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OXIDATION AND COMPLEX FORMATION OF SOME FORMAZANS

A. M. A. VERWEIJ

OXIDATION AND COMPLEX FORMATION
OF SOME FORMAZANS

VRIJE UNIVERSITEIT TE AMSTERDAM

OXIDATION AND COMPLEX FORMATION
OF SOME FORMAZANS

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad van Doctor in de Wiskunde en Natuur-
wetenschappen aan de Vrije Universiteit te Amsterdam , op gezag
van de Rector Magnificus Mr. W.F. de Gaay Fortman, Hoogleraar
in de Faculteit der Rechtsgeleerdheid, in het openbaar te verdedigen
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Woestduincentrum, Woestduinstraat 16 te Amsterdam

door ANTHONIE MARINUS ARIE VERWEIJ

geboren te Leerdam

Aan de nagedachtenis van mijn vader

Aan mijn vrouw

Aan Joke

CONTENTS

CHAPTER 1

INTRODUCTION

As early as 1892 von Pechman (92 P) and Bamberger (92 B) discovered the formazans, a class of compounds having the chain of atoms

$$-N \overset{1}{=} N \overset{|}{\underset{3}{-C}} \overset{2}{=} N \overset{H}{\underset{5}{-N}}-$$

in common and nearly always having phenyl groups attached to the outmost nitrogen atoms N_1 and N_5, for instance:

1, 3, 5-Triphenylformazan.

Formazans have received several important applications:

1. The oxidation products of formazans, the tetrazolium salts (Chapter 2), are used in biology (41 K, 55 N) for identification of enzymatic reduction processes.

2. Formazans can form complexes (Chapter 2), which receive applications in industry as dyeing agents for wool, cotton and synthetic fibers (15 P, 55 N, 68 W).

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3. In analytical chemistry certain formazans are used as colorimetric and as extracting reagents: Zincon and Dithizone (58 I, 37 F) are well-known examples.

Formazans were chosen as subject of our investigations owing to their importance in analytical chemistry and on account of the already existing experience in this laboratory on similar compounds (62 B).

The aim of this thesis is to study some aspects of the oxidation of formazans.

In the oxidation of ligands with metal complexes two possibilities can be distinguished (67 S):

First the oxidation can proceed by way of an "inner sphere" electron transfer process, in which complex formation of the ligand to be oxidized and the oxidizing reagent take place in the intermediate state of the reaction. This is found to be the case, for instance in the oxidation of hydroxyethylene-diaminetriacetic acid by vanadate (V) ions (66 J).

Secondly the oxidation can proceed by way of an "outer sphere" electron transfer mechanism, in which no complex formation of the ligand and the oxidizing reagent is found. Oxidations by hexacyanoferrate (III) anions are generally assumed to proceed according to this mechanism (68 Wi); the oxidation of EDTA by the hexacyanoferrate (III) anion (66 L) is an example of this kind of electron transfer process.

An "outer sphere" mechanism is also expected for the oxidation of formazans by hexacyanoferrate (III) anions. A study of this oxidation process is treated in Chapter 4.

As a consequence of the ability of formazans to form complexes (Chapter 2) with metal ions like copper (II), it is possible that the oxidation of formazans by copper (II) proceeds by way of an "inner sphere" electron transfer mechanism. In order to investigate this possibility, we first have to study the complex formation of formazans.

Most formazans are oxidized rather rapidly by copper (II) so that no complex formation can be observed.

One exception is found, however: Copper (II) rapidly forms complexes with 1,3-Diphenyl-5-o-carboxyphenylformazan, whereas the oxidation of this formazan by copper (II) appears to be very slow. Consequently complex

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formation of this formazan can be studied independently of oxidation (Chapter 5). In this way results as regards complex formation are obtained which can be used in interpreting the copper(II) oxidation of the simple formazans (Chapter 6).

Comparison of the several studies and final conclusions will be given in Chapter 7.

CHAPTER 2

REVIEW OF LITERATURE

In this Chapter a survey of those aspects of the literature on formazans will be given, which are of direct importance of the work dealt with in this thesis.
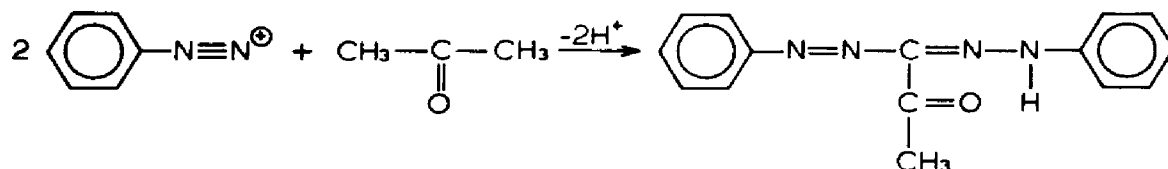
2.1 PREPARATION OF FORMAZANS

Since 1892 innumerable formazans have been synthesized mainly according to the following routes:

1. Treatment of an arylhydrazone (a) or a compound with an active methylene or methylgroup (b) with aryldiazonium salts under alkaline conditions, e.g.:
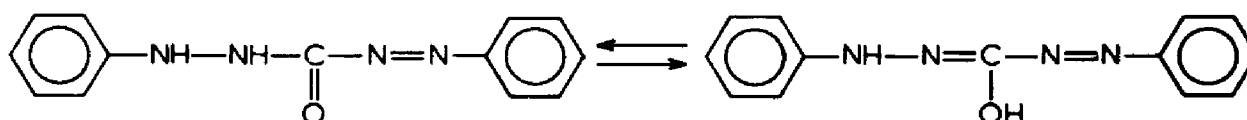
a.
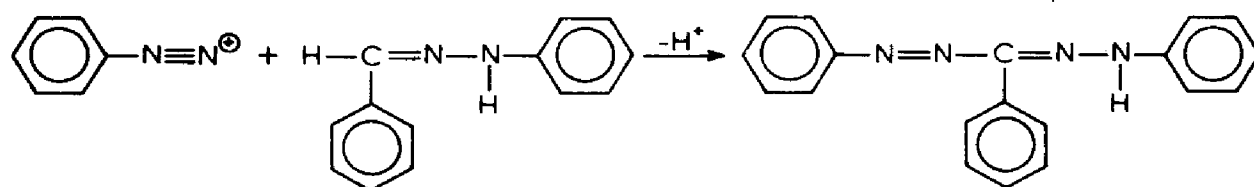
b.

2. Condensation of carbonic acid derivatives with arylhydrazines followed by dehydrogenation of the condensation product, e.g.:

$$2\ C_6H_5{-}NH{-}NH_2 + COCl_2 \longrightarrow C_6H_5{-}NH{-}NH{-}\underset{\underset{O}{\|}}{C}{-}NH{-}NH{-}C_6H_5 \xrightarrow{-H_2}$$

$$C_6H_5{-}NH{-}NH{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}C_6H_5 \rightleftharpoons C_6H_5{-}NH{-}N{=}\underset{\underset{OH}{|}}{C}{-}N{=}N{-}C_6H_5$$
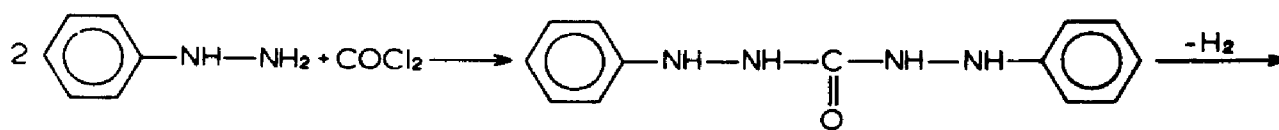
3. Synthesis by modification of other formazans, for example:

$$C_6H_5{-}N{=}N{-}\underset{\underset{CN}{|}}{C}{=}N{-}NH{-}C_6H_5 \xrightarrow{NaOH} C_6H_5{-}N{=}N{-}\underset{\underset{COOH}{|}}{C}{=}N{-}NH{-}C_6H_5$$
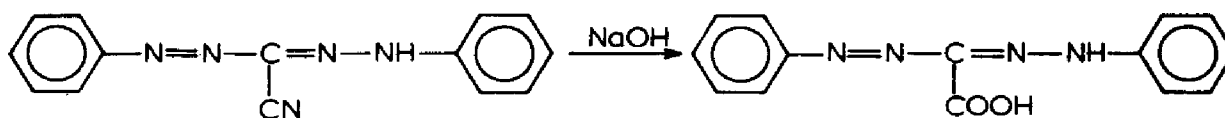
Excellent and comprehensive reviews on the preparation of formazans are given by Nineham (55 N) and Pütter (65 P).

2.2 PHYSICAL PROPERTIES OF FORMAZANS

Due to the organic character of formazans, these compounds show a reasonably good solubility in solvents like ethanol, benzene and chloroform. When a proper substitution has been made in the phenyl groups at N_1 or N_5 (Chapter 1) or at the carbon atom C_3 (for instance of -COOH, -OH or $-SO_3H$) a moderate water solubility of the formazan is obtained. This water solubility is enhanced when the groups mentioned are deprotonated by a base.

Solutions of formazans show strong absorption bands in the UV and in the visible region of the spectrum (55 N). Detailed studies of IR spectra of several formazans have been reported (59 F, 69 S, 69 O). Also NMR studies of some formazans are known (60 T, 68 M, 68 F).

Geometrical isomerism is possible with formazans. The structure of a formazan in solution is influenced by the nature of the solvent, by visible light irradiation and by the presence of catalysts (e.g. metal ions) (41 H, 53 K, 53 Ku).

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Two forms of formazans are observed: a "red" form and a "yellow" form. One assumes that in the "red" form the hydrogen atom is between N_1 and N_5 (see II), whereas in the "yellow" form the hydrogen atom of N_5 is rotated from N_1 (see III).
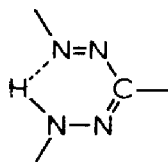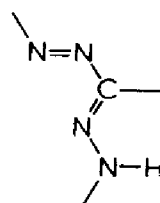
II   III

2.3 CHEMICAL PROPERTIES OF FORMAZANS

As our main interest in formazans is directed to their behaviour towards oxidizing reagents we will now give some remarks on these properties of formazans.

Formazans can be oxidized to the generally colorless tetrazolium salts by mild oxidizing reagents like isoamylnitrite, mercury(II) oxide, lead tetraacetate and halogenoamides (51 L, 41 K, 53 K, 55 N), e.g.:
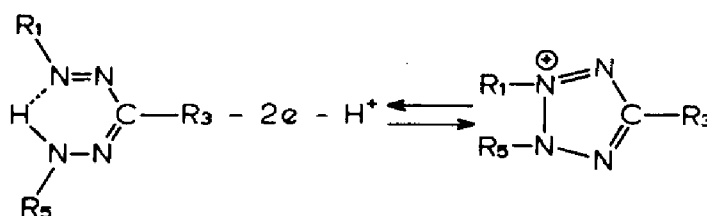
This process is reversible: hence tetrazolium salts can be reduced to their corresponding formazans by mild reducing agents like ammonium sulphide and alkaline solutions of ascorbinic acid or hydroxylamine (96 W, 53 K, 55 N).

Furthermore formazans can act both as acids and bases. For a limited number of formazans containing sulfonic or benzimidazole groups, protonation constants for the nitrogen atom possessing a lone pair and deprotonation constants of the imino group are published (62 T, 68 S, 69 I).

From these reports it can be concluded that formazans are weak acids and bases. Furthermore the simple formazans show a poor water solu-

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bility (usually $\approx 10^{-5}$ M), that is why it is understandable that no work on protonation and deprotonation constants has been done on the simple formazans.

Formazans show a reasonable resistance to strong alkaline solutions, although under these conditions they are liable to air oxidation (37 K). The formazan skeleton is destroyed (92 B, 55 N, 67 Sc) in concentrated mineral acid solutions (especially at elevated temperatures).

At last we will mention here the complex forming properties of formazans. With some metal ions formazans can form complexes. A number of classes can be distinghuished:

1. Unstable solid saltlike compounds can be formed by reaction of alkali metal ions and silver ions with formazans (92 Ba, 01 B, 46 R). The compounds obtained in this reaction are easily hydrolysed by water, and have the composition of one metal ion to one formazan molecule. Very little about this type of complexes is known; perhaps in this case the formazan acts as a monodentate ligand.

2. Complexes of formazans with divalent metal ions like copper(II), nickel(II), cobalt(II) and palladium(II) can be prepared (41 Hu, 60 E, 60 Z, 68 W), in which the metal ion is supposed to be surrounded by two formazan molecules in this way:

$$H_5C_6 \quad C_6H_5$$
$$| \qquad \quad |$$
$$N=N \quad N=N$$
$$H_5C_6-C \underset{N=N}{\overset{}{\Big(}} M \overset{}{\Big)} C-C_6H_5$$
$$N=N \quad N=N$$
$$| \qquad \quad |$$
$$H_5C_6 \quad C_6H_5$$
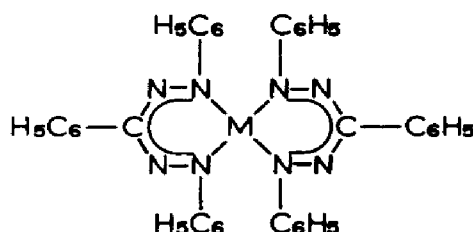
In these complexes the formazans behave like bidentate ligands.

