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Kinetics of the Oxidation of Formazans. II. Nickel(II) and Copper(II) Complexes of 1,3-Diphenyl-5-*o*-carboxyphenylformazan

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A study is reported of the complex formation between 1,3-diphenyl-5-o-carboxyphenyl formazan and nickel-(II) or copper(II) in ammoniacal ethanol (45.5 wt%)-water solutions. Constant ionic strength (0.09) and constant temperature (23°C) were employed. The reactions were found to proceed to an equilibrium. The influence of pH, ammonia and ammonium nitrate concentrations on the reaction rates have been determined. A detailed reaction mechanism, consistent with the experimental findings, has been worked out. Also the oxidation of the two formazan complexes by the hexacyanoferrate(III) ion is reported.

Introduction

In a foregoing article[1] the oxidation of a selected number of formazans by the hexacyanoferrate(III) anion has been described. Before considering the copper(II) oxidations of the formazans and the role of complex formation therein, we report here a study on complex formation of copper(II) and nickel(II) with 1,3-diphenyl-5-*ortho*-carboxyphenylformazan (DPC$_o$–PF), a formazan that is oxidized extremely slowly by copper(II) in ammonia containing solutions, so that no interference from oxidation needed to be feared. Also the hexacyanoferrate(III) oxidation of the two complexes is described.

It is hoped that the results obtained can be used for interpreting the copper(II) oxidations of the formazans under study[1]. Therefore the main emphasis in the present work lies on reactions in ammonia-ammonium nitrate buffers in ethanol-water mixtures, the medium employed in the redox reactions.

Experimental Section

DPC$_o$–PF was synthesized according to the method of Wizinger and Biro[2]. The copper(II) and nickel(II) complexes of this formazan were prepared in the following way: for the copper(II) complex a hot filtered solution of 2.4 g copper(II) nitrate hexahydrate in 30 ml ethanol was poured into a hot solution of 5 g DPC$_o$–PF in 400 ml ethanol 96%. The instantly formed precipitate was filtered and washed thoroughly, first with water and then with ethanol 96%. After drying over phosphorus pentoxide during a night the compound was analysed for copper: 15.53% (theoretical value for a 1:1 complex 15.65%). For the nickel(II) 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 and washed thoroughly with water and ethanol 96%. After drying over phosphorus pentoxide during a night the complex was analysed for nickel: 14.48% (theoretical value for a 1:1 complex 14.64%).

All other chemicals used were reagent grade.

The reaction set up and the apparatus used have been described in the preceeding article.[1] The reactions have been studied at constant temperature (23.0± 1.0°C) and unless stated otherwise, at constant ionic strength (0.09 M $NH_4NO_3+KNO_3$) in 45.5 wt% ethanol-water mixtures.

The experiments on the decomposition of the copper and the nickel complex were performed in the following 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 of water was added containing the various chemicals to make up the medium. The nickel complex was dissolved directly into the selected medium. The experiments were carried out at four different concentrations of the complexes$(1.0–4.0)\times10^{-5}$ M for the copper and $(6.0–10.0)\times10^{-5}$ M for the nickel complex and at least four different concentrations of ammonia. The ammonium nitrate concentration was also varied, while the ionic strength was kept constant (0.09 M) by adding potassium nitrate. The concentration of the metal complexes during the decomposition was determined spectrophotometrically using the separately determined molar absorbancy indices for the complexes and the formazan. It was found that the whole spectrum could be accounted for on the basis of the presence of DPC$_o$–PF and its metal complex. The absorbance of the copper and nickel ammine complexes in the concentrations used can be neglected compared to the formazan absorbance.

In the formation experiments exactly the same circumstances have been used as in the decomposition experiments using equal concentrations of the for-

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(1) A.M.A. Verwey and S. Balt, *Inorg. Chim. Acta*, *3*, 178 (1969).

(2) R. Wizinger and V. Biro, *Helv. Chim. Acta*, *32*, 901 (1949).

mazan and the metal salt. For least squares calculations and variation analysis use was made of an I.B.M. 1130 computer..

