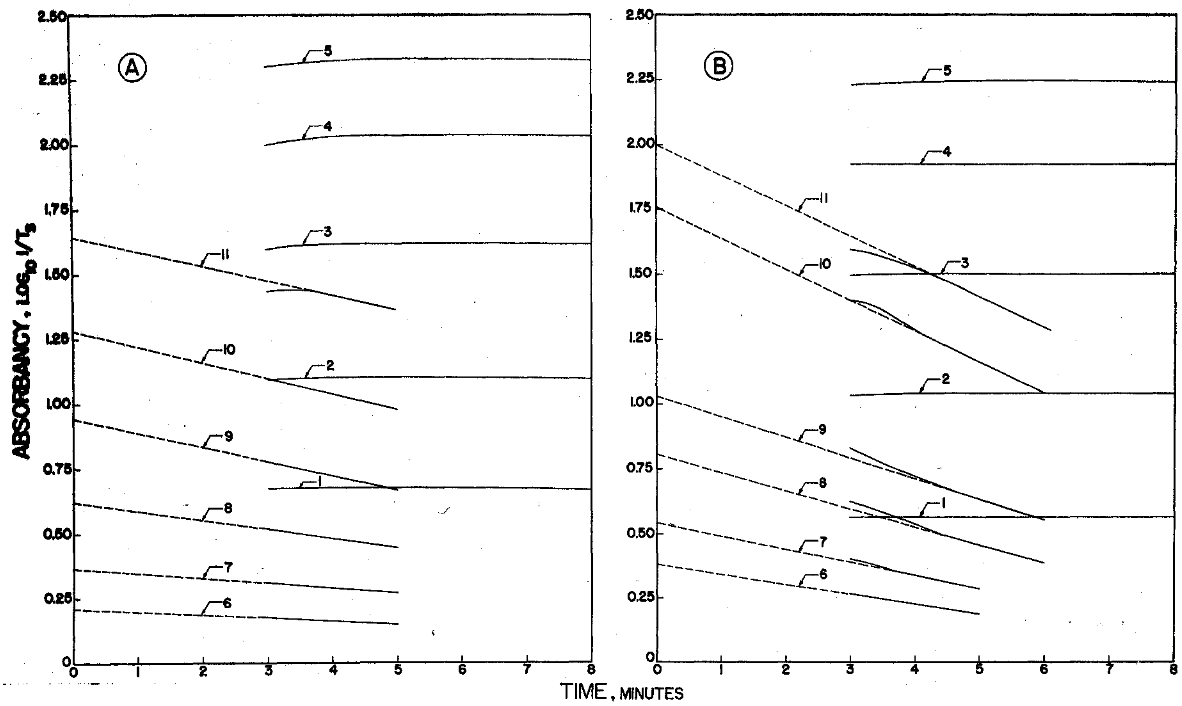

FIG. 20 – TIME CURVES FOR COMPLEX A BY SLOPE RATIO METHOD.

NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLES XIV & XV.
ABSORBANCY MEASURED IN 5.0 cm.
CUVETTES vs. DISTILLED WATER AT 443 mμ.
(A) 1,2-CYCLOHEPTANEDIONEDIOXIME
(B) 2,3-BUTANEDIONEDIOXIME

