

Kinetics of Complex Formation between 1-(2-Hydroxyphenyl)-3,5-diphenylformazan and Ammineaquacopper(II) Complexes

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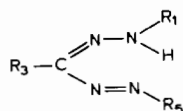
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Received August 17, 1976

A kinetic study is reported on the reaction between copper(II) perchlorate and the tridentate ligand 1-(2-hydroxyphenyl)-3,5-diphenylformazan in ammoniacal ethanol–water mixtures at constant ionic strength. A detailed analysis of medium effects has resulted in the elucidation of the mechanism of the reaction. Coordination of an amminecopper(II) complex to the formazan is shown to occur in discrete steps. A rather stable bicoordinated intermediate could be studied in solution. A comparison with earlier results has clarified some of the factors that determine the attack of metal ions on the formazans.

Introduction

Formazans (the general formula of which is given below) and their metal complexes, beside being important colour reagents and pigments [1], are



widely used in various redox systems [2]. It has been established [3] that in the metal ion catalyzed oxidation of the formazans the rate determining step is monodentate coordination of the formazans to the oxidizing metal ion. Studies in ammonia buffers have shown [4] that metal ion complex formation with the tridentate 1-(2-carboxyphenyl)-3,5-diphenylformazan occurs in discrete steps. Initially the role of coordinated ammonia in the mechanism seemed to be contradictory to postulates about the geometry of the metal complexes, but this discrepancy has recently been removed [5].

We report here a kinetic study of complex formation between copper(II) and 1-(2-hydroxyphenyl)-3,5-diphenylformazan. Especially the essential difference in mechanism of metal complex formation

between the hydroxy and the carboxy substituted formazan has helped to understand the mechanism in more detail.

Experimental

Chemicals

The preparation of 1-(2-hydroxyphenyl)-3,5-diphenylformazan and its copper complexes has been described [6].

Ethanol–water mixtures used as solvent have been made up from boiled out demineralized water and ethanol saturated with nitrogen. It has been checked that further purification of the solvent did not change the reaction rates measured. The chemicals used were of reagent grade.

Kinetic Runs

All experiments have been performed under nitrogen to prevent oxidation of the formazan by air oxygen. In all cases the solvent is a 50 wt % ethanol–water mixture, to which ammonia and ammonium perchlorate have been added to make up the medium. The ionic strength has been kept constant by adding the calculated amount of sodium perchlorate up to a final perchlorate concentration of 0.10 *M* (further denoted as *I* = 0.10 *M*). The formazan and the metal complexes could be dissolved rapidly by using an ultrasonic technique. It has been ascertained that in this way no colloidal solutions were made. For the reaction of copper(II) perchlorate with the formazan the reaction medium was made up for each of the reactants separately, after which equal volumes of these were added together. The temperature for all reactions was 25.0 ± 0.1 °C.

Two different methods have been used for measuring reaction rates:

Method A (for reactions with half-lives smaller than 1 sec) uses a stopped-flow spectrophotometer described previously [7].

Method B for slower reactions: solutions of the reactants were kept in thermostatted syringes that were then emptied via a mixing chamber into a flow-

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through cell placed in a Zeiss PM QII spectrophotometer. In this way complete mixing could be obtained in a second. The spectrophotometer was equipped with a logarithmic amplifier and a recorder to monitor the absorbance as a function of time. The reactions were followed from 10 to 95% completion. In a few cases only keeping this range was impossible in view of the small excess of one of the reactants.

Photometric rate measurements have been made at the strong absorption bands of the complexes in the visible region (generally between 15,000 and 22,000 cm^{-1}). As in all cases studied the observed reaction rate has been found to be independent of the wavenumber used, for each series of reactions one single wavenumber has been chosen where the difference in absorption between starting and final product is optimal.

For all reactions the measured absorbance as a function of time obeyed a first-order rate law within 1%. (Pseudo) first-order rate constants have been computed by using the published [8] LSG program.

Acid Dissociation Constant of the Formazan

1-(2-hydroxyphenyl)-3,5-diphenylformazan (denoted as H_2F) is a dibasic acid. The phenolic part is the strongest acid and can be titrated to give HF^- . The second, amide, proton is only split off on complex formation. The first acid dissociation constant (of the phenolic part) of the formazan has been determined photometrically in the medium employed for the kinetic experiments. We define:

$$K_{\text{H}_2\text{F}} = \frac{(\text{HF}^-)(\text{NH}_4^+)}{(\text{H}_2\text{F})(\text{NH}_3)}$$

At four different wavenumbers (between 16,000 and 22,000 cm^{-1}) the absorbance has been measured of a $4.4 \times 10^{-5} \text{ M}$ solution of the formazan as a function of

$$p \frac{(\text{NH}_3)}{(\text{NH}_4^+)}$$

This has been realized by varying the ammonia concentration from 0.05 to 4.00 M and the ammonium perchlorate concentration from 0.01 to 0.10 M , at constant ionic strength ($I = 0.10 \text{ M}$). In this way for each wavenumber 20 measurements have been made in the dissociation region of the formazan. $K_{\text{H}_2\text{F}}$ was then calculated, with the separately determined molar absorption coefficients of the unionized formazan and the anion HF^- , as $K_{\text{H}_2\text{F}} = 0.043 \pm 0.003$ ($25.0 \pm 0.1^\circ \text{C}$).