3. By introducing of one complex forming group (e.g. -COOH or -OH) at the ortho position of one phenyl group on the outmost nitrogen atoms, complexes (45 B, 49 W, 68 W) of copper(II) and nickel(II) can be formed, having the composition of one metal ion to one formazan. The following structure is suggested for these complexes (57 K, 57 Ki, 57 F, 58 F, 60 E):
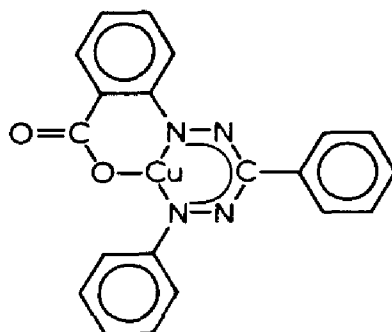
Complexes of this kind of formazans with cobalt(III) and chromium(III) can also be prepared (63 B, 64 S, 68 W). In these complexes (see VI) the metal ion is coordinatively saturated; the complex is negatively charged and consists of one metal ion and two formazan molecules.
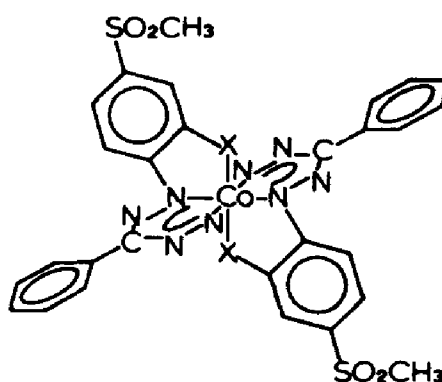
VI

In all the complexes of class three the formazan acts as a tridentate ligand.

4. Complex forming properties of formazans can be enhanced by introducing a complex forming group in the ortho position of both outmost phenyl groups. Complexes of this type show a very good acid resistance and can be used succesfully for dyeing purposes (68 W).

Of the complexes mentioned here we are especially interested in bi- and tridentate formazan complexes and for this reason we will discuss some properties of these complexes in detail. We refer to the review of Wizinger (68 W) for a complete survey of work done on formazan complexes.

The copper(II), nickel(II) and cobalt(II) complexes of type 2 and 3 are generally thought to be planar. This conclusion was drawn from magnetic

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susceptibility measurements (57 F, 58 F, 60 E, 60 I) performed on powders of nickel(II) and cobalt(II) complexes. This conclusion seems to be premature because the following arguments:

1. The nickel complexes were found to be diamagnetic, no diamagnetic correction for the ligand part of the molecule, however, was applied by the authors (57 F, 58 F, 60 E, 60 I).

   We have applied these corrections using Pascal constants and found μ_{eff} varying between 0.4 and 0.7 B.M.

2. Copper(II) complexes may be expected to retain one unpaired electron whatever the structure of these complexes is. Some of the copper(II)-formazan complexes have anomalous magnetic properties (57 K, 57 Ki, 58 K), probably due to interactions between neighbouring copper atoms, causing a lowering af magnetic moments (64 K). The same effect may also influence the magnetic moments of the nickel(II) complexes.

Cobalt(III) complexes of tridentate formazans with -COOH as complex forming group (VI) (in which the formazan rest is coordinated in 6,6 fused rings) can be separated in coordinative stereomers by chromatography over alumina; consequently a Pfeiffer (41 P) or sandwich structure (VII) must be adpoted for this complex.

No coordinative stereomerism could be demonstrated with 1 : 2 cobalt(III) complexes containing the formazan rest coordinated in 5,6 fused rings (with -OH as extra complex forming group) and a Drew-Pfitzner structure (39 D, 50 P) is adopted for those complexes (VIII) (63 B).

o nitrogen

● oxygen

VII   VIII
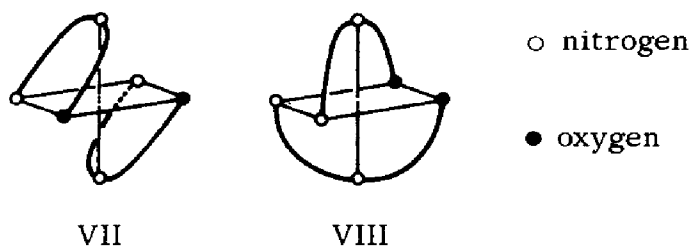
It is often suggested that the copper(II) and nickel(II) complexes of tridentate formazans can possess the unusual coordination number three (52 T, 68 W), which can be augmented to four by the addition of ammonia or pyridine, producing a notable change in spectrum (68 W, 52 T). This addition is not always possible and is influenced by the nature of the formazan

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and the complex forming group in the formazan. For instance: the tendency of the metal ion in the formazan complex to become four coordinated by addition of an ammonia or a pyridine molecule, is promoted when the extra complex forming group is -OH instead of -COOH. Substitution of the phenyl group at the C_3 position in the formazan by -CN has a similar effect. The causes of this tendency are not known. Undoubtedly steric factors must play a part, but this cannot explain all facts found, and inductive effects may be of importance too.

CHAPTER 3

EXPERIMENTAL

3.1 CHEMICALS

The following formazans were studied (referring to the formula below)

$$R_1$$
$$\backslash$$
$$N{=}N$$
$$H \quad \diagup \quad \diagdown$$
$$\diagdown C{-}R_3$$
$$N{-}N \diagup$$
$$\diagup$$
$$R_5$$
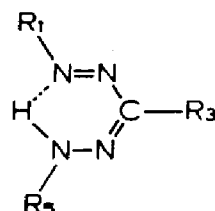
R_1	R_3	R_5	
C_6H_5	H	C_6H_5	1,5-Diphenylformazan (DPF)
C_6H_5	C_6H_5	C_6H_5	1,3,5-Triphenylformazan (TPF)
C_6H_5	COOH	C_6H_5	1,5-Diphenyl-3-carboxyformazan (DPF-C)
C_6H_5	C_6H_5	C_6H_4 - o - COOH	1,3-Diphenyl-5-o-carboxyphenylformazan (DPC$_o$-PF)
C_6H_5	C_6H_5	C_6H_4 - p - COOH	1,3-Diphenyl-5-p-carboxyphenylformazan (DPC$_p$-PF)

In parentheses the abbreviations used for the formazans.

TPF was obtained in purum quality from Fluka A.G.; DPF was synthesized according to Von Pechman (92 P); DPF-C according to Bamberger (02 B); for DPC$_o$-PF the method of Wizinger (49 W) was used; the same method was applied in the synthesis of DPC$_p$-PF, only 4-aminobenzoïc acid was taken instead of 2-aminobenzoïc acid.

Analysis (in parentheses the calculated percentages)

	C in %	H in %
DPF	69.82 (69,62)	5.43 (5.39)
DPF-C	62.71 (62.67)	4.56 (4.51)
DPC_o-PF	69.70 (69.75)	4.71 (4.65)
DPC_p-PF	68.59 (69.75)	4.64 (4.65)

For complex dissociation studies the copper(II) and nickel(II) complexes of DPC_o-PF were prepared in this way:

For the copper(II) complex a hot filtered solution of 2.4 g copper(II)-nitrate hexahydrate in 30 ml ethanol 96% was poured into a hot solution of 5 g DPC_o-PF in 400 ml ethanol 96%. The precipitate that instantly formed was filtered, washed thoroughly, first with water and then with ethanol 96%. After drying over phosphorus pentoxide for a night the compound was analysed for copper: 15.53% (theoretical value for 1 : 1 complex 15.65%).

For the nickel complex a hot filtered solution of 4 g nickel(II) nitrate hexahydrate in 30 ml ethanol 96% was mixed with a hot solution of 5 g DPC_o-PF in 300 ml ethanol 96%. After refluxing for three hours, the precipitate formed was filtered, washed thoroughly with water and ethanol 96%. After drying over phosphorus pentoxide for a night the complex was analysed for nickel: 14.48% (theoretical value for a 1 : 1 complex 14.64%).

Sodium hexacyanoferrate(III) was prepared by chlorine oxidation (66 C) of sodium hexacyanoferrate(II), to which a few drops of 2 N sodium hydroxide had been added. The reddish brown solution was poured into twenty times its volume of ethanol. The precipitate was filtered, washed with ethanol, dried and analysed. Analysis yielded (in parentheses the calculated percentages).

$Fe(CN)_6^{3-}$	66.56%	(66.87%)
Fe	17.86%	(17.62%)
N	27.17%	(26.52%)

All other reagents used were reagent grade.

3.2 REACTION CONDITIONS

General

On account of the poor water solubility of formazans and their complexes, all work was carried out in a medium consisting of an ethanol (45.5 wt %) - water mixture. Whenever possible the reactions were also performed in water.

Ionic strength was kept constant (0.09) either by adding ammonium nitrate or by adding a mixture of ammonium nitrate and potassium nitrate or sodium nitrate.

As many equilibria are present in the solutions under investigation, of which temperature dependencies are hardly known under the conditions used in the experiments, it did not seem fruitful to us to perform oxidation as well as complex formation studies at more than one temperature.

All solutions were intensively treated with nitrogen to prevent air oxidation of the formazans.

3.3 OXIDATION

Acidic solutions (pH $<$ 2.0) of the formazans under study are instable. The oxidations performed in the pH traject 3.0 - 6.0 are found to be very slow. For these reasons the reactions were performed under alkaline conditions; ammonia was used as a base giving as a further advantage that no hydrolysis occurred of the copper(II) solutions. As a result it was necessary to work in a pH traject between pH 8.0 and 11.0 (A potassium hydroxide titration of the carboxylic formazans proved the carboxylic group to be completely dissociated under these conditions). Under these circumstances the decrease of the formazan concentration could be observed photometrically and the reactions ended in a reasonable time.

As the oxidation reaction was found to liberate hydrogen ions it was inevitable to buffer the solutions; to this end and for keeping ionic strength constant, ammonium nitrate was added.

The oxidations were performed in this way:
Solutions containing a fixed concentration of the formazan (usually between $(0.9 - 4.0) \times 10^{-5} M$) were treated with a ten- to fiftyfold excess of the oxidizing reagent. The varying concentrations were obtained by diluting more

concentrated stock solutions of the formazans and potassium hexacyano-ferrate(III) or copper(II) ammine complexes. The stock solutions were prepared freshly every day in order to prevent air oxidation of the formazan (37 K) and hydrolysis of the hexacyanoferrate(III) (66 C) and the copper(II) solutions. Temperature was kept constant during the reactions $(25.0 \pm 0.1)°C$.

The decrease in concentration of the formazans was followed at 435 mμ for DPF, DPC_o-PF and DPF-C and at 485 mμ for TPF and DPC_p-PF. Because the hexacyanoferrate(III) anion also showed an appreciable absorption at the wavelengths used for measuring the formazan concentrations, the reference was made up to contain a compensating quantity of potassium hexacyano-ferrate(III). When the formazans were oxidized by copper(II) solutions no compensation for copper(II) ammine complexes was necessary.

3.4 COMPLEX DISSOCIATION AND FORMATION STUDIES

In the experiments on dissociation and formation of nickel(II) and copper(II) complexes of DPC_o-PF the same medium was used as in the oxidation experiments.

The composition of the metal complexes in the ammoniacal solutions (45.5 wt % ethanol) was studied by the continuous variation method (28 J), in a constant sum concentration - metal ion plus formazan - of 1.0×10^{-4}M. For each system seven different mole fractions were prepared of which the absorption spectra were measured at regular time intervals. After completion of the reaction - one week for the nickel and one day for the copper complex - Job curves were plotted for the wavelength of maximum complex absorbance (corrected for the reagent contribution): $\lambda = 660$ mμ (Ni) and 550 mμ (Cu). The ammonia concentration was also varied: 0.133 and 0.333 M for the nickel and 0.1, 0.2, 0.3, 0.4 and 0.5 M for the copper system.

The experiments on dissociation of the complexes were carried out in this way:
To aliquots of solutions of the copper complex in ethanol 96%, in which solvent no appreciable decomposition was found to occur, a measured portion cf water as added containing the various chemicals (NH_4NO_3, NH_4NO_3 + KNO_3 resp. NH_3) to make up the desired medium. The nickel complex was dissolved directly into the selected medium.

The experiments were performed at four different concentrations of the complexes $(1.0 - 4.0) \times 10^{-5}$M for the copper and $(6.0 - 10) \times 10^{-5}$M for

the nickel complex and with at least four different concentrations of ammonia. The ammonium nitrate concentration was also varied, while the ionic strength was kept constant (0.09) by adding potassium nitrate.

The concentration of the complexes was determined spectrophotometrically using the separately determined absorbancy indices for the complexes and the formazan. No correction had to be made for the metal ammine complexes, because their absorbances could be neglected as compared with the absorbancies of the formazan and the formazan complexes at the wavelengths used for measurements (455 mμ and 550 mμ for the copper case and 660 mμ in the nickel case).

In the formation experiments exactly the same circumstances have been used as in the decomposition experiments using equal concentrations of the formazan and the metal salt.

The oxidation of the complexes by hexacyanoferrate(III) ions has been done under the same conditions as those used in the oxidation of the formazans by hexacyanoferrate(III) ions.

All studies on complex dissociation and formation have been done at $(23 \pm 1)°C$.

3.5 STABILITY CONSTANTS OF COPPER(II) AMMINE COMPLEXES

As yet these constants have not been determined in (45.5 wt %) ethanol - water (64 Si). By means of the pH method of Bjerrum (41 B) the stepwise stability constants for the copper(II)-ammine system in ethanol (45.5 wt %) water containing 0.09 M NH_4NO_3 have been determined at $(25.0 \pm 0.1)°C$.

3.6 APPARATUS

In observing the reactions an Optica CF 4 DR of a Zeiss PM QII spectrofotometer was used, both equipped with thermostated, stoppered 10 or 40 mm glass cells.

The pH was measured with an E.I.L. 46 A pH meter fitted with a G.H.S. N 33 glass electrode and a R.J. 23 calomel reference electrode.

For least-squares calculations and variation analysis an I.B.M. 1130 computer was used.

CHAPTER 4

KINETICS OF THE OXIDATION OF SOME FORMAZANS BY THE HEXACYANOFERRATE (III) ANION

In this Chapter the oxidation of several formazans by the hexacyano-ferrate (III) anion (an outer sphere oxidizing reagent) is discussed.

The reactions are performed in water as well as in ethanol (45.5 wt%) - water mixtures at a temperature of $25°C$ and at an ionic strength of 0.09 (fixed by adding ammonium nitrate to the solutions).