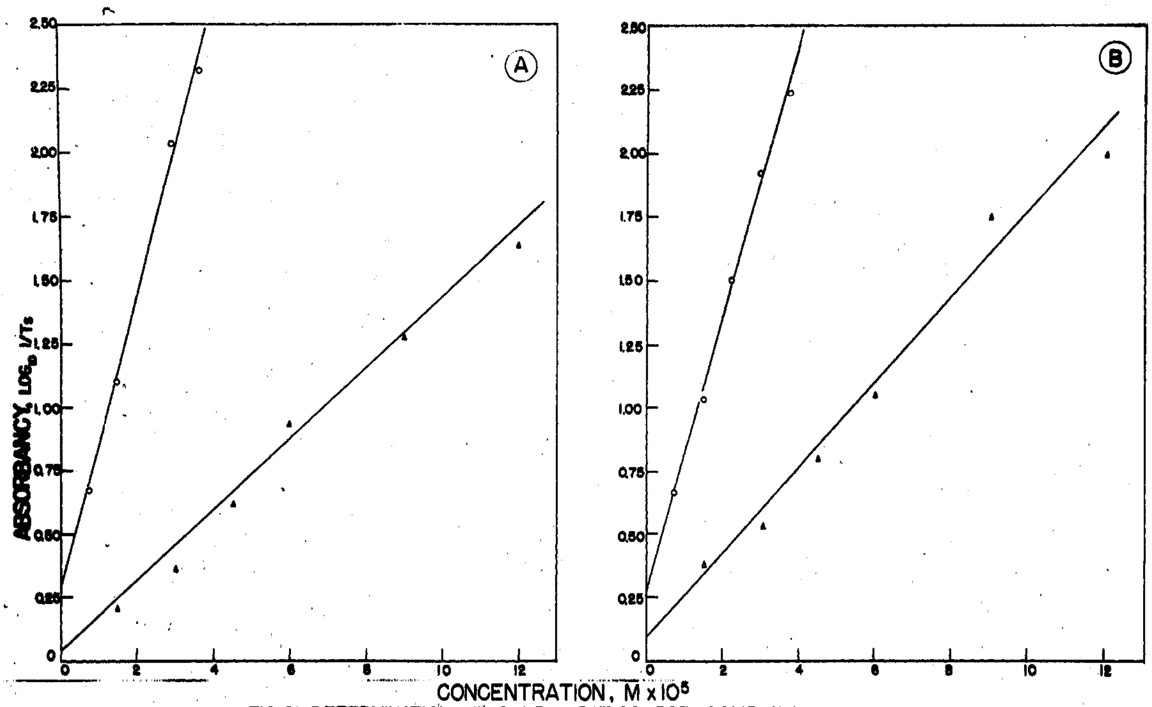

FIG. 21-DETERMINATION OF SLOPE RATIOS FOR COMPLEX A, DATA TAKEN FROM FIGURE 20 FOR 1,2-CYCLOHEPTANEDIONEDIOXIME (A) AND FOR 2,3-BUTANEDIONEDIOXIME (B).

Δ CONSTANT EXCESS OF DIOXIME
O CONSTANT EXCESS OF NICKEL

of vic-dioxime to nickel ion of 3.2:1 was obtained from the ratio of the calculated slopes.

This method gave rather poor results when applied to Complex A prepared with 1,2-cycloheptanedionedioxime. A ratio of vic-dioxime to nickel ion of 4:1 was obtained in this case. If it is again assumed that the reaction is retarded when the nickel ion is in excess over the vic-dioxime, this high ratio can be explained. The ratio approaches 3:1, when the points representing solutions 10 and 11 in Table XIV are neglected.

It was concluded from the above results that the ratio of vic-dioxime to nickel ion in Complex A is probably 3:1.

VI. DISCUSSION

A. Stable Complex (Complex B)

When the results reported above are reviewed, it seems most likely that Complex B represents a case of an unfamiliar oxidation state of a metal ion, which has been stabilized through complex formation. This study, as well as the results of others, confirms the presence of an oxidized product connected with the complex. The electrometric experiments indicate an electron change of two associated with decomposition of Complex B. It does not appear reasonable to ascribe an electron change of two to one, or more, of the three vic-dioximes bound to the nickel ion. A more likely explanation for all of the facts can be found by assuming an oxidation state of four for the complexed nickel ion.

The oxidation of nickel(II) ion to nickel(IV) ion makes two-3d orbitals available for bond formation. Consequently, strong covalent bonds can be formed by d^2sp^3 hybridization. These six bonds can be filled by electron-pairs from the six oxime nitrogen atoms. Stabilization of nickel(IV) ions would not be unexpected when such an octahedral complex can be formed and, in fact, the complex should be strong. The data presented above indicate Complex B is a relatively strong complex.