Results and Discussion

Composition and Structure of the Complexes Formed

When equimolar amounts of ammoniacal solutions of copper(II) perchlorate and the formazan are added

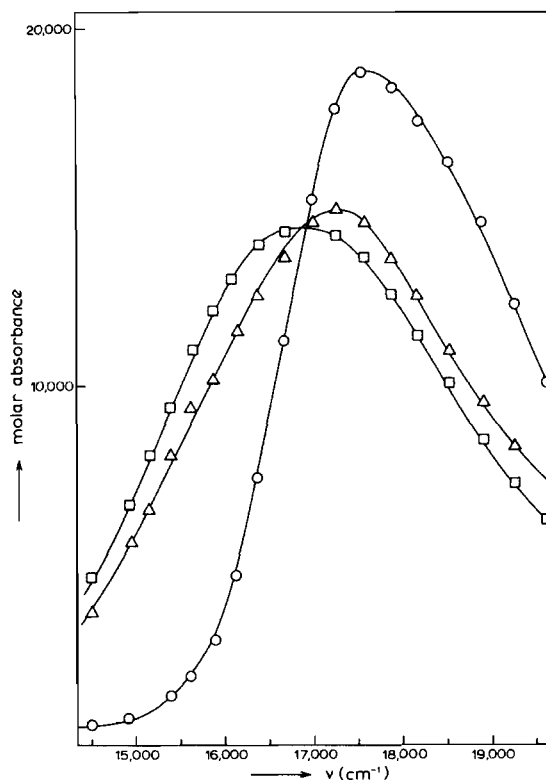


Figure 1. Visible absorption spectra of the copper(II) formazan complexes: I (Δ); II (\square) and III (\circ) (see text) with $(\text{NH}_3) = 0.66 \text{ M}$, $(\text{NH}_4^+) = 0.02 \text{ M}$ and $I = 0.10 \text{ M}$.

together a blue product (complex I) is immediately formed. The visible spectrum of this compound is given in Figure 1. Each absorbance has been obtained individually by extrapolation to zero time, using method B of mixing (this is because of a slow consecutive reaction to be described hereafter).

The formation of complex I is accompanied by a drop in pH. Titration showed that for equimolar mixtures of copper(II) and formazan the quantity of acid liberated in complex formation is equivalent to the splitting off of two protons from the ligand. The coordinated formazan is consequently present in the dianion form.

When an excess (over the equimolar ratio) of copper(II) is used, a different product spectrum in the visible is displayed. The composition of the products formed has been determined by the mol ratio method. This has been done by measuring the absorbance of rapidly mixed (method B) solutions of copper(II) perchlorate and formazan as a function of time. Figure 2 exhibits the absorbance extrapolated to zero time for a constant total formazan concentration (Form_{tot}) of $6.0 \times 10^{-5} \text{ M}$ and varying mol ratio $(\text{Cu}_{\text{tot}})/(\text{Form}_{\text{tot}})$ at two different wavenumbers. It is clear that an equilibrium exists between two complexes, with the stoichiometry $\text{Cu} : \text{Form} = 1:1$ and $2:1$ respectively. The first complex must necessarily

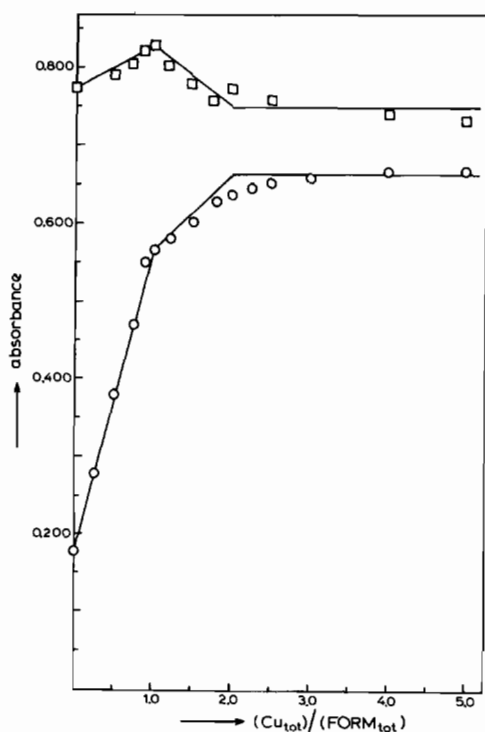
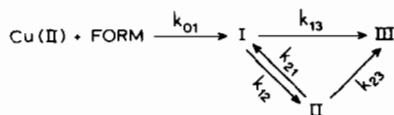