The influence of the ammonium ion concentration on the reaction rate was determined by a variation of the ammonium nitrate concentration. In these experiments the ionic strength was kept constant by adding sodium nitrate. Under these conditions two competing reactions were found: the oxidation of the formazan anion by the $Fe(CN)_6^{3-}$ and by the $NH_4Fe(CN)_6^{2-}$ anion. The predominant reaction was found to be the oxidation of the formazan anion by $Fe(CN)_6^{3-}$.

For detailed reaction conditions we refer to Chapter 3.

4.1 RESULTS

A. Spectra

The visible absorption spectra of the formazans (in concentrations of $(1.0 - 5.0) \times 10^{-5}M$) were recorded in the same medium as that used for the redox reactions (Chapter 3). In ethanol (45.5 wt%) water mixtures, DPF, DPF-C and DPC_o-PF had an absorption maximum between 435 and 455 mμ; TPF and DPC_p-PF had a maximum at 485 mμ. In water only the absorption maximum of DPC_p-PF changed to 435 mμ, the other maxima remained in the same position.

B. Redox kinetics at constant ammonium nitrate concentration

Of a solution of formazan, potassium hexacyanoferrate (III), ammonia and ammonium nitrate in water or a water - ethanol mixture, the formazan absorbance was measured at 435 or 485 mμ . A logarithmic plot of this absorbance versus time showed straight lines at various concentrations of the reactants, but at constant ammonium nitrate concentration (0.09 M). Figure 4_1 shows some representative plots.
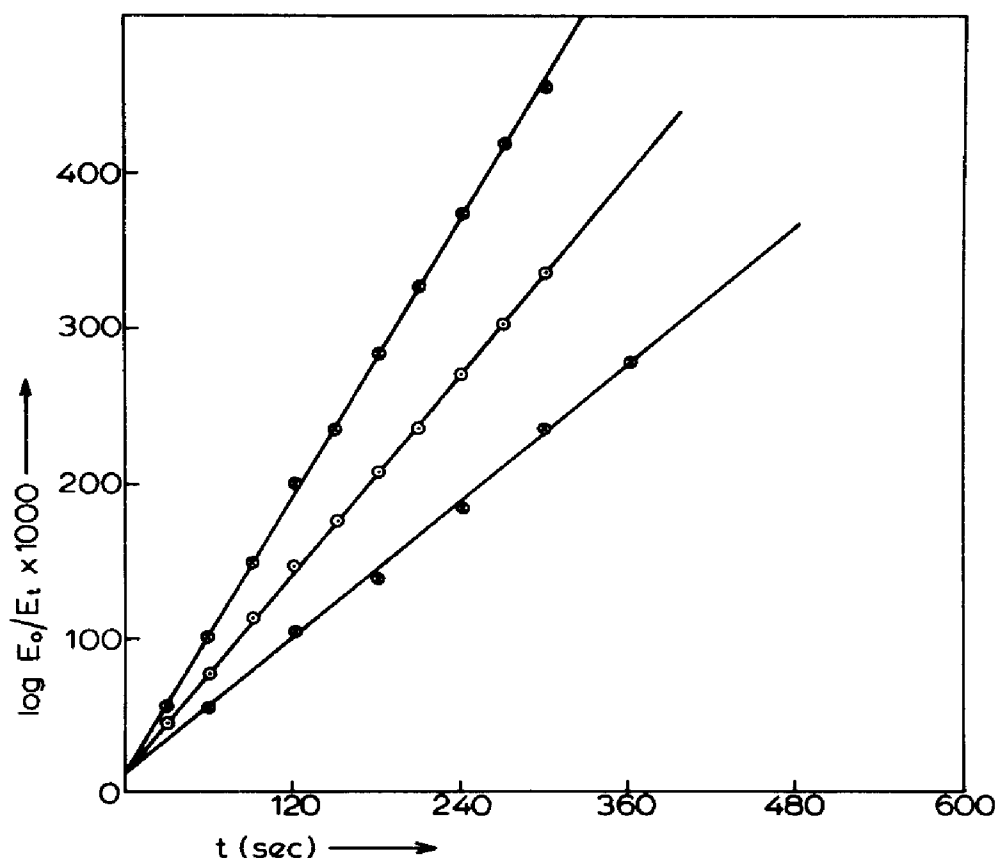
Figure 4_1.

Plots of log Eo/Et versus time for TPF (3.6 x 10^{-5}M) in a 45.5 wt % ethanol - water mixture at constant ammonium nitrate concentration (0.09 M) and ammonia concentration (0.604 M).

+ $K_3Fe(CN)_6$ = 8.0 x 10^{-4}M   x $K_3Fe(CN)_6$ = 16.0 x 10^{-4}M

. $K_3Fe(CN)_6$ = 12.0 x 10^{-4}M

This result proves the reactions to be first order in the formazan. In this Chapter we will denote the undissociated formazan by FNH, the dissociated formazan by FN$^-$ and concentrations by (- - - -).

Defining the rate of the reaction as:

$$s_{Fe} = - \frac{d\,(FNH)}{dt} \tag{1}$$

The former result means

$$s_{Fe} = k'_{Fe} \cdot (FNH) \tag{2}$$

where k'_{Fe} is computed from the logarithmic plots. The influence of the excess potassium hexacyanoferrate(III) concentration $(Fe\,(CN)_6^{3-})_t$ (t = total) and the ammonia concentration (NH_3) on k'_{Fe} could be expressed by:

$$k'_{Fe} = k_{Fe} \cdot (NH_3) \cdot (Fe\,(CN)_6^{3-})_t \tag{3}$$

Experimental results for k_{Fe} are given in Table 4_1.

Table 4_1.

Reaction conditions and rate constants[*] (in units $sec^{-1} \cdot M^{-2}$) for the formazan-hexacyanoferrate(III) oxidations in 0.09 M ammonium nitrate.

DPF[a**)]	0.9	1.35	1.80	
114	119.6	115.4	113.7	
152	119.6	113.3	117.4	
229	119.6	117.3	118.6	
305	112.5	111.9	111.0	
TPF[a]	8.0	12.0	16.0	20.0
483	3.63	3.68	3.67	3.70
604	3.60	3.57	3.59	3.69
724	3.46	3.48	3.45	3.53
966	3.71	3.52	3.46	3.58
DPF-C[a]	4.32	5.76	7.20	
381	10.63	10.98	10.94	
305	10.69	10.53	10.56	
228	11.18	11.40	10.79	
191	11.15	10.84	11.31	
DPF-C[b]	4.32	5.76	7.20	
3.8	4094	3661	3924	
5.7	3238	3339	3404	
7.6	3451	3461	3458	
11.4	3401	3296	--	

$DPC_p\text{-}PF^a$	6.0	10.0	14.0
477	2.42	2.39	2.33
286	2.17	2.30	2.26
$DPC_p\text{-}PF^b$	4.0	6.0	8.0
1.91	1370	1461	1431
0.76	1539	1513	1433
$DPC_o\text{-}PF^b$	4.0	10.0	20.0
327	17.4	18.9	--
167	18.0	18.0	18.3
67	19.9	18.5	--

*) For each formazan k_{Fe} has been given as a function of: horizontally $(Fe(CN)_6^{3-})$ in units $10^{-4}M$ and vertically (NH_3) in units $10^{-3}M$.

**) a. The formazan is dissolved in 45.5 wt % ethanol in water;

b. The formazan is dissolved in water.

The average k_{Fe} values from Table 4_1 are given in Table 4_2.

Table 4_2.

Reaction conditions and rate constants (in units $sec^{-1} . M^{-2}$) for the formazan-hexacyanoferrate (III) oxidations in 0.09 M ammonium nitrate.

Formazan	(FNH) *)	$(Fe(CN)_6^{3-})$ **)	(NH_3) ***)	Solvent ****)	k_{Fe}
DPF	0.9	0.9- 1.8	114-305	a	116 ± 3
TPF	3.6	8.0-20.0	302-966	a	3.6 ± 0.1
DPF-C	3.6	4.3- 7.2	191-382	a	11.0 ± 0.3
DPF-C	3.6	4.3- 7.2	3.8-11.4	b	3520 ± 250
$DPC_p\text{-}PF$	4.0	6.0-14.0	286-477	a	2.3 ± 0.1
$DPC_p\text{-}PF$	4.0	4.0- 8.0	0.76-1.91	b	1450 ± 50
$DPC_o\text{-}PF$	4.0	10.0-30.0	66-328	b	18.3 ± 0.9

*) (FNH) in units $10^{-5}M$.

**) $(Fe(CN)_6^{3-})$ in units $10^{-4}M$.

***) (NH_3) in units $10^{-3}M$.

****) a. 45.5 wt % ethanol in water; b. water.

The simplest explanation of the (NH_3) dependence of the reaction rates is that the hexacyanoferrate(III) ion oxidizes the weakly acidic formazans as the anion: FN^- (of which only a very small amount can be present (Chapter 2)). In this case the oxidation of the "neutral" formazans can be neglected, since no (NH_3) independent part is observed. The term "neutral" only refers to the dissociation of the iminogroup, the carboxylic acid group being completely dissociated (see Chapter 3).

This interpretation implies the acid dissociation to be rapid, compared with the oxidation of the anion. The very rapid proton exchange between the terminal nitrogen atoms in some formazans points in this direction (68 F).

Only for DPC_0-PF in 45.5 wt % ethanol - water mixtures the oxidation was found to be independent of (NH_3):

$$\frac{k'_{Fe}}{(Fe(CN)_6^{3-})} = (4.5 \pm 0.1) \times 10^{-3} \ sec^{-1}.M^{-1}$$

Consequently this formazan is oxidized in the "neutral" form.

In order to investigate the effect of dielectric constant of the reaction medium, the percentage of ethanol was varied between 0 and 45.5 wt % for DPF-C.

Results in k_{Fe} are given in Table 4_3.

Table 4_3.

Rate constants (in units $sec^{-1}.M^{-2}$) for the DPF-C $Fe(CN)_6^{3-}$ reaction as a function of the percentage of ethanol, at constant ammonia, ammonium nitrate and hexacyanoferrate(III) concentrations.

%	k_{Fe}	%	k_{Fe}
0	3381	22.1	188
4.0	1836	29.1	54
6.6	1194	45.5	11
14.0	512		

C. Redox kinetics at varying ammonium nitrate concentration but at constant ionic strength

It is known (67 Sw, 61 D, 67 C) that univalent ions have a considerable augmenting effect on the reaction rate of anion-anion redox reactions. The exact role of the univalent ion in the activated complex is not clear (67 K, 60 Ln, 65 S). The metal ion may act as an actual bridge for electron transfer (67 K) or simply as a means of bringing together the two negatively charged ions (in casu FN^- an $Fe(CN)_6^{3-}$). This means that the cation NH_4^+ may influence the rate considerably. No study on ion pairing between ammonium and hexacyanoferrate(III) has been reported. Ion pairing occurs (37 H, 50 J) between K^+ and $Fe(CN)_6^{3-}$ and in all probability not between Na^+ and $Fe(CN)_6^{3-}$ (67 Sw). The NH_4^+ effect on the reaction rates can only be evaluated by varying the NH_4^+ concentration. This has been done for TPF in the following way: The variation of k_{Fe}' with varying (NH_4^+) at constant ionic strength (addition of Na^+ or K^+) and constant pH (Figure 4_2) proves the effect of ion pairing on the oxidation rates in the NH_4^+-$Fe(CN)_6^{3-}$ system to be approximately the same as it is in the K^+-$Fe(CN)_6^{3-}$ system.

Figure 4_2.
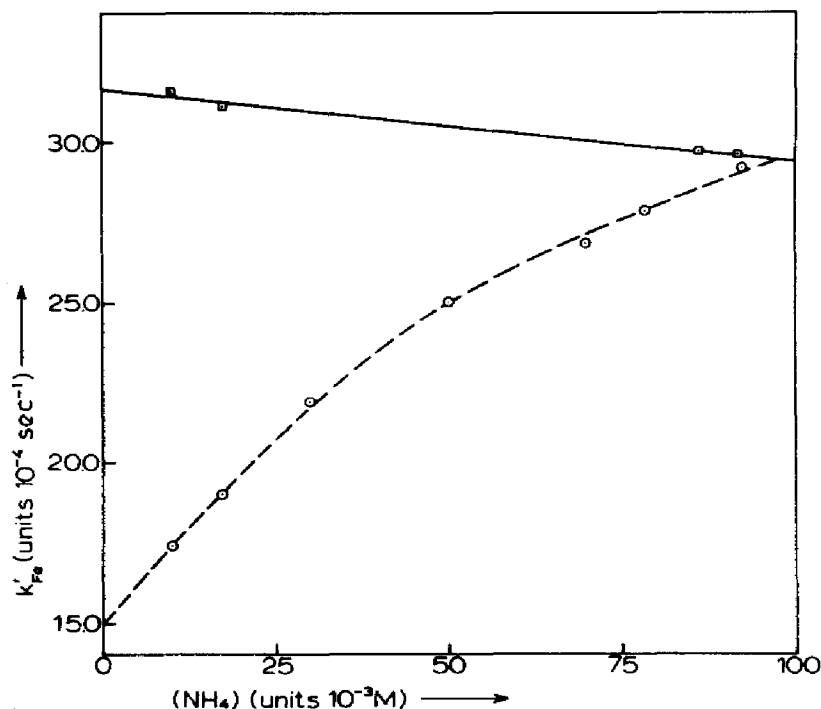
Reaction rate k_{Fe}' for the hexacyanoferrate(III) oxidation of TPF (3.6 x 10^{-5}M) as a function of (NH_4) in 45.5 wt % ethanol water mixtures. The quotient of the ammonia concentration and the ammonium nitrate concentration is 6.42.
Solid line : $(K_3[Fe(CN)_6]) = 12$ x 10^{-4}M; $(K) + (NH_4) = 0.1$ M
Dotted line: $(Na_3[Fe(CN)_6]) = 12$ x 10^{-4}M; $(Na) + (NH_4) = 0.1$ M

These results mean that in the oxidation of the anion FN^- two competing reactions must be considered:

$$Fe + FN \xrightarrow{\ k_{1Fe}\ }$$
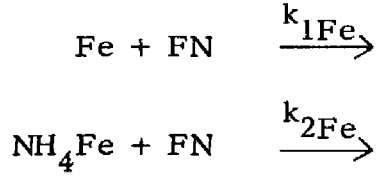
$$NH_4Fe + FN \xrightarrow{\ k_{2Fe}\ }$$

Here and in the continuation of this section ionic charges will be dropped.

$$Fe = Fe(CN)_6^{3-}.$$
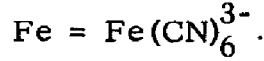
The rate constants of equation (3) can now be decomposed as follows:

$$k'_{Fe}\cdot(FNH) = k_{1Fe}\cdot(Fe).(FN) + k_{2Fe}\cdot(NH_4Fe).(FN) \qquad (4)$$

Defining the concentration constants:

$$\alpha = \frac{(FN).(NH_4)}{(FNH).(NH_3)} \ ; \qquad \beta = \frac{(NH_4Fe)}{(NH_4).(Fe)}$$

and the pseudo constant

$$\alpha' = \frac{(FN)}{(FNH)}$$

then when working at constant ionic strength and constant $\dfrac{(NH_3)}{(NH_4)}$ (adjusted by fixing the pH) and varying (NH_4), k'_{Fe} of equation (4) can be expressed as:

$$\frac{k'_{Fe}}{(Fe)_t} = k^*_{Fe} = \frac{k_{1Fe}\cdot\alpha' + k_{2Fe}\cdot\alpha'.\beta.(NH_4)}{1 + \beta.(NH_4)} \qquad (6)$$

When (NH_4) is very small, the amount of NH_4Fe is negligible compared with $(Fe)_t$ and equation (6) reduces to (after neglecting terms in $(NH_4)^2$ and higher):

$$k^*_{Fe} = k'_{1Fe} + (k'_{2Fe} - k'_{1Fe}.\beta).(NH_4) \qquad (7)$$

with $k'_{1Fe} = k_{1Fe}\cdot\alpha'$ and $k'_{2Fe}\cdot\alpha'.\beta$.