The study of the acidic dissociation constants of the vic-dioximes indicates that $D^{=}$ is the predominate species present in solutions having a pH of about 13. Since the complex was shown to carry one or more negative charges, both oxime hydrogen atoms on each vic-dioxime molecule present in the complex are undoubtedly absent.

It is therefore concluded, that Complex B exists in aqueous solution as the ion, $NiD_3^{=}$, and the vic-dioxime molecules are attached to the nickel(IV) ion in an octahedral arrangement by bonds between the nickel(IV) ion and the oxime nitrogen atoms.

No attempt was made to obtain results in each experiment above for Complex B prepared with each vic-dioxime. It has been assumed that the conclusions reached above apply to Complex B prepared with the three vic-dioximes employed in this study. It is believed that this assumption is valid and can be extended to other vic-dioximes which form Complex B.

B. Unstable Complex (Complex A)

The great instability of Complex A caused most of the emphasis in this study to be placed on Complex B. Time limitations prevented extension of the experimental work concerning the unstable complex. However, it is possible to deduce a probable structure for Complex A.

The pK_1 values for the vic-dioximes studied indicates that the ion, DH^-, is the predominate species present in concentrated ammoniacal solution. The possibility that a proton is lost by reaction with nickel ion cannot be eliminated. However, it seems likely that the vic-dioxime molecules are present in Complex A as the ion, DH^-.

The absorption curves presented in Figure 12 suggest that the structure of Complex A might be intermediate between that for the 1,2-bis(vic-dioximo-N,N')nickel(II) and that for Complex B. It is believed that the best formulation would result from assuming a nickel(III) complex, $Ni(DH)_3$.

Attempts to extract the complex into organic solvents such as benzene, chloroform, carbon tetrachloride and diethyl ether failed. However, diisopropyl ether caused the aqueous layer to become pale yellow without imparting a visible color to the organic phase. This simple test does not constitute proof of solubility and indirect proof of a neutral complex.

Only one-3d orbital is available for bonding in the nickel(III) ion and one-3d electron remains unpaired. It is not known if such an electron can be promoted to an orbital of higher principle quantum number in this case. If promotion occurs, the resultant structure would be expected to be unstable. The use of orbital arrangements such as $3d4s4p^34d$ and $3d4s4p^35s$ are expected to be much less stable than ordinary octahedral type bonding. In either case, an unstable complex would be predicted.

It is suggested that Complex A is a nickel(III) complex having three <u>vic</u>-dioxime molecules attached to the nickel ion by bonds to the oxime nitrogen atoms, $Ni(DH)_3$. The complex is predicted to be paramagnetic.

VII. APPLICATION TO THE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL

Unfortunately, the above results do not provide the analyst with a superlative method for the determination of microgram quantities of nickel. However, the above conclusions explain the necessity for rigid control of variables in the existing methods utilizing these so-called "oxidized" complexes.

Application of the term, "stabilized oxidation state", to Complex A is perhaps a misnomer. It is a well known fact that the stability of this complex is a rather transient phenomenon. It seems unlikely that a rapid oxidant, capable of producing Complex A without concurrent destruction of the *vic*-dioxime, will be found. Furthermore, there are no methods available that will prevent the unstable complex from changing into an apparently more stable state, *i.e.*, Complex B.

The formation of Complex B by air oxidation has been shown to be extremely slow. Here again oxidants, such as peroxydisulfate ion, destroy the *vic*-dioxime and consequently the complex.

It would appear that a new type of reagent for the spectrophotometric determination of nickel is required. This conclusion, perhaps, is the most valuable result of this study insofar as the analyst is concerned.

VIII. SUMMARY

1. The literature pertaining to the +3 and +4 oxidation states of nickel has been reviewed with special emphasis being placed on complex compounds.