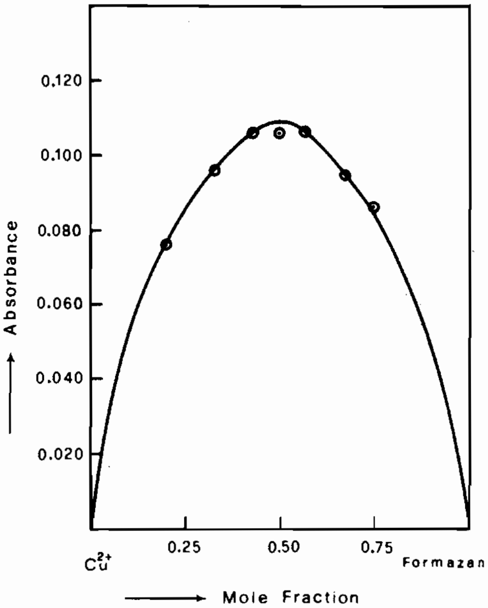

Figure 1. Corrected continuous variation plot for the system Cu^{2+}—DPC_o—PF; $(Cu^{2+})+(DPC_o—PF)=10^{-4}$ *M*, $(NH_3)=0.4$ *M*; $\lambda=550$ mμ.

Results and Discussion

Composition of the metal complexes in solution. The composition of the metal complexes in the ammoniacal solutions (45.5 wt% ethanol) was studied by the continuous variation method[3] 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[3] were plotted for the wavelength of maximum complex absorbance (corrected for the reagent contribution): $\lambda = 660$ mμ (Ni) and $\lambda = 550$ 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. All plots (of which figure 1 shows a representative one for copper) had a symmetrical or nearly symmetrical maximum for the mole proportion M^{2+}: Formazan = 1:1. This result proves the composition of the complexes in solution and in the solid state to be the same.

Stability constants of the ammine complexes. For separating 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. As yet these constants have not been determined[4] in 45.5 wt% ethanol-water. It may however be assumed that the values in this medium do not differ much from those measured in aqueous solution, because no neutralisation of charge is involved in the complex formation.[5,6] This assumption has been tested by a determination of the copper(II)-ammonia constants in ethanol (45.5 wt%)-water containing 0.09 *M* NH_4NO_3, using the pH method of Bjerrum.[7] 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[5,7] 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.

Absorption spectra. The spectra of the copper and nickel complexes 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: $\lambda_{max} = 550 \pm 5$ mμ
$\varepsilon_{max} = (16.69 \pm 0.20) \times 10^3\ M^{-1}\ cm^{-1}$
Ni: $\lambda_{max} = 660 \pm 5$ mμ
$\varepsilon_{max} = (6.23 \pm 0.18) \times 10^3\ M^{-1}\ cm^{-1}$

Reactions 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, the results of which will be given here because of their relevance for interpretating 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 $k = 1.8 \times 10^{-5}$ 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 this reason the reaction rates have been determined at varying ammonia and ammonium nitrate

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[3] J. Job, *Ann. Chim.*, 9, 113 (1928).
[4] L.G. Sillen and A.E. Martell, «Stability Constants of Metal Ion Complexes» Special Publication no. 17, The Chemical Society, London, 1964.
[5] F.C. Rossotti and H. Rossotti, « The Determination of Stability Constants», McGraw Hill, New York, 1961.
[6] A.A. Frost and R.G. Pearson, «Kinetics and Mechanism», John Wiley and Sons, New York, London 1961, page 186.
[7] J. Bcrrum, «Metal Ammine Formation in Aqueous Solutions», P. Haase and Son, Copenhagen, 1941.

concentrations, as has been described in the experimental section.

The final results obtained could be interpreted[6] by assuming a first order decomposition and a second order formation reaction with rates:

$$s'\,(\text{formation}) = k' \, . \, (M)_t \, . \, (HFo) \qquad (1)$$

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

MFo denotes the metal formazan complexes, HFo the parent ligand (with a dissociated COOH group[1]), ( ) denotes a concentration. $(M)_t$ denotes the total metal ion concentration. 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.[6] It is clear that k and k′ are pseudo constants whose values are dependent upon the medium, as the results in Table I and II show. The values for $(NH_4) = 0.09\,M$, the medium selected for the redox reactions, have been obtained by averaging at least three independent runs. For comparison also other NH_4^+-concentrations have been used. For NiFo only a few formation rates have been obtained from decomposition reactions; in the other cases the decomposition rate constant k was calculated from the first 10% reaction obeying a first order rate law. The reason for this procedure is the slowness of the reaction taking a week ore more for completion.