Indeed plots of k'_{Fe} versus (NH_4) (of which Figure 4_2 gives a representative one for TPF) approach straight lines at low (NH_4). From these

plots k'_{1Fe} and $(k'_{2Fe} - k'_{1Fe} \cdot \beta)$ can be obtained. At higher (NH_4) the plot deviates from the initial straight line; in this case we get from (6):

$$\frac{k^*_{Fe} - k'_{1Fe}}{(NH_4)} = k'_{2Fe} - k^*_{Fe} \cdot \beta .$$ (8)

Plotting the left hand term of (8) versus k^*_{Fe} gives β (see Figure 4_3).
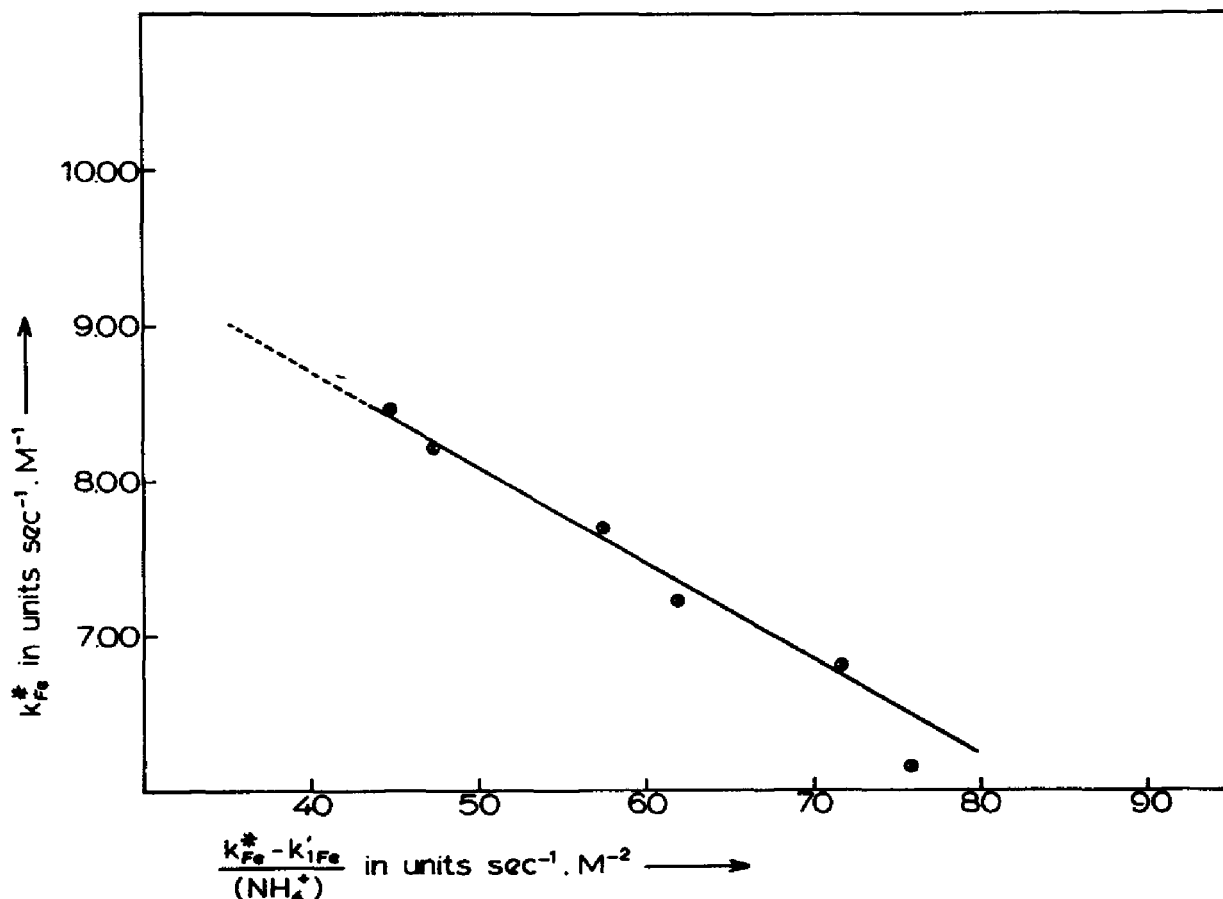
Figure 4_3.

Plot of $\dfrac{k^*_{Fe} - k'_{1Fe}}{(NH_4)}$ versus k^*_{Fe} for DPF, ionic strength 0.10, $\dfrac{(NH_3)}{(NH_4)} = 0.66$,

$(Na_3 \left[Fe(CN)_6 \right]) = 12.0 \times 10^{-4}$ M.

In this way values of $\dfrac{k'_{1Fe}}{k'_{2Fe}} = \dfrac{k_{1Fe}}{k_{2Fe} \cdot \beta}$ and of β have been obtained for three formazans at different ionic strengths.

Experimental conditions and results are in Table 4_4.

Rate constants and reaction conditions[*] for experiments with variation of the ammonium nitrate concentration.

Formazan	Ionic Strength	$\dfrac{(NH_3)}{(NH_4)}$	k'_{1Fe}	$(k'_{2Fe} - k'_{1Fe} \cdot \beta)$	β	$\dfrac{k_{2Fe}}{k_{1Fe}}$
TPF	0.10	6.42	1.2	21	14	2.2
TPF	0.15	7.60	1.7	24	11	2.3
DPF	0.075	0.66	3.7	96	20	2.3
DPF	0.10	0.66	5.4	74	17	1.8
DPF-C	0.10	0.52	6.6	17	18	7.5

[*] DPF and TPF were dissolved in ethanol (45.5 wt %)-water, DPF-C was dissolved in water; (FNH) $= 3.6 \times 10^{-5}$M; $(Na_3[Fe(CN)_6]) = 12.0 \times 10^{-4}$M.

The results in Table 4_4 have a semiquantitative character, because of the difficult nature of the experiments.

4.2 DISCUSSION

The reaction rates measured in water differ considerably from the rates measured in water - ethanol mixtures, as can be seen from Table 4_2 and 4_3. The effect of ethanol addition on the rates may be explained from the corresponding change in dielectric constant. Table 4_3 shows a smooth change, indeed. The ionic strength is too high (61 F) to connect this behaviour quantitatively with the proposed reaction mechanism.

The rate constants for the different formazans can only be compared in 45.5 wt % ethanol - water mixtures, in which all formazans could be dissolved. Here k_{Fe} increases in the order:

$$DPF > DPF - C > TPF \approx DPC_p - PF >> DPC_o - PF$$

The rate constants for the first four formazans are all of the same order of magnitude, whereas the rate constant for DPC_o-PF is extremely small as compared to the other rate constants. Furthermore the rate constant of DPC_o- PF is independent of the ammonia concentration; this means that under these circumstances no oxidation of the DPC_o-PF anion is observed. The analogous para substituted DPC_p-PF, however, is oxidized as the anion with

$k_{Fe} = 2.33$ comparable with k_{Fe} for TPF (3.60). The independence of k'_{Fe} for DPC_o-PF from the ammonia concentration may therefore be ascribed to a steric ortho effect: an internal proton bridging between the terminal nitrogen atom and the anionic ortho-carboxylic group in the formazan. This proton bridging will depress the N-H dissociation constant and since the formazan anion is supposed to be responsible for the pH dependent part of the oxidation reaction, this part of the reaction will be much slower for DPC_o-PF.

Some more can be said about the sequence of the first four constants. As is known formazans show (Chapter 3) geometrical isomerism; two of the possible isomers are relatively stable, an open "yellow" and a closed "red" form, the latter having proton bridging between the terminal (1,5) N-atoms. As the names already suggest these two stable forms may be identified by their visible absorption spectra: the yellow form tends to have an absorption band around 430 mμ, while the red form has a band at 490 mμ. From the spectra it can be concluded that DPF, DPF-C and DPC_o-PF are in the yellow form and TPF and DPC_p-PF are in the red form under the conditions used in the experiments. Thus comparing the reaction rates of DPF and TPF, DPC_p-PF there are indications that the yellow form (DPF) is somewhat more easily oxidized than the red form (TPF, DPC_p-PF).

Since oxidation is proceeded by acid dissociation the cause of the difference observed may also be that the red form is a weaker acid on account of its proton bridging capacity. The difference in rate constant between DPF and DPF-C (both being in the yellow form) can possibly be ascribed to proton bridging in DPF-C (see Chapter 2 formula III).

In varying the ammonium nitrate concentration the ratio $\dfrac{k_{2Fe}}{k_{1Fe}}$ is found to be greater than one for all formazans. As discussed earlier (Chapter 4.1 C) the enhancing effect of a cation on a anion-anion reaction may be expected.

The values found for β are of the same order as the stability constants for the K^+ - $Fe(CN)_6^{3-}$ ion associate in water.

The rate constants obtained in this Chapter refer to the first one-electron transfer step giving a formazan radical. Most probably this step is followed by a very rapid consecutive reaction forming the tetrazolium salt.

CHAPTER 5

KINETICS OF COMPLEX FORMATION AND COMPLEX DISSOCIATION OF 1,3-DIPHENYL-5-o-CARBOXYPHENYL FORMAZAN WITH NICKEL(II) AND COPPER(II) IONS.

In this Chapter the complex formation between 1,3-Diphenyl-5-o-carboxyphenylformazan $(DPC_o\text{-}PF)$ and nickel(II) or copper(II) in ammoniacal ethanol (45.5 wt %)-water mixtures will be discussed. This formazan was chosen because it forms complexes with copper(II) and nickel(II), at a measurable rate, while on the other hand the copper complex is not oxidized by an excess of copper(II). The system metal ion + formazan could be described by way of an equilibrium. A detailed reaction mechanism, consistent with the experimental findings, will be worked out. Also attention will be paid to the hexacyanoferrate(III) oxidation of the copper(II) and the nickel(II) complexes of $DPC_o\text{-}PF$.

For the reaction conditions we refer to Chapter 3.

5.1 RESULTS

A. Stability constants of the copper(II) ammine complexes

In the reaction medium used for the complex formation experiments copper(II) and nickel(II) occurs as ammine complexes $(M (NH_3)_n(H_2O)_{6-n})^{2+}$. In order to separate the contributions of the various ammine complexes to the measured reaction rates, it is necessary to know the values of the corresponding stepwise stability constants of these complexes. In the literature no values of these constants measured under the conditions used in the ex-

34

periments, are mentioned. It may, however, be assumed that the values measured in 45.5 wt % ethanol-water do not differ much from those measured in aqueous solutions, because no neutralisation of charge is involved in the complex formation (61 R, 61 F). This assumption has been tested by a determination of the copper(II) ammonia constants in 45.5 wt % ethanol-water (see Chapter 3). The values obtained were:

$$\log K_1 = 4.26 \ (4.06)$$
$$\log K_2 = 3.46 \ (3.41)$$
$$\log K_3 = 2.80 \ (2.80)$$
$$\log K_4 = 2.13 \ (2.04)$$

K_n denotes the stepwise stability constant (61 R, 41 B) for the complex $Cu(NH_3)_n(H_2O)_{6-n}^{2+}$; in parentheses we have given the values obtained by Bjerrum for aqueous solutions containing 0.09 M ammonium nitrate. Because of the small differences between the two sets, the original Bjerrum values were used in our calculations.

B. Spectra

The spectra of the copper and nickel complexes of DPC_o-PF have been recorded in ethanol 96% and in ethanol (45.5 wt %)-water, with and without 0.09 M NH_4NO_3 and in varying concentrations of ammonia (0.1 to 0.4 M). Changes in the medium had only minor effects on the initial absorption maxima and the molar absorbancy indices of the complexes:

Cu : $\lambda_{max} = 550 \pm 5 \ m\mu$

$\epsilon_{max} = (16.69 \pm 0.20) \times 10^3 M^{-1}.cm^{-1}$

Ni : $\lambda_{max} = 660 \pm 5 \ m\mu$

$\epsilon_{max} = (6.23 \pm 0.18) \times 10^3 M^{-1}.cm^{-1}$

C. Composition of the metal complex in solution

The composition of the nickel(II) and copper(II) complexes of DPC_o-PF in ammoniacal solution (45.5 wt %) ethanol-water was studied by the continuous variation method (28 J).