Figure 2. Mol ratio plot for the complex formation between copper(II) and 1-(2-hydroxyphenyl)-3,5-diphenylformazan. The total formazan concentration is constant ($6.0 \times 10^{-5} M$), while the concentration of copper(II) perchlorate varies. (NH_3) = 0.66 M; (NH_4^+) = 0.02 M; I = 0.10 M. The absorbance (extrapolated to zero time, see text) at 15,630 (○) and 17,860 (□) cm^{-1} is given.

be identified with the above discussed compound I. The second 2:1 compound will be denoted as complex II. The visible spectrum of compound II is given in Figure 1. Compounds I and II in the medium employed slowly rearrange to form a violet complex (III). During this reaction the pH does not change, showing that the coordinated formazan remains in the anion form. Visible (Figure 1) and ESR spectra [5] in solution show this compound to be identical to ammine [1-(2-hydroxyphenyl)-3,5-diphenylformazanato]copper(II). In the ammine complex the central ion has slightly distorted square planar coordination [5, 6]. We may sum up the compounds and reactions observed in the following scheme:



In the following the kinetics of the reactions will be described.

Formation of Complex I

The formation of complex I is rapid compared to subsequent reactions. When an excess of formazan or

equivalent amounts of copper and formazan are employed, the product of the initial rapid reaction is complex I, while all copper present is found to be converted into the complex. So no reverse or side reaction can obscure the measured rate under these conditions. By keeping the formazan in excess, a pseudo first-order rate could be maintained. The first-order rate constants have been obtained by the stopped-flow technique (method A) as a function of the medium. In the first place, by varying the formazan concentration, between 1.4×10^{-5} and $7.0 \times 10^{-5} M$ (for a copper (II) concentration of $3.0 \times 10^{-6} M$) at several fixed values of the ammonia and the ammonium perchlorate concentration, we observed that the rate constant is proportional to the formazan concentration: $k_{(\text{obsd})} = k_{01} (\text{Form}_{\text{tot}})$, if the formazan is in excess. Also k_{01} is independent of the copper concentration, varied between 3.0×10^{-6} and $1.0 \times 10^{-5} M$. Table I and Table II contain the observed rate constant as a function of the concentration of ammonia and ammonium perchlorate at constant excess formazan, ionic strength and temperature. From these values we can determine the reactive aminocopper(II) complexes and the form in which the ligand reacts with the metal complexes [3]. From pH measurements and absorption spectra [9] we concluded that under the present circumstances hydrolysis of copper(II) never exceeds 1%.

If now we assume generally that each aminocopper(II) complex $\text{Cu}(\text{NH}_3)_n^{2+}$ (omitting coordinated water) reacts at its individual rate with both the neutral formazan (rate constant $k_{01}^{0,n}$) and the phenoxide anion ($k_{01}^{1,n}$) of the formazan, the rate constant k_{01} defined above can be split into its component parts as follows:

TABLE I. Rate Constant for the Reaction between Copper (II) Perchlorate and 1-(2-Hydroxyphenyl)-3,5-diphenylformazan as a Function of the Concentration of Ammonium Perchlorate at Constant Ammonia Concentration^a.

(NH_4^+) M	$10^{-4} k_{01}$ $M^{-1} \text{sec}^{-1}$	
	Obsd	Calc ^b
0.010	208	209
0.020	163	162
0.030	133	132
0.040	114	111
0.060	83	85
0.080	69	68
0.100	53	57

^a(NH_3) = 0.534 M; I = 0.10 M; $t = 25.0 \pm 0.1^\circ \text{C}$, in 50 wt % ethanol-water; measured at $16,650 \text{ cm}^{-1}$. (FORM_{tot}) = $6.2 \times 10^{-5} M$; (Cu_{tot}) = $6.2 \times 10^{-6} M$. ^bCalculated from equation (2), using the parameter values given in the text.

TABLE II. Rate Parameters for the Reaction between Copper(II) Perchlorate and 1-(2-Hydroxyphenyl)-3,5-diphenylformazan as a Function of the Ammonia Concentration at Constant pH^a.