2. Estimates of the acidic dissociation constants of three vic-dioximes have been obtained from spectrophotometric data. The values for these thermodynamic constants may be summarized as follows:

	pK_1	pK_2
2,3-butanedionedioxime	10.6 ± 0.1	11.9 ± 0.3
1,2-cyclohexanedionedioxime	$10.5_5 \pm 0.1$	12.4 ± 0.5
1,2-cycloheptanedionedioxime	10.7 ± 0.2	12.3 ± 0.5

3. An extensive study has lead to the conclusion that the vic-dioxime-nickel ion complex, which has been designated Complex B, is a diamagnetic nickel(IV) complex that exists in aqueous solution as the ion, $NiD_3^{=}$. Such a formulation indicates an octahedral structure with the bonds being between the nickel(IV) ion and the oxime nitrogen atoms. The molar formation constant for Complex B prepared with 2,3-butanedionedioxime was found to be about 1×10^9 at an ionic strength of 0.1.

4. The unstable vic-dioxime-nickel ion complex, which

has been designated Complex A, has been shown to be a 3:1 complex. It is suggested that Complex A is a paramagnetic nickel(III) complex having the formula, $Ni(DH)_3$.

IX. SUGGESTIONS FOR FURTHER WORK

As mentioned previously, a more satisfactory reagent for the spectrophotometric determination of nickel would be useful. The synthesis of a vic-dioxime containing one or more sulfonic acid groups should be carried out. Such a compound might react with nickel(II) ion in the manner of an ordinary vic-dioxime yielding a soluble, colored compound. Such a reagent would be extremely valuable.

A more complete study of the polarographic behavior of both Complex A and Complex B might provide much useful information. Further attempts to isolate the complexes in solid form should be undertaken. An X-ray crystallographic study of the solid complexes should provide valuable information concerning their actual structures.

The present study of Complex A was brief and further experiments are definitely indicated. The determination of the magnetic susceptibility of the complex is only one line of attack that could be pursued.

Experimental studies should be instigated to obtain information concerning the difference in the reactivities of the several vic-dioximes. Such a study would provide much needed fundamental knowledge concerning the stabilities of all complex compounds.

X. LITERATURE CITED

1. Abbey, S., Anal. Chem., 20, 630-634 (1948).

2. Ackermann, H., Prue, J. E. and Schwarzenbach, G., Nature, 163, 723-724 (1949).

3. Ackermann, H. and Schwarzenbach, G., Helv. Chim. Acta, 32, 1543-1554 (1949).

4. Auwers, K., Ber., 60B, 2122-2142 (1927).

5. Auwers, K., Ber., 61B, 1041-1049 (1928).

6. Babko, A. K., Zhur. Anal. Khim., 3, 284-289 (1948). Original not available for examination; abstracted in C. A., 43, 8935 (1949).

7. Babko, A. K. and Mikhelson, P. B., Zhur. Anal. Khim., 6, 267-272 (1951). Original not available for examination; abstracted in C. A., 45, 9971 (1951).

8. Back, E. and Steenberg, B., Acta Chem. Scand., 4, 810-815 (1950).

9. Bobtelsky, M. and Jordan, J., J. Am. Chem. Soc., 67, 1824-1831 (1945).

10. Burriel-Marti, F. and Pino-Perez, F., Anal. Chim. Acta, 4, 333-339 (1950).

11. Cooper, M. D., Anal. Chem., 23, 880-883 (1951).

12. Crémoux, J. and Mondain-Monval, P., Bull. soc. chim. France, 1949, 700-704.

13. Delsal, J. L., J. chim. phys., 35, 314-326 (1938).

14. Derr, P. F. and Vosburgh, W. C., J. Am. Chem. Soc., 65, 2408-2411 (1943).

15. Diehl, H. "The applications of the dioximes to analytical chemistry." Columbus, Ohio, The G. Frederick Smith Chemical Co. 1940.