After completion of the reaction "Job curves" (28 J) were plotted for the wavelengths of maximum absorbance. The plots (of which Figure 5_1 gives a representative one for copper) had a symmetrical or nearly symmetrical maximum for the mole proportion M^{2+} : DPC_o-PF = 1 : 1. This result proves the mole proportion of these complexes in the solution to be the same as in the solid state.
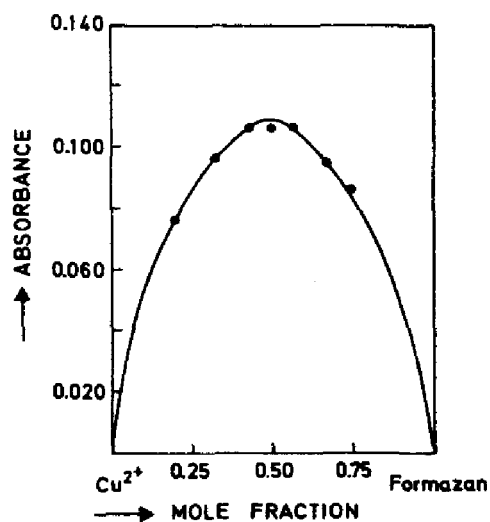
Figure 5_1.

Corrected (61 R) continuous variation plot for the system Cu^{2+} - DPC_o-PF;

(Cu^{2+}) + $(DPC_o$-PF) = 10^{-4}M, (NH_3) = 0.4 M; λ = 550 mμ.

D.1 Reaction kinetics

The kinetic work on the complexes was started with a preliminary survey of the pH dependence of the decomposition rates for the nickel and the copper complexes of DPC_o-PF, the results of which will be given here, because of their relevance for interpreting the results of ammonia containing solutions.

Both complexes were found to be rapidly destroyed by acid. For pH > 8.0 the rate of decomposition of the copper complex was nearly independent of the pH, when the pH was adjusted with KOH (pH = 9-11): The first 10% decomposition obeyed a first order law with k = 1.8 x 10^{-5}sec^{-1}. The rate increased considerably (10 - 100 fold) on using NH_3 to make up the pH. The rate also increased on the addition of ammonium nitrate; other salts (sodium and potassium nitrate) did not show this effect.

The rate of decomposition of the nickel complex in the absence of ammonium nitrate depended on the pH, whether it had been made up by adding potassium hydroxide or ammonia. Addition of ammonium nitrate (but not of potassium or sodium nitrate) to solutions of the nickel complex increased the reaction rate about 10 fold.

For these reasons the reaction rates have been determined at varying ammonia and ammonium nitrate concentrations, as has been described (Chapter 3).

The final results obtained could be interpreted (61 F) by assuming a pseudo first order decomposition and a pseudo second order formation reaction with rates:

$$s' \text{ (formation)} = k' . (M)_{tot} . (HFo) \tag{1}$$

$$s \text{ (decomposition)} = k . (MFo) \tag{2}$$

MFo denotes the metal formazan complexes, HFo the parent ligand (DPC_o-PF) (with a dissociated - COOH group (Chapter 4)), (--) denotes a concentration. $(M)_{tot}$ denotes the total metal ion concentration present as metal ammine complexes. For convenience ionic charges have been dropped. The k and k' values have been obtained by applying the usual analysis for this type of reversible reaction (61 F).

In our case (i.e. when the concentrations of ammonia and ammonium nitrate are kept constant) k and k' are pseudo constants and can be determined by the following procedure:

$$MFo \underset{k}{\overset{k'}{\rightleftarrows}} M_{tot} + HFo$$
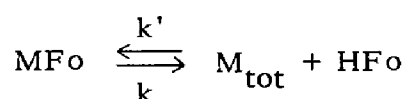
Then

$$-\frac{d(MFo)_t}{dt} = k . (MFo)_t - k' . (M_{tot})_t . (HFo)_t \tag{3}$$

and for the decomposition reaction at t = o

$$(M_{tot})_o = (HFo)_o = o$$

then

$$(HFo)_t = (M_{tot})_t = (MFo)_o - (MFo)_t \tag{4}$$

Introducing the equilibrium concentration $(MFo)_e$ and using equation (3) and (4) gives:

$$k \cdot (MFo)_e = k' \left\{ (MFo)_0 - (MFo)_e \right\}^2 \tag{5}$$

now substitution of (5) into (3) gives:

$$-\frac{d(MFo)_t}{dt} = k \cdot \left[(MFo)_t - \frac{(MFo)_e}{\left\{ (MFo)_0 - (MFo)_e \right\}^2} \cdot \left\{ (MFo)_0 - (MFo)_t \right\}^2 \right] \tag{6}$$

which can also be written as:

$$-\frac{d\left\{ (MFo)_t - (MFo)_e \right\}}{dt} = k \cdot \frac{(MFo)_e \cdot \left\{ (MFo)_t - (MFo)_e \right\}}{(MFo)_0 - (MFo)_e{}^2} \cdot$$

$$\cdot \left[\frac{\left\{ (MFo)_0^2 - (MFo)_e^2 \right\}}{(MFo)_e} - (MFo)_t - (MFo)_e \right] \tag{7}$$

When proper substitutions have been made the integrated result is:

$$\ln \frac{(MFo)_0^2 - (MFo)_e \cdot (MFo)_t}{\left\{ (MFo)_t - (MFo)_e \right\} (MFo)_0} = k \cdot \left[\frac{(MFo)_0 + (MFo)_e}{(MFo)_0 - (MFo)_e} \right] \cdot t \tag{8}$$

From this equation k can be evaluated with the help of a graph (of which Figure 5_2 gives a representative example). The rate constant k' then follows from equation (5).
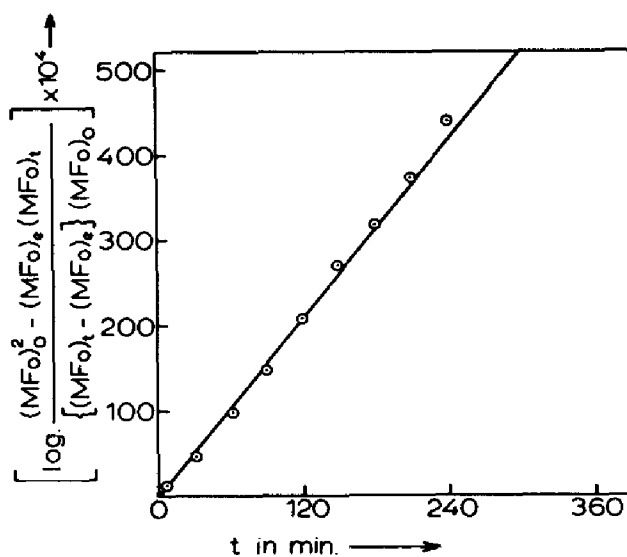

Figure 5_2.

Plot of log. $\dfrac{(MFo)_0^2 - (MFo)_e \cdot (MFo)_t}{\left\{ (MFo)_t - (MFo)_e \right\} \cdot (MFo)_0}$ versus time for copper complex of DPC_0-PF

$(2.0 \times 10^{-5} M)$ at $(NH_3) = 0.163$ M and $(NH_4^+) = 0.09$ M.

For complex formation when, $(MFo)_0 = o$ and if $(M_{tot})_0$ and $(HFo)_0$ have the same concentrations, a similar derivation can be made resulting into equations from which k and k' can be calculated.

It is clear that the values of k. and k' are dependent upon the medium as the results in Table 5_1 and Table 5_2 show.

The values obtained for $(NH_4) = 0.09$ M, the medium selected for the redox reactions, have been obtained by averaging over at least three independent runs.

By way of comparison, other NH_4^+ concentrations have also been used. Only a few formation rates for NiFo have been obtained from decomposition experiments; in the other experiments only the decomposition rate constant k was calculated from the first 10% reaction obeying a first order rate law. The cause of this procedure is the slowness of the reaction.

Table 5_1.

Rate constants for the Cu^{2+} - DPC$_o$ -PF reaction at varying of (NH_3) and (NH_4NO_3); (from the decomposition experiments).

	(NH_3) in M	(NH_4NO_3) in M	k in $10^{-4} sec^{-1}$	k' in $sec^{-1}.M^{-1}$
A.	0.109	0.09	4.3	18.7
	0.163	0.09	5.5	10.3
	0.217	0.09	8.4	8.8
	0.271	0.09	10.9	7.9
	0.326	0.09	14.0	5.9
	0.380	0.09	16.2	5.8
	0.434	0.09	18.1	4.6
B.	0.162	0.015	1.2	11.6
	0.162	0.03	2.2	11.6
	0.162	0.045	2.8	11.3
	0.162	0.06	3.9	11.1
	0.162	0.075	4.7	10.2
	0.162	0.09	5.9	11.2
C.	0.241	0.015	1.9	8.0
	0.241	0.03	3.2	7.1
	0.241	0.045	4.7	8.0
	0.241	0.06	6.6	7.6
	0.241	0.075	7.2	7.3
	0.241	0.09	8.5	7.7
D.	0.365	0.015	2.5	5.1
	0.365	0.03	5.3	6.1
	0.365	0.045	7.5	5.3
	0.365	0.06	9.8	5.0
	0.365	0.075	11.3	5.4
	0.365	0.09	13.5	4.7

Rate constants for the Ni^{2+} - DPC -PF reaction at varying of (NH_3) and (NH_4NO_3); (from the decomposition reactions).

	(NH_3) in M	(NH_4NO_3) in M	k in $10^{-7}sec^{-1}$	k' in $10^{-2}sec^{-1}.M^{-1}$
A.	0.092	0.09	9.7	9.5
	0.139	0.09	11.0	5.7
	0.147	0.09	13.1	4.5
	0.170	0.09	15.3	3.4
	0.197	0.09	22.9	3.2
	0.241	0.09	24.1	2.0
	0.253	0.09	26.0	1.7
	0.288	0.09	28.0	1.5
	0.362	0.09	48.0	
	0.497	0.09	63.3	
	0.543	0.09	85.4	
	0.575	0.09	87.4	
	0.608	0.09	89.2	
	0.663	0.09	111	
	0.723	0.09	137	
	0.904	0.09	196	
	1.085	0.09	296	
B.	0.102	0.03	5.1	
	0.102	0.045	6.4	
	0.102	0.06	7.6	
	0.102	0.075	9.4	
	0.102	0.09	10.3	
C.	0.306	0.03	14.1	
	0.306	0.045	18.6	
	0.306	0.06	22.8	
	0.306	0.075	26.0	
	0.306	0.09	31.2	
D.	0.442	0.03	26.8	
	0.442	0.045	33.5	
	0.442	0.06	42.0	
	0.442	0.075	50.0	
	0.442	0.09	57.5	
E.	0.663	0.03	50.9	
	0.663	0.045	68.1	
	0.663	0.06	78.7	
	0.663	0.075	91.2	
	0.663	0.09	111.3	
F.	0.723	0.03	55.7	
	0.723	0.045	81.6	
	0.723	0.06	99.8	
	0.723	0.075	166.1	
	0.723	0.09	138.0	

D.2 Analysis of the kinetics of complex decomposition

A survey of Table 5_1 reveals that for the copper complex as a first approximation the decomposition rate constant k is proportional to both (NH_3) and (NH_4). To investigate the possibility of a $(NH_3)^2$ dependent term in k, the values of Table 5_{1A} (constant (NH_4) were analysed for the two relations:

(I) $k = k_0 + k_1 \cdot (NH_3)$

(II) $k = k_0 + k_1 \cdot (NH_3) + k_2 \cdot (NH_3)^2$

by means of a Polynomial Regression Program. Use of a variation analysis as described in the Appendix resulted in rejection of formula (II); it turned out that formula (I) gives an adequate fit. The values of $k_0(I)$ and $k_0(II)$ appeared to be small compared to k_1 and k_2 and had no physical reality $(k_0(I) = -0.28.10^{-3}sec^{-1}$ and $k_0(II) = -0.11.10^{-3}sec^{-1})$.

After this, all values of Table 5_1 were analysed by a Multiple Regression Program using the functions:

(III) $k = k_0 + k_{1.1} \cdot (NH_3) \cdot (NH_4)$

(IV) $k = k_0 + k_{1.0} \cdot (NH_3) + k_{1.1} \cdot (NH_3) \cdot (NH_4)$

Applying the variation analysis as described in the Appendix turned out that formula (III) gives an adequate fit. The value of $k_0(III)$ was found to be negative and small ($(-0.28 \pm 0.24) \times 10^{-4}sec^{-1}$) compared to $k_{1.1}$. Inclusion of a term proportional to $(NH_3) \cdot (NH_4)^2$ turned out to be of no significance. The values of Table 5_1 can therefore be fitted adequately by the equation $k = k_{1.1} \cdot (NH_3) \cdot (NH_4)$; with $k_{1.1} = (4.4 \pm 0.4) \times 10^{-2}sec^{-1} \cdot M^{-2}$.