A survey of Table I reveals that for the copper complex as a first approximation the decomposition rate constant k is proportional to both (NH_3) and (NH_4). This suggests to write the rate constant k as:

$$k = k_{1,1} \, . \, (NH_3) \, . \, (NH_4) \qquad (3)$$

Table I. Rate constants for the Cu^{2+}—DPC_o—PF reaction in dependence of (NH_3) and (NH_4NO_3) (from the decomposition).

	(NH_3), *M*	(NH_4NO_3), *M*	k, 10^{-4} sec^{-1}	k′, 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

Using equation (3) the values of table I yield

$$k_{1,1} = (4{,}4 \pm 0.4) \times 10^{-2} \ sec^{-1} \, M^{-2}$$

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 II^{A} (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 $II^{B,C,D,E,F}$ 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). The three points mentioned suggest that the simplest way to write k is:

$$k = k_{1,0} \, . \, (NH_3) + k_{-1,1} \, . \, (NH_3)^{-1} \, . \, (NH_4) + k_{2,1} \, . \, (NH_3)^2 \, . \, (NH_4) \quad (4)$$

The $k_{-1,1}$ term is proportional to (H) and represents the pH dependence. To test the significance of this equation (4) variation analysis was applied on the

Table II. Rate constants for the Ni^{2+}—DPC_o—PF reaction in dependence of (NH_3) and (NH_4NO_3); (from the decomposition).

	(NH_3) *M*	(NH_4NO_3) *M*	k, 10^{-7} sec^{-1}	k′, 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	
F.	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	
G.	0.723	0.03	55.7	
	0.723	0.045	81.6	
	0.723	0.06	99.8	
	0.723	0.075	116.1	
	0.723	0.09	138.0	

(8) P.D. Lark, B.R. Craven, and R.C.L. Bosworth, «The Handling of Chemical Data», Pergamon, London, 1968.

experimental values using a Multiple Regression Program. For this fit the F test[8] yielded F = 1468, compared with a theoretical F for a 1% probability level of 5,14. This means that equation (4) gives a very good fit to the experimental results.

The constants involved were found to be:

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

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

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

Table I and II also contain the pseudo second order formation rate constants k′ obtained from the application of the formula[6] mentioned to the dissociation results. 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 I and II refer to the total metal ion concentration $(M)_t$: using the overall stability constants β_n for the metal ammine complexes given by Bjerrum,[7] $(M)_t$ may be expressed as:

$$(M)_t = (M) . S(NH_3) \qquad (5)$$

with

$$S(NH_3) = \sum_{n=o}^{6} \beta_n . (NH_3)^n$$

(M) refers to the concentration of the 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 $k_n{}^o$, then the rate of the formation reaction may be expressed as:

$$s' = \frac{1}{S(NH_3)} . (M)_t . (HFo) . \sum_{n=o}^{6} k'_n . (NH_3)^n \qquad (6)$$

with

$$k'_n = k_n{}^o . \beta_n .$$

This result may also be expressed in the k′ value obtained from the Frost and Pearson[6] formula using equation (1):

$$k' . S(NH_3) = \sum_{n=o}^{6} k_n' . (NH_3)^n \qquad (7)$$

Calculations on the values of k′ in Tables I and II 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 concentration.

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

$$k_3{}^o(\text{CuFo}) = (240 \pm 15) \text{ sec}^{-1} \text{ M}^{-1}$$

$$k_3{}^o(\text{NiFo}) = (31 \pm 3) \times 10^{-2} \text{ sec}^{-1} \text{ M}^{-1}$$

The results obtained above have been checked in a limited number of 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[6] in the constants k and k′ defined above, by using the quoted formula.[6] Table III and Table IV give the calculated results. The values of k and k′ were interpreted as above, giving:

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

$$\text{Cu+HFo:} \quad k_3{}^o = (280 \pm 20) \text{ sec}^{-1} . \text{M}^{-1}$$

For the more complicated nickel decomposition no rate constants were calculated; instead the experimental rates have been compared with the rates calculated from equation (4), using the constants obtained in the decomposition experiments (Table IV). It is seen that agreement between the formation and decomposition results is reasonable.