16. Dietrich, K. and Schmitt, K., *Z. anal. Chem.*, *109*, 25-31 (1937).

17. Douglas, B. E., *J. Chem. Ed.*, 29, 119-129 (1952).

18. Edelman, L. E., *J. Am. Chem. Soc.*, *72*, 5765-5766 (1950).

19. Eichler, O. and Meyer, G., *Naturwissenschaften*, *35*, 93-94 (1948).

20. Feigl, F., *Ber*, *57B*, 758-761 (1924).

21. Ferguson, R. C. and Banks, C. V., *Anal. Chem.*, *23*, 448-453 (1951).

22. Ferguson, R. C. and Banks, C. V., *Anal. Chem.*, *23*, 1486-1487 (1951).

23. Field, F. H. and Vosburgh, W. C., *J. Am. Chem. Soc.*, *71*, 2398-2401 (1949).

24. Furman, N. H. and McDuffie, B. M-4234. 1947.

25. Gayer, K. H. and Garrett, A. B., *J. Am. Chem. Soc.*, *71*, 2973-2975 (1949).

26. Gayer, K. H. and Woontner, L., *J. Am. Chem. Soc.*, *74*, 1436-1437 (1952).

27. Gibson, K. S. "Spectrophotometry." Washington, D. C., National Bureau of Standards Circular 484. 1949.

28. Gilbert, E. C. and Evans, W. H., *J. Am. Chem. Soc.*, *73*, 3516-3518 (1951).

29. Glemser, O. and Einerhand, J., *Z. anorg. Chem.*, *261*, 26-42 (1950).

30. Gould, R. K. and Vosburgh, W. C., *J. Am. Chem. Soc.*, *64*, 1630-1634 (1942).

31. Haim, G. and Tarrant, B., *Ind. Eng. Chem., Anal. Ed.*, *18*, 51-52 (1946).

32. Hall, N. F. and Willeford, Jr., B. R., *J. Am. Chem. Soc.*, *73*, 5419-5423 (1951).

33. Harvey, A. E., Jr. and Manning, O. L., *J. Am. Chem. Soc.*, *72*, 4488-4493 (1950).

34. Harvey, J. L., Tewksbury, C. I. and Haendler, H. M., *J. Am. Chem. Soc.*, 71, 3641-3643 (1949).

35. Hooreman, H., *Anal. Chim. Acta*, *3*, 606-627 (1949).

36. Hooreman, H., *Anal. Chim. Acta*, *3*, 635-641 (1949).

37. Hüber, W. and Brüch, R., *Naturwissenschaften*, *36*, 312-313 (1949).

38. Ives, D. J. G. and Riley, H. L., *J. Chem. Soc.*, *1931*, 1998-2012.

39. Jensen, K. A. and Nygaard, B., *Acta Chem. Scand.*, *3*, 474-480 (1949).

40. Job, P., *Ann. Chim.*, (10) *9*, 113-203 (1928).

41. Johnson, J. E. and Hall, N. F., *J. Am. Chem. Soc.*, *70*, 2344-2348 (1948).

42. Johnson, W. C. and Simmons, M., *Analyst*, *71*, 554-556 (1946).

43. Jonassen, H. B. and Douglas, B. E., *J. Am. Chem. Soc.*, *71*, 4094-4097 (1949).

44. Jonassen, H. B. and Meibohm, A. W., *J. Phys.* and *Colloid Chem.*, 55, 726-733 (1951).

45. Jones, H. W., Monk, C. B. and Davies, C. W., *J. Chem. Soc.*, *1949*, 2693-2695.

46. Kinney, C. R. and Harwood, H. J., *J. Am. Chem. Soc.*, *49*, 514-516 (1927).

47. Kuraš, M. and Ruzicka, E., *Chem. Listy*, 45, 100-102 (1951). Original not available for examination; abstracted in *C. A.*, *45*, 9423 (1951).

48. Kuraš, M. and Ruzicka, E., *Chem. Listy*, *45*, 233-234 (1951). Original not available for examination; abstracted in *C. A.*, *46*, 2498 (1952).

49. Lander, J. J., *Acta Cryst.*, *4*, 148-156 (1951).

50. Lander, J. J. and Wooten, L. A., *J. Am. Chem. Soc.*, *73*, 2452-2454 (1951).

51. Latimer, W. M. "The oxidation states of the elements and their potentials in aqueous solution." New York, Prentice-Hall, Inc. 1938.