The analysis of the dissociation of NiFo appeared to be rather complicated. In the first place it must be remembered that the dissociation is pH dependent; secondly it can be seen from Table 5_{2A} (constant $(NH_4) = 0.09$ M) that the dissociation rate must include a term proportional to $(NH_3)^2$; thirdly it was found that plotting the k values of Tables $5_{2B, C, D, E, F}$ against (NH_4) (at constant (NH_3) and ionic strength), gave straight lines with intercepts on the k axis, which were proportional to (NH_3). With these three points in mind we tried to fit k with the formula:

$$k = k_{1,0} \cdot (NH_3) + k_{1,1} \cdot (NH_3) \cdot (NH_4) + k_{-1,1} \cdot (NH_3)^{-1} \cdot (NH_4) +$$

$$+ k_{2,1} \cdot (NH_3)^2 \cdot (NH_4) \qquad (9)$$

The $k_{-1,1}$ term is proportional to (H) and represents the pH dependence. The term $k_{1,1} \cdot (NH_3) \cdot (NH_4)$ was added because it played an important part in the dissociation experiments of the copper complex. To test the significance of the different terms in equation (9) the number of terms in this equation was varied and each variation analysed with the help of a Multiple Regression Program. The following survey gives the various equations. together with their F values and their theoretical F for P = 0.99:

(V) $\quad k = k_{1,0} \cdot (NH_3) + k_{1,1} \cdot (NH_3) \cdot (NH_4) + k_{-1,1} \cdot (NH_3)^{-1} \cdot (NH_4) +$

$$+ k_{2,1} \cdot (NH_3)^2 \cdot (NH_4)$$

$$F = 1255, \quad F\ (P = 0.99) = 4.28$$

(VI) $\quad k = k_{1,0} \cdot (NH_3) + k_{-1,1} \cdot (NH_3)^{-1} \cdot (NH_4) + k_{2,1} \cdot (NH_3)^2 \cdot (NH_4) \qquad (10)$

$$F = 1468, \quad F\ (P = 0.99) = 5.14$$

(VII) $\quad k = k_{1,0} \cdot (NH_3) + k_{1,1} \cdot (NH_3) \cdot (NH_4) + k_{2,1} \cdot (NH_3)^2 \cdot (NH_4)$

$$F = 719, \quad F\ (P = 0.99) = 5.14$$

(VIII) $\quad k = k_{1,1} \cdot (NH_3) \cdot (NH_4) + k_{-1,1} \cdot (NH_3)^{-1} \cdot (NH_4) + k_{2,1} \cdot (NH_3)^2 \cdot (NH_4)$

$$F = 278, \quad F\ (P = 0.99) = 5.14$$

(IX) $\quad k = k_{1,0} \cdot (NH_3) + k_{-1,1} \cdot (NH_3)^{-1} \cdot (NH_4) + k_{1,1} \cdot (NH_3) \cdot (NH_4)$

$$F = 137, \quad F\ (P = 0.99) = 5.14$$

Selection VI was chosen in the usual way (Appendix).

The constants involved were found to be

$$k_{1,0} = (2.6 \pm 0.2) \times 10^{-6} \sec^{-1} . M^{-1}$$

$$k_{-1,1} = (5.9 \pm 0.3) \times 10^{-7} \sec^{-1}$$

$$k_{2,1} = (2.5 \pm 0.2) \times 10^{-4} \sec^{-1} . M^{-2}$$

D.3 Analysis of the kinetics of complex formation

Table 5_1 and 5_2 also contain the pseudo second order formation rate constants k' obtained from the application of the formula (5). Variation of

the ammonium nitrate concentration had no influence on the formation rate of CuFo or NiFo when (NH_3) was kept constant.

The values of k' in Table 5_1 and 5_2 refer to the total metal ion concentration $(M)_{tot}$: Using the overall stability constants β_n for the metal ammine complexes given by Bjerrum (41 B), $(M)_{tot}$ may be expressed as:

$$(M)_{tot} = (M) \cdot S(NH_3) \tag{11}$$

with $\quad S(NH_3) = \sum_{n=0}^{6} \beta_n \cdot (NH_3)^n$

(M) refers to the concentration of hexaquo ion. Assuming now that each ammine complex $M(NH_3)_n (H_2O)_{6-n}^{2+}$ reacts with the formazan at its own rate given by the rate constant k_n^o, the rate of the formation reaction may be expressed as:

$$s' = \frac{1}{S(NH_3)} \cdot (M)_{tot} \cdot (HFo) \cdot \sum_{n=0}^{6} k_n' \cdot (NH_3)^n \tag{12}$$

with $\quad k_n' = k_n^o \cdot \beta_n$.

This result may also be expressed in the k' value; using equation (1):

$$k' \cdot S(NH_3) = \sum_{n=0}^{6} k_n' \cdot (NH_3)^n \tag{13}$$

Calculations on the values of k' in Table 5_1 and 5_2 revealed k'. $S(NH_3)/(NH_3)^3$ to be nearly constant, while the values of k'. $S(NH_3)/(NH_3)^2$ and k'. $S(NH_3)/(NH_3)^4$ increased respectively decreased on increasing ammonia concentrations.

The k_3' term thus plays the most important part in complex formation, from these:

$$k_3^o (CuFo) = (235 \pm 10) \ sec^{-1} \cdot M^{-1}$$

$$k_3^o (NiFo) = (31 \pm 2) \times 10^{-2} sec^{-1} \cdot M^{-1}$$

The results obtained above have been checked in a limited number of complex formation experiments by adding together metal ions and formazan in equal concentrations in exactly the same circumstances as already described above. The results obtained were expressed in the usual way in the constants k and k' defined above.

Table 5_3 and Table 5_4 give the calculated results. The values of k

and k' were interpreted as above, giving:

$$CuFo \quad : k_{1,1} = (3.3 \pm 0.4) \times 10^{-2} sec^{-1} . M^{-2}$$

$$Cu + HFo : k_3^o = (280 \pm 15) \, sec^{-1} . M^{-1}$$

$$Ni + HFo : k_3^o = (31 \pm 3) \times 10^{-2} sec^{-1} . M^{-1}$$

For the more complicated nickel decomposition no rate constants were calculated; instead, the experimental rates have been compared with the rates calculated from equation (10), using the constants obtained in the decomposition experiments (Table 5_3). It is seen that agreement between the formation and decomposition results is reasonable.

Table 5_3

Rate constants for the Ni^{2+} - DPC_o-PF reaction at varying (NH_3) and constant $(NH_4NO_3) = 0.09$ M; (from the formation experiments).

(NH_3) in M	k(exp.) in $10^{-7} sec^{-1}$	k(calc.) in $10^{-7} sec^{-1}$	k' in $10^{-3} sec^{-1} . M^{-1}$
0.404	49.3	47.3	6.8
0.354	34.8	37.8	8.9
0.303	29.6	29.6	11.3
0.254	22.9	21.4	15.9

Each entry is the mean of at least three independent kinetic runs.

Table 5_4.

Rate constants for the Cu^{2+} - DPC_o-PF reaction at varying (NH_3) and constant $(NH_4NO_3) = 0.09$ M; (from the formation experiments).

(NH_3) in M	k in $10^{-4} sec^{-1}$	k' in $sec^{-1} . M^{-1}$
0.097	2.5	21.1
0.137	4.1	17.5
0.190	5.8	12.1
0.287	10.1	9.6

Each entry is the mean of at least three independent kinetic runs.

E. Oxidation of the complexes

The kinetics of the oxidation of CuFo and NiFo by the hexacyano-ferrate (III) anion have been studied in the way described (in Chapter 3) for

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the formazan - $Fe(CN)_6^{3-}$ system. The reactions were observed spectrophoto-metrically. The initial concentration of the complexes in most cases was $2.0 \times 10^{-5}M$. The reaction of NiFo was found to be first order in ammonia, hexacyanoferrate (III) and NiFo:

$$s^* = k^* . (Fe(CN)_6^{3-}) . (NH_3) . (NiFo)$$

with $k^* = (2.8 \pm 0.1) \ sec^{-1} . M^{-2}$.

Table 5_5.

Pseudo first order rate constant (in $10^{-4} sec^{-1}$) for the oxidation of NiFo by excess hexacyanoferrate (III) ion at varying (NH_3) and constant $(NH_4NO_3) = 0.09$ M.

(NH_3) in M	$(K_3Fe(CN)_6)$ in $10^{-4}M$		
	4.0	6.0	8.0
0.257	2.9	3.8	5.9
0.314	3.6	5.0	6.7
0.425	4.6	6.4	8.8
0.522	6.4	8.5	12.0
0.627	7.4	10.1	14.6

Comparison of k^* with the dominating decomposition rate constant $k_{2,1}$ in section D.2 reveals that the dissociation of NiFo is much slower (10,000 times) than the oxidation and therefore the NiFo is oxidized as a complex by hexacyanoferrate (III). It is remarkable that NiFo is oxidized at about the same rate as TPF ($(3.6 \pm 0.1) sec^{-1} . M^{-2}$) and DPC_p-PF ($(2.3 \pm 0.1) sec^{-1} . M^{-2}$).

The oxidation of CuFo by the hexacyanoferrate (II) anion could be fitted best by the equation

$$s^* = k^* . (NH_3) . (CuFo)$$

with $k^* = (4.5 \pm 0.4) \times 10^{-3} sec^{-1} . M^{-1}$

Table 5_6.

Pseudo first order rate constant (in $10^{-4} sec^{-1}$) for the oxidation of CuFo by excess hexacyanoferrate (III) ion at varying (NH_3) and constant $(NH_4NO_3) = 0.09$ M.

| (NH_3) in M	$(K_3Fe(CN)_6)$ in $10^{-4}M$			
	2.0	4.0	6.0	8.0
0.189	8.3	9.2	9.1	9.2
0.270	10.7	11.0	11.0	11.1
0.351	16.0	16.2	16.2	16.5

In section D.2 we found the value $(4.0 \pm 0.4) \times 10^{-3} \sec^{-1}.M^{-1}$ for the pseudo dissociation rate constant (for constant NH_4^+). From these results it is clear that CuFo dissociates only, but is not oxidized by hexacyanoferrate (III).

It was attempted to oxidize the complex CuFo by a very large excess (1,000 fold) of Cu^{2+} but even after weeks no change in spectrum was observed. Addition of a large excess of Cu^{2+} to NiFo only produces metal ion exchange in this complex.

5.2 DISCUSSION

Before considering the detailed complex formation reaction we give a short summary of what is known about coordination in the two formazan complexes. It is generally agreed upon (57 Ki, 57 K, 57 F, 52 T) that three-coordination is of common occurrence in the complexes, both in the solution and in the solid state, and that the fourth coordination place, marked by $\otimes$, in the MN_2O plane of the complex schematically represented by formula (IX), is difficult to fill. The reason for this fact is not known.
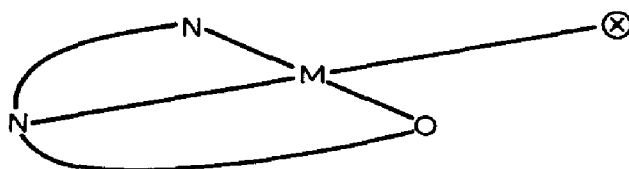
M = Ni, Cu

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A molecular model of the complexes clearly showed interference between a group coordinated to the "empty" site ($\otimes$) and the remainder of the molecule. It must however be remembered that filling the fourth coordination place in these formazan complexes presents a very subtle equilibrium; so four-coordination is rather easy in C-cyano and N-ortho-hydroxyphenyl, N'-ortho-chlorophenyl formazan complexes (68 W, 52 T). This perhaps means that it is not solely a case of steric hindering. Filling of the "empty" site ($\otimes$) with for instance ammonia produces a notable change in the absorption spectrum (52 T, 68 W). Therefore the similarity between the absorption spectra, in water and ethanol, with and without ammonia as found in section B guarantees that under the experimental circumstances this fourth

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coordination place is not occupied by ammonia.

Of the two reactions under study the easiest to deal with is that between nickel(II) and the formazan; the decomposition rate is represented by equation (10):

The term, $k_{-1,1} \cdot (NH_3)^{-1} \cdot (NH_4)$, may be called a pH term as it is proportional to the hydrogen ion concentration and in this way represents the "tail" of the acid-dependent decomposition reaction (section D.1). Therefore this very small term (only a few per cent) is of no interest in the scope of our investigations on the reactions in ammonia buffers. From the remaining two terms the term $k_{1,0} \cdot (NH_3)$ explains less than 15% of the observed rate in the buffer medium NH_3/NH_4^+ with $(NH_4) = 0.09$ M employed in the redox reaction studied. This term is difficult to interpret and will be neglected.

There remains as the main decomposition reaction:

$$NiFo + 2NH_3 + NH_4^+ \longrightarrow$$
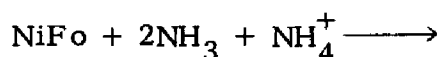
with $\quad s = k_{2,1} \cdot (NH_3)^2 \cdot (NH_4) \cdot (NiFo)$

The corresponding formation rate is given by:

$$s' = k_3^o \cdot (Ni(NH_3)_3^{2+}) \cdot (HFo)$$

referring to the reaction:

$$Ni(NH_3)_3^{2+} + HFo \longrightarrow$$
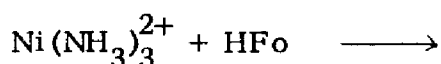
(For the sake of simplicity, coordinated water will not be indicated unless confusion may arise.) This reaction is preceded by a fast equilibrium between all ammine complexes in solution and $Ni(NH_3)_3^{2+}$. The simplest reaction scheme consistent with, but not necessarily proved by, the results given, is:

NI(NH₃)₃²⁺ + N⌒N⌒O
         H

$\xrightleftharpoons[k_b]{k_a}$
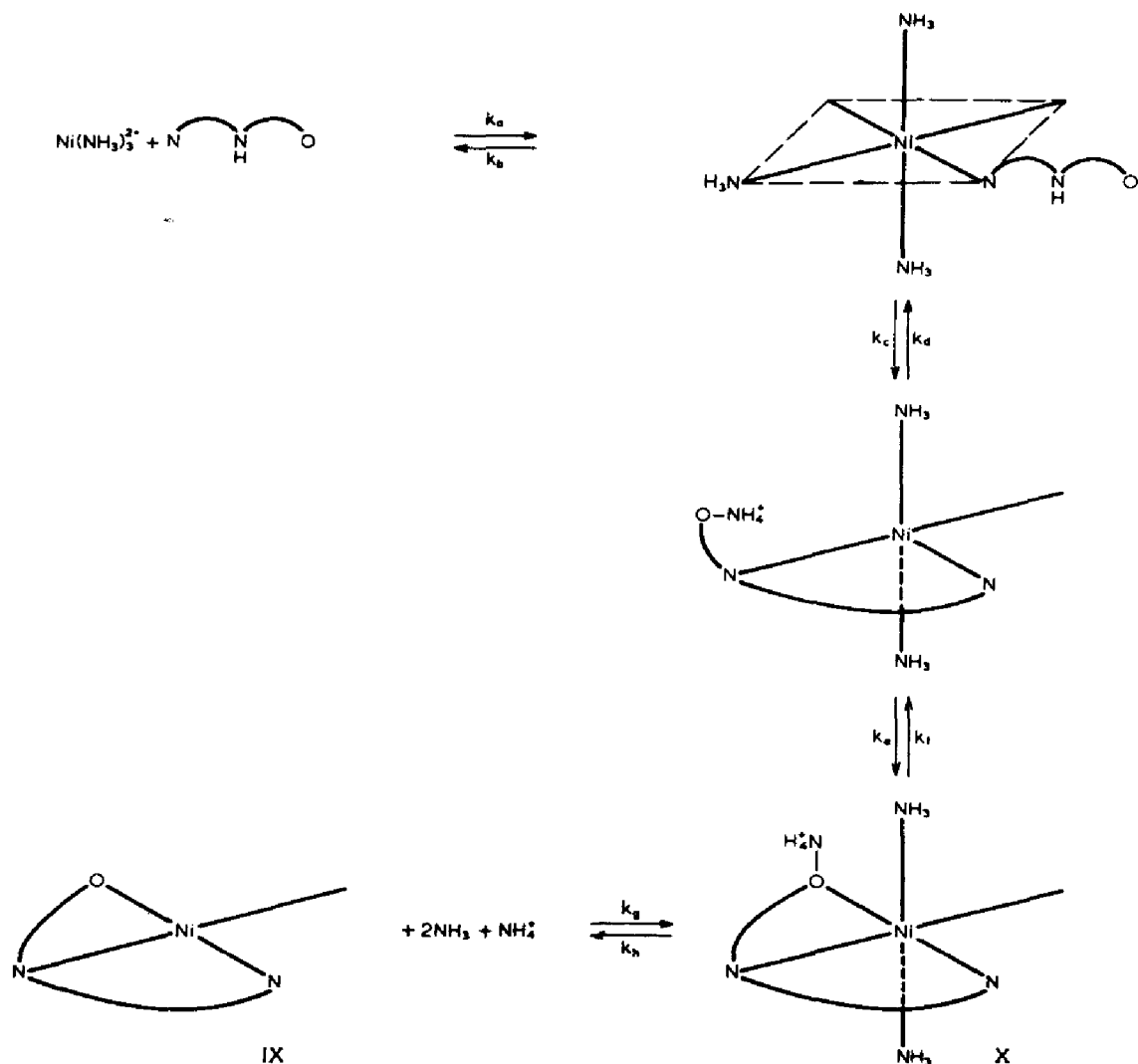
(The formazan is schematically represented by the joint donor atoms as:

N⌒N⌒O .) (N.B. The constants k_a and $k_{2,1}$ are not the same.)
   H
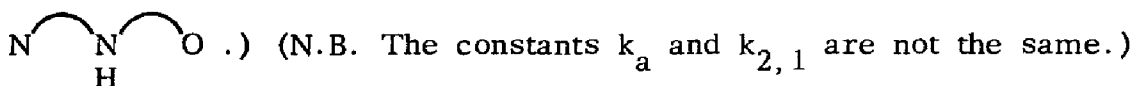
This mechanism supposes that the association of an NH_4^+-ion to the COO⁻ group (and not necessarily to the O coordinated to the metal ion as the simplified scheme seems to suggest) and NH_3 coordination to the Ni^{2+} above and below the formazan plane weakens the Ni-O bond to such an extent that this bond may easily be broken. This mechanism explains the rate law found if it is assumed that X is in a fast equilibrium with IX:

$$IX + NH_4^+ + 2NH_3 \rightleftharpoons X$$
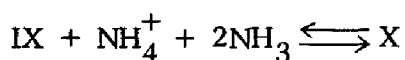
and that no appreciable quantity of X is present.

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The absence of any influence of (NH_4) on the formation rates excludes the formulation of the reaction as:

$$Ni(NH_3)_2^{2+} + (N \frown N \frown O)^-$$
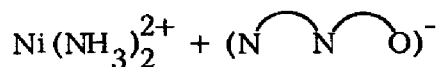
The copper(II) - formazan system presents a slightly more difficult case than the system discussed above because at first sight there is a difference in the number of molecules involved in the formation and that in the decomposition reaction:

formation: $s' = k_3^o \cdot (Cu(NH_3)_3^{2+}) \cdot (HFo)$

or $\quad Cu(NH_3)_3^{2+} + HFo \quad \longrightarrow$

decomposition: $s = k_{1,1} \cdot (CuFo) \cdot (NH_3) \cdot (NH_4)$

or $\quad CuFo + NH_3 + NH_4^+ \quad \longrightarrow$

This difference necessitates changing the scheme elaborated for NiFo in this way: For mixed aquo complexes of copper(II) in aqueous solutions the addition of a fifth or sixth ligand is not easily accomplished (66 Co). Mutatis mutandis this means for the complex CuFo, where the fourth coordination site is "blocked", that attachment of an extra molecule perpendicular to the CuN_2O-plane of (IX) is rather unfavourable, while adding a second ammonia molecule as it was postulated to occur for NiFo will be even more difficult energetically.

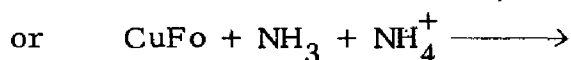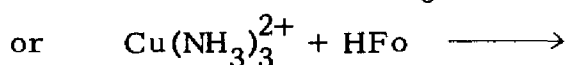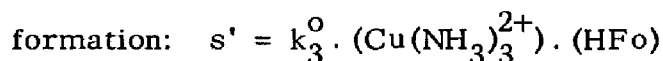On the other hand, although the fourth coordination place in the CuN_2O plane cannot easily be used by ammonia, it may be assumed that at least on the "open" side the complex is preferably solvated by ammonia molecules in the second coordination sphere. At the moment that the Cu-O bond breaks (reaction k_f in the Ni scheme) coordination is possible and immediately an ammonia ligand comes in; all this results in a stable planar coordination of the copper (with perhaps two water molecules above and below the plane at larger distances). The following reactions and the rate constants expressions are in this case the same as those already given in the nickel case.

The extension of the NiFo mechanism worked out for CuFo resembles the one generally (67 B) assumed for the S_N1 anation of cobalt(III) complexes. As already referred to it implies saturated solvation in the vulnerable coordination side.

The reaction scheme given follows the general assumption (52 T,

68 W, 55 N) that the formazan complexes have planar structures. However, if the metal-oxygen bond might be perpendicular to the plane of the metal-nitrogen bonds the mechanism may easily be adjusted to this effect without essentially changing its content.

CHAPTER 6

KINETICS OF THE OXIDATION OF SOME FORMAZANS BY COPPER(II) AMMINE COMPLEXES

In this Chapter the oxidation of some formazans by copper(II) ammine complexes will be dealt with. The reaction conditions are equal to those used in the oxidation of the same formazans by the hexacyanoferrate(III) anion. The initial stage of the oxidation is found to be analogous to the complex formation reaction of copper(II) with 1,3-Diphenyl-5-o-carboxyphenylformazan.

For detailed reaction conditions we refer to Chapter 3.

6.1 RESULTS

A logarithmic plot of the measured absorbance at the formazan maximum versus time showed straight lines in all cases. This result proves the reaction to be first order in the total formazan, indicated by FNH; in this section the same abbreviations and symbols as in Chapter 4 are used. The pseudo first order constant k_{Cu} obtained from the logarithmic plots is proportional to the total copper(II) concentration $(Cu)_t$ (dropping ionic charges):

$$s_{Cu} = k'_{Cu} \cdot (FNH) = k_{Cu} \cdot (Cu)_t \cdot (FNH) \tag{1}$$

$(s_{Cu}$ = reaction rate).

Results in k_{Cu} are given in Table 6_1.

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Reaction conditions and rate constants [*] (in units $sec^{-1} . M^{-1}$) for the formazan-copper(II) ammine oxidations in 0.09 M ammonium nitrate.

TPF[a] [**]	5.4	8.1	10.8	DPF[a]	5.4	8.1	10.8
144	4.40	4.30	4.38	155	5.32	5.27	5.29
216	3.67	3.49	3.56	216	3.84	3.86	3.75
310	2.91	2.80	2.82	310	2.59	2.62	2.59
432	2.46	2.38	2.35	432	1.90	1.89	1.84

DPF-C[a]	2.7	3.3	4.05	DPF-C[b]	1.8	2.7	3.6
150	33.70	-	33.20	297	73.89	74.44	-
224	22.67	21.97	22.67	446	50.39	49.26	49.17
299	17.44	16.21	17.09	595	37.22	35.19	37.50
449	11.33	10.94	11.03	744	30.56	29.58	29.17

DPC$_p$-PF[a]	4.0	6.0	8.0
201	2.55	2.59	2.68
306	2.28	2.14	2.18
400	-	1.95	1.95
471	1.69	1.71	1.66

[*] For each formazan k_{Cu} has been given as a function of: horizontally (Cu^{2+}) in units $10^{-4} M$ and vertically (NH_3) in units $10^{-3} M$.

[**] a. The formazan is dissolved in 45.5 wt % ethanol - water;
   b. The formazan is dissolved in water.

In order to analyse the ammonia dependence of the rate constants the various copper(II)- ammonia equilibria must be taken into account. Following the analysis of the complex formation experiments in Chapter 5, we may separate the contributions of each ammine complex (equation (12) of Chapter 5).

$$s_{Cu} = \frac{(Cu)_t \cdot (FNH) \sum_{n=o}^{6} k_{n\,Cu} \cdot (NH_3)^n}{S(NH_3)} \tag{2}$$

with $(Cu)_t = (Cu) \cdot S(NH_3)$, $S(NH_3) = \sum_{n=o}^{6} \beta_n \cdot (NH_3)^n$ and $k_{n\,Cu} = k^o_{n\,Cu} \cdot \beta_n$

(Cu) = concentration of the hexaquo ion; β_n and $k^o_{n\,Cu}$ are the overall stability constant (41 B) and the redox rate constant for the complex $Cu(NH_3)_n(H_2O)_{6-n}^{2+}$ respectively; because during the reactions the spectra did not show any evidence (49 V, 58 F, 41 Hu, 65 H, 60 E, 60 I, 60 H) of complex formation no appreciable quantity of the formazans is bound to Cu^{2+}, so that for (FNH) the total formazan concentration may be used.

Combination of the equations (1) and (2) gives:

$$k_{Cu} \cdot S(NH_3) = \sum_{n=o}^{6} k_{n\,Cu} \cdot (NH_3)^n \tag{3}$$

From the values in Table 6_1 $k_{Cu} \cdot S(NH_3)$ in a first approximation is proportional to $(NH_3)^3$ with probably a slight increase on increasing (NH_3). Therefore the values referred to have been analysed with a Multiple Regression Program on an I.B.M. 1130 computer for the relations.

(I) $\quad k_{Cu} \cdot S(NH_3) = k_o + k_{3\,Cu}(NH_3)^3$

(II) $\quad k_{Cu} \cdot S(NH_3) = k_o + k_{3\,Cu}(NH_3)^3 + k_{4\,Cu}(NH_3)^4$

(III) $\quad k_{Cu} \cdot S(NH_3) = k_o + k_{4\,Cu}(NH_3)^4$

The results obtained for the various formazans are in Table 6_2, together with the calculated F values and the F values for P = 0.99 (68 L). From Table 6_2 and with the help of a variation analysis as described in the Appendix, it appeared that relation I gives the best fit for all formazans except TPF, where an appreciable contribution of k_4 is found. In all cases k_o was found to be very small as compared to k_3 and k_4 (<1%).

Table 6_2.

Least squares analysis results for the rate constants of Table 6_1.

Formazan[*)	Test	k_o in 10^{10} sec^{-1} . M^{-1}	$k_{3\,Cu}$ in 10^{12} sec^{-1} . M^{-4}	$k_{4\,Cu}$ in 10^{12} sec^{-1} . M^{-5}	F	F(P = 0.99)
DPF[a]	I	-0.16	2.00 + 0.03	- -	2783	10.04
	II	+0.04	1.6 + 0.3	0.9 + 0.7	2671	8.02
	III	+0.95	- -	4.3 + 0.1	1553	10.04
DPF-C[a]	I	-0.44	12.1 + 0.1	- -	15361	10.56
	II	-0.09	11.5 + 1.3	1.2 + 0.3	6986	8.65
	III	7.2	- -	25.2 + 0.6	1555	10.56
DPF-C[b]	I	-40.4	52.7 + 0.8	- -	4757	10.56
	II	13.9	42.2 + 8.1	19.5 + 10.1	3095	8.65
	III	168	- -	72.2 + 1.8	1571	10.56
DPC$_p$-PF[a]	I	-0.93	2.00 + 0.03	- -	6732	10.56
	II	-0.46	1.4 + 0.2	1.1 + 0.5	5311	8.65
	III	7.62	- -	4.0 + 0.1	2018	10.56
TPF[a]	I	-0.78	2.6 + 0.1	- -	2671	10.04
	II	0.01	1.0 + 0.3	3.5 + 0.6	6479	8.02
	III	0.53	- -	5.6 + 0.1	5264	10.04

[*) a. The formazan is dissolved in 45.5 wt % ethanol-water;
   b. The formazan is dissolved in water.

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Table 6_3 gives the resulting $k^o_{n\,Cu}$ values for the least squares fit.

Table 6_3.

Rate constants $k^o_{3\,Cu}$ and $k^o_{4\,Cu}$ (in $sec^{-1}.M^{-1}$) for the oxidation of the formazans by the copper(II) ammine complexes.