Table III. Rate constants for the Cu^{2+}—DPC_o—PF reaction at varying (NH_3) and constant $(NH_3NO_3) = 0.09$ *M*; (from the formation). [a]

(NH_3) *M*	k, 10^{-4} sec^{-1}	k′, 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

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

Table IV. Rate constants for the Ni^{2+}—DPC_o—PF reaction at vaying (NH_3) and constant $(NH_4NO_3) = 0.09$ *M* (from the formation). [a]

(NH_3) *M*	k (exp.), 10^{-7} sec^{-1}	k (calc.) 10^{-7} sec^{-1}	k′ (exp.), 10^{-3}sec^{-1}M^{-1}	k′ (calc.), 10^{-3}sec^{-1}M^{-1}
0.404	49.3	47.3	6.8	5.3
0.354	34.8	37.8	8.9	7.4
0.303	29.6	29.6	11.3	10.9
0.254	22.9	21.4	15.9	15.8

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

Table V. Pseudo first order rate constant (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, *M*	$(K_3Fe(CN)_6)$, 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

Table VI. Pseudo first order rate constant (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, *M*	$(K_3Fe(CN)_6)$, 10^{-4} *M*			
	2.0	4.0	5.0	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

Oxidation of the complexes. The kinetics of the oxidation of CuFo and NiFo by the hexacyanoferrate(III) anion has been studied in the way described earlier[1] for the formazan-$Fe(CN)_6^{3-}$ system. The reactions were followed spectrophotometrically. The initial concentration of the complexes was $2.0 \times 10^{-5}\,M$. The reaction of NiFo was found to be first order in ammonia and hexacyanoferrate(III):

$$s^* = k^* . (Fe(CN)_6) . (NH_3) . (NiFo)$$

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

In the same way the oxidation of CuFo by the hexacyanoferrate(III) anion could be fitted by the equation:

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

with

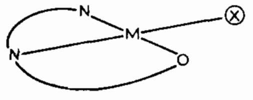
$$k^* = (4.5 \pm 0.4) \times 10^{-3} \text{ sec}^{-1} . M^{-1} \text{ (Table VI)}$$

Assuming the redox reaction to be controlled by dissociation of the complex, k* from the results obtained above would be $(4.0 \pm 0.4) \times 10^{-3}$ sec^{-1} M^{-1}, a value that is nearly identical with the k* found.

It was also attempted to oxidize the complex CuFo by a very large excess (1000 fold) of Cu^{2+} but even after some weeks no change in spectrum was observed. Addition of a large excess of Cu^{2+} to NiFo only produces metal ion exchange in the complex.

Conclusion

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[9,10,11,12] that three coordination is of common occurrence in the complexes, both in solution and in the solid state and that the fourth coordination



M=Ni,Cu

(A)

place, marked by ⊗, in the MN_2O plane of the complex schematically represented by formula (A), is difficult to fill. The reason for this fact is not well known. A molecular model of the complexes clearly showed interference between a group coordinated to the « empty » site ⊗ 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 much easier in C-cyano and N-*ortho*-hydroxyphenyl, N′-*ortho*-chlorophenyl formazan complexes.[13] This perhaps means that it is not solely a case of steric hindering. Filling of the « empty » site ⊗ produces a notable change in the absorption spectrum.[12,13] Therefore the similarity between the absorption spectra, in water and ethanol, with and without ammonia, combined with the strong indications[9,10,11,13] that in weakly basic aqueous solutions only three coordination occurs quarantee that under the experimental circumstances this fourth coordination place is not occupied.

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 (5):

The first term, $k_{-1,1} . (NH_3)^{-1} . (NH_4)$, 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. This very small term therefore is of no interest in the scope of our investigations into the reactions in ammonia buffers. From the remaining two terms the term $k_{1,0} . (NH_3)$ 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 reactions studied. This term is difficult to interpret; it may be due to a systematic error in the experiments.