52. Lifschitz, I., Bos, J. G. and Dijkema, K. M., Z. anorg. allgem. Chem., 242, 97-116 (1939).

53. Long, F. A., J. Am. Chem. Soc., 73, 537, 540 (1951).

54. Makepeace, G. R. and Craft, C. H., Ind. Eng. Chem., Anal. Ed., 16, 375-377 (1944).

55. McKenzie, H. A., Mellor, D. P., Mills, J. E. and Short, L. N., J. Proc. Roy. Soc. N. S. Wales, 78, 70-80 (1944).

56. Mills, J. E. and Mellor, D. P., J. Am. Chem. Soc., 64, 181-182 (1942).

57. Milone, M., Gazz. chim. ital., 59, 829-838 (1929).

58. Mitchell, A. M. "A spectrophotometric study of colorimetric methods for the determination of nickel." Unpublished M. S. Thesis. Lafayette, Ind., Purdue University. 1945.

59. Mitchell, A. M. and Mellon, M. G., Ind. Eng. Chem., Anal. Ed., 17, 380-382 (1945).

60. Nyholm, R. S., J. Chem. Soc., 1950, 2061-2071.

61. Nyholm, R. S., J. Chem. Soc., 1951, 2602-2607.

62. Okáč, A. and Polster, M., Collection of Czechoslov. Chem. Communs., 13, 561-572 (1948).

63. Okáč, A. and Polster, M., Collection of Czechoslov. Chem. Communs., 13, 572-581 (1948).

64. Paterson, A. M. and Capell, L. T. "The ring index." New York, Reinhold Publishing Corp. 1940.

65. Ponzio, G., Gazz. chim. ital., 60, 49-96 (1930).

66. Rauh, E. G., Smith, G. F., Banks, C. V. and Diehl, H., J. Org. Chem., 10, 199-204 (1945).

67. Roberts, G. L. and Field, F. H., J. Am. Chem. Soc., 72, 4232-4235 (1950).

68. Rogers, L. B. and Reynolds, C. A., J. Am. Chem. Soc., 71, 2081-2085 (1949).

69. Rollet, A. -P., Compt. rend., 183, 212-213 (1926).

70. Samuel, A., J. chim. phys., 40, 207-216 (1943).

71. Sandell, E. B. and Perlich, R. W., Ind. Eng. Chem., Anal. Ed., 11, 309-311 (1939).

72. Scholl, R., Ber., 23, 3490-3505 (1890).

73. Schwarzenbach, G. and Freitag, E., Helv. Chim. Acta, 34, 1503-1508 (1951).

74. Stenström, W. and Goldsmith, N., J. Phys. Chem., 30, 1683-1687 (1926).

75. Stromberg, A. G., Zhur. Fiz. Khim., 23, 969-980 (1949).

76. Stromberg, A. G. and Zelyanskaya, A. I., Zhur. Anal. Khim, 4, 286-291 (1949). Original not available for examination; abstracted in C. A., 44, 2828 (1950).

77. Ter Haar, K. and Westerveld, W., Rec. trav. chim., 67, 71-82 (1948).

78. Vander Haar, R. W., Voter, R. C. and Banks, C. V., J. Org. Chem., 14, 836-838 (1949).

79. Vosburgh, W. C. and Cooper, G. R., J. Am. Chem. Soc., 63, 437-442 (1941).

80. Voter, R. C. and Banks, C. V., Anal. Chem., 21, 1320-1323 (1949).

81. Voter, R. C., Banks, C. V., Fassel, V. A. and Kehres, P. W., Anal. Chem., 23, 1730-1735 (1951).

82. Willis, J. B. and Mellor, D. P., J. Am. Chem. Soc., 69, 1237-1240 (1947).

83. Wulff, P. and Lundberg, A., Beih. Z. Ver. deut. Chem., A: Chem., B: Chem. Tech., No. 48, 76-83 (1944).

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