Formazan[*)]	$k^o_{3\,Cu}$ in $sec^{-1}.M^{-1}$	$k^o_{4\,Cu}$ in $sec^{-1}.M^{-1}$
DPF[a]	105 + 2	- -
DPF-C[a]	639 + 5	- -
DPF-C[b]	3052 + 44	- -
DPC$_p$-PF[a]	106 + 3	- -
TPF	52 + 13	1.7 + 0.3

[*)] a. The formazan is dissolved in 45.5 wt % ethanol - water.
 b. The formazan is dissolved in water.

The influence of the solvent on the reaction rate has been investigated for DPF-C; the same was done in Chapter 4 for the hexacyanoferrate(III) oxidation. For this formazan the reaction was performed in different weight percentages of ethanol (between 0 and 45.5 wt %), keeping the ammonia and copper(II) concentration constant. Results are in Table 6_4.

Table 6_4.

Rate constants (in units $sec^{-1}.M^{-1}$) for the Cu^{2+} - DPF-C reaction as a function of the percentage of ethanol, at constant ammonia and ammonium nitrate concentration[*)].

wt % ethanol	k_{Cu}
0	20.7
4.0	18.4
6.6	16.4
14.0	11.8
22.1	9.7
29.1	7.2
45.5	4.6

[*)] (NH_4^+) = 0.09 M
 (NH_3) = 1.10 M

Addition of a thousand-fold excess of the nitrates of zinc (II), cadmium (II) or nickel (II) to the reaction mixture did not change the rate of the reactions.

6.2 DISCUSSION

The absence of a spectral indication (49 W, 58 F, 41 Hu, 65 H, 60 E, 61 I, 60 H) for complex formation and the fact that even a thousand-fold excess of Zn^{2+}, Cd^{2+} or Ni^{2+} ions over the formazans did not change the rate of the oxidation, prove that no appreciable quantity of the metal formazan complex is present under the experimental conditions. On the other hand DPC_o-PF (Chapter 5) in contrast with the other formazans under study, rapidly forms complexes. This complex formation of DPC_o-PF has been studied in detail (Chapter 5) and it has been found that this formazan reacts with the triammine complex of copper (II).

It is found in the oxidation of formazans by copper (II) that the copper (II) triammine complex also plays the most important part. An exception is found, however. For TPF the third and fourth ammine complex react with the formazan, the reaction rates of these copper complexes are of the same order, but after correction for β it was found that the third complex is more favourable for the oxidation (compare $k^o_{3\,Cu}$ and $k^o_{4\,Cu}$).

The importance of the third copper (II) ammine complex both in the complex formation (Chapter 5) and the oxidation reaction (Chapter 6) may be taken as a strong indication that at least in the initial stage the mechanism is the same for complex formation and oxidation. For reasons of analogy it may be assumed that in the rate determining step of the oxidation reaction the formazan molecule reacts with the triammine copper (II) complex; this in contradiction to the hexacyanoferrate (III) - formazan reactions, for which indications have been found that the anion is the reactive species (Chapter 4).

At this moment it is not yet possible to say where the complex formation mechanism elaborated for the Cu^{2+} - DPC_o-PF system breaks off and electron transfer occurs. For DPC_o-PF, where no oxidation, but only complex formation is observed, metal oxygen bonding seems to prevent this electron transfer process.

Table 6_3 shows a slight decrease in k_{Cu}, when the dielectric constant decreases. Since this effect is small and ionic strength differs from zero

(61 F), no quantitative interpretation can be given.

The values of $k_3^O{}_{Cu}$ for the copper(II) oxidation reactions will be discussed in the following Chapter and be compared with the results obtained in the oxidation by hexacyanoferrate(III).

CHAPTER 7

CONCLUSIONS

In this Chapter we will summarize the conclusions obtained in the preceding Chapters and compare the various results.

In Chapter 4 it was found that the hexacyanoferrate(III) oxidation of the formazans under study proceeded by an "outer sphere" mechanism. In the presence of NH_4^+ ions, two competing reactions were found: The oxidation of the formazan anion by the hexacyanoferrate(III) anion and by the ammoniumhexacyanoferrate(III) anion. The predominant reaction appeared to be the oxidation of the formazan anion by the hexacyanoferrate(III) anion.

One exception was found, however: DPC_o-PF in a 45.5 wt % ethanol - water mixture was oxidized at a much slower rate than the other formazans and from the kinetics it was concluded that in this case the "neutral" formazan molecule was oxidized. This exception was ascribed to a possible internal proton bridging in DPC_o-PF, which prevents the deprotonation of the imino group.

The results obtained for the other formazans in a 45.5 wt % ethanol - water mixture are summarized in Table 7_1.

Table 7_1.

Reaction rate constants for the hexacyanoferrate(III) and the copper(II) oxidation of several formazans.

Formazan	k_{Fe} in sec^{-1}.M^{-2}	$k^o_{3\ Cu}$ in sec^{-1}.M^{-1}	$k^o_{4\ Cu}$ in sec^{-1}.M^{-1}
TPF	3.6 ± 0.1	52 ± 13	1.7 ± 0.3
DPF	116 ± 3	105 ± 2	-
DPF-C	11.0 ± 0.3	639 ± 5	-
DPC_p-PF	2.3 ± 0.1	106 ± 3	-

The significant difference in oxidation rate between the "red" TPF and DPC_p-PF on the one hand and the "yellow" DPF on the other hand was ascribed to the greater acidic strength of the "yellow" formazan. The difference in rate constant between the "yellow" DPF and DPF-C was suggested to be caused by proton bridging in the "yellow" DPF-C.

In Chapter 5 the complex formation between copper(II) and DPC_o-PF was studied and no interference from formazan oxidation was found. It is supposed that the stability of the copper(II) complex of DPC_o-PF must be ascribed to the favourable possibilities of coordination present here: a tridentate complex can easily be formed without disturbing the π-system of the ligand.

Under the experimental conditions used here, no complexes of the other formazans with copper(II) have been observed, but instead the formazans were oxidized by copper(II). It is possible, however, to prepare the copper complexes of these formazans, if other experimental conditions are used. We suppose that these complexes are less stable than the DPC_o-PF complexes, because in the complexes the ligand is a bidentate (TPF) or a tridentate with a disturbed π-system (DPF-C).

An analysis of the kinetics of the complex formation between copper(II) and DPC_o-PF taught that the important step in this complex formation is the reaction between the copper(II) triammine complex and the "neutral" formazan molecule.

In Chapter 6 the oxidation of the other formazans by copper(II) was studied. Here, too, an analysis of the kinetics revealed that the important step is the reaction between the copper(II) triammine complex and the "neutral" formazan molecule.

An analogy was found therefore between the complex formation reaction of copper(II) with DPC_o-PF and the oxidation reaction of the other formazans by copper(II).

This analogy strongly indicates that at least the initial step of both the complex formation of DPC_o-PF and the copper(II) oxidations of the other formazans are similar and that therefore the oxidation proceeds by an "inner sphere" mechanism.

The rate constants found in the copper oxidations are all of the same order of magnitude. These rate constants are approximately equal to the rate constant found for the complex formation reaction of the Cu^{2+}-DPC_o-PF system ($k^o_{3\,Cu} \approx 260\ sec^{-1}.M^{-1}$). This is another indication of the im-

portance of complex formation in the copper oxidations.

As a first step in the copper(II) oxidation, the copper(II) triammine complex is attached to the formazan molecule probably via the lone pair of the outmost nitrogen atom: In the complex formation reaction of copper(II) with DPC_O-PF the next step is coordination of the copper to the other outmost nitrogen atom, thus forming a bidentate. The second step of the oxidation process, however, presents two possibilities:

a. An immediate oxidation of the formazan in the copper(II) triammine-formazan system.

b. A further complexation of copper to the other nitrogen atom in the formazan (as with DPC_O-PF) followed by an internal oxidation.

From the experimental results obtained in this work we cannot decide between the two possibilities mentioned above. The fact, however, that the rate constants found for the oxidation of the formazans and in the complex formation of DPC_O-PF are of the same order of magnitude suggests that the rate determining step is the same for both processes.

Inspection of Table 7_1 reveals that the oxidation rate constants for TPF, DPF and DPC_p-PF with copper are approximately equal; this in contrast to the rate constants for the oxidation of the same formazans with the hexacyanoferrate(III) anion. The fact that for the copper oxidation the same rate constants are found for the "yellow" and the "red" formazans indicates that in the copper oxidation the formazans are oxidized not as anion but as "neutral" molecule. This once more supports the proposed mechanism.

The higher reaction rate in the oxidation of the "yellow" DPF-C with copper may be due to the carboxylic group favouring complex formation.

SUMMARY

In this thesis an investigation of the kinetics and the mechanism of the oxidation in solution of a number of formazans is described. As oxidizing agents copper(II) and hexacyanoferrate(III) ions were used.

The oxidations were performed in an ethanol-water mixture at constant ionic strength and temperature. The medium was buffered by an ammonia/ammonium nitrate mixture since during the oxidation reactions protons were released.

The oxidations of the formazans by the "outer sphere" oxidizing hexacyanoferrate(III) anion were found to involve the formazan anion. This was concluded from the rate law found and supported by the fact that the reaction rates increased when univalent ions (capable of forming "outer sphere" ions associates with the hexacyanoferrate(III) anion) were added. Confirmation of the supposed reaction mechanism was also obtained from the change in reaction rate when the dielectric constant of the reaction medium was varied.

It is known that formazans can form complexes with copper(II). One of the formazans under study (DPC_o-PF) formed complexes with copper(II) at a measurable rate, while the formazan was not oxidized, not even by a large excess of copper(II). The complex formation of this formazan was studied in detail and it was found that as a first step the copper triammine complex reacted with the formazan molecule.

The other formazans were rapidly oxidized by copper(II) solutions. An analysis of the oxidation rates revealed, that in this case the copper(II) triammine complex also played the most important part in the oxidation of the formazan molecule. That is why it was concluded that in the oxidation of the formazans by copper(II), complex formation must play a role. Further-

more there were indications that the reaction of the formazan molecule with the copper(II) triammine complex is the rate determining step. An "Inner sphere" oxidation mechanism is thus found in the copper(II) oxidations of the formazans.

APPENDIX

CURVE FITTING

In order to come to a simple representation of the values measured for the rate constant, a number of equations was taken of which could be expected from experiments that they fitted more or less correctly the experimental values.

With the help of regression analysis the coefficients of the various equations were calculated.

From these results the equation that fits best the experimental observations had to be selected. This was done with the help of an analysis of variance for the different regression lines. In this analysis the total variability of the measured rate constants about their mean value is split into a component given by the variance of the regression line about the mean of the measured k values (reduction due to regression) and into a component which represents the variance of the measured k values about the calculated regression line (residual). The quotient of these variances (the common F value (68 L)) is used as a measure for fit.

When regression lines were compared with the same degrees of freedom, the line which had the highest F value was chosen.

When regression lines of different degrees of freedom were compared, further analysis was performed in which the significance of the additional term was tested. To this end (68 L) the total variation term was split into components which represented the reduction due to regression obtained by the original equation and in a component representing the reduction due to regression obtained by the additional term.

The latter reduction (expressed in mean squares) was divided by the

mean squares of its corresponding residual and when the F value obtained in this way surpassed the F (P = 0.99) value, significance of the additional term was accepted. For an extensive description of this method of variation analysis we refer to Chapter V of the Book: "The Handling of Chemical Data" (68 L).

As an example of curve fitting of k_{Cu} values to equations of different degrees of freedom we give here the fitting to the functions:

$$k_{Cu} \cdot S(NH_3) = k_0 + k_{3\ Cu}(NH_3)^3 \tag{1}$$

$$k_{Cu} \cdot S(NH_3) = k_0 + k_{3\ Cu}(NH_3)^3 + k_{4\ Cu}(NH_3)^4 \tag{2}$$

We want to know whether $k_{4\ Cu}$ is of significance in fitting the experimental results. The curve fitting was done for DPF-C as well as TPF with the experimental values of k_{Cu} from Table 6_1.

Test of the significance of adding the term $k_{4\ Cu}(NH_3)^4$ to equation (1), (for DPF-C).

Component of variation	Sum of squares	f	Mean square	Ratio	F (P = 0.99)
Total	$0.190849\ 10^{25}$	10			
Reduction due to $k_0 + k_{3\ Cu}(NH_3)^3$	$0.190737\ 10^{25}$	1	$0.190737\ 10^{25}$	15361	10.56
Residual from the line $k_0 + k_{3\ Cu}(NH_3)^3$	$0.117521\ 10^{22}$	9	$0.130578\ 10^{21}$		
Reduction due to adding the $k_{4\ Cu}(NH_5)^4$ term	$0.008536\ 10^{22}$	1	$0.08536\ 10^{21}$	0.55	11.26
Residual from the line $k_0 + k_{3\ Cu}(NH_3)^3 + k_{4\ Cu}(NH_3)^4$	$0.109216\ 10^{22}$	8	$0.161520\ 10^{21}$		

The term in $(NH_3)^4$ can be skipped, because $F_{calc.} < F$ (P = 0.99).

Test of the significance of adding the term $k_{4\,Cu}(NH_3)^4$ to equation (1), (for TPF)

Component of variation	Sum of squares	f	Mean square	Ratio	F (P = 0.99)
Total	$0.722740 \ 10^{23}$	11			
Reduction due to $k_0 + k_{3\,Cu}(NH_3)^3$	$0.720044 \ 10^{23}$	1	$0.720044 \ 10^{23}$	2671	9.65
Residual from line $k_0 + k_{3\,Cu}(NH_3)^3$	$2.69504 \ 10^{20}$	10	$0.269504 \ 10^{20}$		
Reduction due to adding the $k_{4\,Cu}(NH_3)^4$ term	$2.19337 \ 10^{20}$	1	$2.19337 \ 10^{20}$	39.4	10.04
Residual from the line $k_0 + k_{3\,Cu}(NH_3)^3 + k_{4\,Cu}(NH_3)^4$	$0.501667 \ 10^{20}$	9	$0.5574 \ 10^{20}$		

The k values can be fitted best by equation (2), because in this case $F_{calc.} > F$ (P = 0.99).

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STELLINGEN

I

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