There then remains as the main decomposition reaction:

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

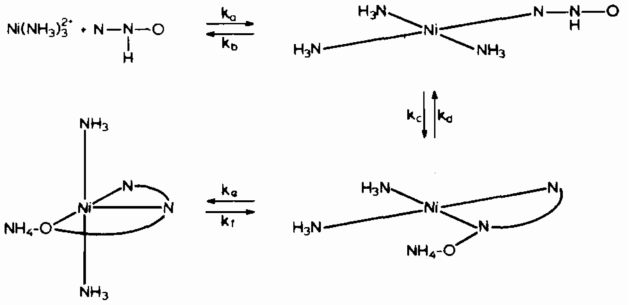
The corresponding formation rate is given by:

$$s' = k_3^{\circ} . (Ni(NH_3)_3) . (HFo)$$

referring to the reaction (but also see further on):

$$Ni(NH_3)_3^{2+} + HFo \longrightarrow$$

(For simplicit coordinated water will not be indicated unless confusion may arise), preceeded 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 expression given and of course of speculative nature, is:



(B)

(The formazan is schematically represented by the joint donor atoms as: $N{-}\underset{H}{N}{-}O$). This mechanism supposes that the association of an NH_4^+-ion to the $-COO^-$ group (and not necessarely to the O coordinated to the metal ion as the simplified scheme seems

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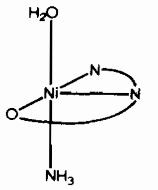
(9) M. Kishita, Y. Muto, and M. Kubo, *Naturwissenschaften*, *23*, 372 (1957).
(10 M. Kishita, Y. Muto, and M. Kubo, *Naturwissenschaften*, *23*, 612 (1957).
(11) W. Freiesleben and F. Grün, *Chimia*, *11*, 276 (1957).
(12) R. v. Tobel, Thesis Basel (1952).
(13) R. Wizinger, *Chimia*, *22 suppl.*, 82 (1968).

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 B is in a fast equilibrium with A:

$$A + NH_4^+ + 2NH_3 \rightleftarrows B$$

with a stability constant K_B for B and that no appreciable quantity of B is present.

Alternately the reaction may be seen as an attack of NH_3 on the complex



(C)

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

$$Ni(NH_3)_2^{2+} + (N{-}N{-}O)^- \longrightarrow$$

Applying the steady state treatment[14] to the concentrations of the preasumably short-living intermediates and consideration of the preceeding equilibria gives:

$$k_3^{\circ} = \frac{k_a . k_c . k_e}{k_b . k_d + k_b . k_e + k_c . k_e}$$

$$k_{1,1} = K_B . \frac{k_b . k_d . k_f}{k_b . k_d + k_b . k_e + k_c . k_e}$$

Unfortunately nothing is known about the relations between the rate constants k_a, k_b *etc.* and about the value of K_B.

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: $s' = k_3^{\circ} . (Cu(NH_3)_3) . (HFo)$

or: $Cu^{2+} + 3NH_3 + HFo \longrightarrow$

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

or: $CuFo + NH_3 + NH_4^+ = Cu^{2+} + 2NH_3 + HFo \longrightarrow$

This difference necessitates changing the scheme elaborated for NiFo in the following way: for mixed aquo complexes of copper(II) in aqueous solutions the addition of a fifth or sixth ligand is not easily accomplished[15]. 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 (A) 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 preferentially solvated by ammonia molecules in the second coordination sphere. At the moment 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 then the same as those already given in the nickel case.

The extension of the NiFo mechanism worked out for CuFo resembles the one generally[14] assumed for the S_N1 anation of cobalt(III) complexes. As already referred to it implies saturated solvation on the vulnerable coordination side.

The reaction scheme given follows the general assumption[12,13,16] that the formazan complexes have planar structures. However if the M–O bond should be perpendicular to the plane of the M–N bonds the mechanism may easily adjusted to this effect without essentially changing its content.

Concerning the oxidation of the metal complexes it must be remembered that the copper complex dissociates before it can be oxidized, while the much more slowly dissociating NiFo is oxidized directly by the hexacyanoferrate(III) anion. It is noteworthy that NiFo is oxidized according to the same rate law and at about the same rate as triphenylformazan (TPF) and diphenyl-*p*-carboxyphenylformazan(DPC_p–PF).

Compare the rate constant

NiFo 2.8±0.1 $sec^{-1} . M^{-2}$

TPF 3.6±0.1 $sec^{-1} . M^{-2}$

DPC_p–PF 2.3±0.1 $sec^{-1} . M^{-2}$

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