	(NH ₃) M	10 ⁻⁴ k ₀₁ M ⁻¹ sec ⁻¹	10 ⁻⁸ k ₀₁ ¹ M ⁻⁴ sec ⁻¹
A ^a	0.129	420	3.53
	0.257	213	3.55
	0.386	137	3.50
	0.515	106	3.70
	0.644	84.2	3.77
	0.901	54.1	3.56
	1.29	38.3	3.89
B ^a	0.265	326	3.76
	0.529	163	3.92
	0.795	104	3.96
	1.06	71.6	3.83
	1.32	53.6	3.75
	1.85	35.2	3.80
	2.65	21.3	3.74

^aA: (NH₃)/(NH₄⁺) = 12.9; B: (NH₃)/(NH₄⁺) = 26.5. Remaining conditions as in Table I.

$$k_{01} = \sum_{n=0}^5 \frac{\beta_n (\text{NH}_3)^n}{S(\text{NH}_3)} \cdot \frac{k_{01}^{0,n} + k_{01}^{1,n} K_{\text{H}_2\text{F}} (\text{NH}_3) (\text{NH}_4^+)^{-1}}{1 + K_{\text{H}_2\text{F}} (\text{NH}_3) (\text{NH}_4^+)^{-1}} \quad (1)$$

$$\text{with } S(\text{NH}_3) = \sum_{n=0}^5 \beta_n (\text{NH}_3)^n$$

β_n is the overall stability constant of the complex Cu(NH₃)_n²⁺ (in the following the stepwise constant $K_n = \beta_n/\beta_{n-1}$ will also be used). At constant ammonia concentration (results of Table I) equation (1) reduces to:

$$k_{01} = \frac{a_1 + a_2 (\text{NH}_3) (\text{NH}_4^+)^{-1}}{1 + a_3 (\text{NH}_3) (\text{NH}_4^+)^{-1}} \quad (2)$$

Equation (2) has been fitted to the k_{01} values of Table I by a steepest descent procedure using the least-squares criterium. From this a_1 is zero within the experimental error, $a_2 = 133 \times 10^3 \text{ sec}^{-1} \text{ M}^{-1}$ and $a_3 = 0.045$. A comparison of the equations (1) and (2) shows that a_3 must equal $K_{\text{H}_2\text{F}}$.

An independent photometric determination of $K_{\text{H}_2\text{F}}$ has given the value 0.043 ± 0.003 . The agreement is very good. The fact that $a_1 = 0$ means that the formazan only reacts in the anion form.

A further simplification of equation (1) is possible from the observation that at constant pH k_{01} to a first approximation is inversely proportional to the ammonia concentration (Table II). In the ethanol-water mixtures used as solvent we can use [10] for β_n the values published [11] for water. It can then be calculated that under the present experimental condi-

tions copper(II) is mainly present as the tetraammine complex. This suggests to reduce equation (1) to:

$$k_{01}^1 = \frac{k_{01} S(\text{NH}_3)}{f(\text{HF}^-) (\text{NH}_3)^3} = \beta_3 k_{01}^{1,3} + \beta_4 k_{01}^{1,4} (\text{NH}_3) \quad (3)$$

in which $f(\text{HF}^-)$ is the ionized fraction of the formazan. The calculated values of k_{01}^1 are seen to be constant within the experimental error (Table II). This means that only the triammine complex Cu(NH₃)₃⁺ is a reactive species in the complex formation. The averaged calculated values of $k_{01}^{1,3}$ are in Table III.

TABLE III. Calculated Values of Rate and Equilibrium Parameters Used to Describe the Formation of Complex I.

(NH ₃) (NH ₄ ⁺)	10 ⁻⁶ k ₀₁ ^{1,3} M ⁻¹ sec ⁻¹	K ₄ ^b M ⁻¹	K ₄ K ₅ ^b M ⁻²
	(3) ^a	(1) ^a	(1) ^a
12.9	191	235	142(110)
26.5	201	189	100(110)

^aCalculated from fitting to the equation given in parentheses.
^bIn parentheses the values published by Bjerrum [11].

We have also checked whether the use of the aqueous values for β_n did influence the final result. To this end we have kept the stability constants as variable parameters in equation (1) and have assumed that copper(II) is only present as triammine, tetraammine and pentaammine complex and that only the corresponding reactions exemplified by the rate constants $k_{01}^{1,3}$, $k_{01}^{1,4}$ and $k_{01}^{1,5}$ could differ from zero.

Subsequent fitting to the observed rate constants in Table II resulted in values for the various parameters that agree very well with the values obtained from equation (3) and with the aqueous stability constants (see Table III) for the comparison); $k_{01}^{1,4}$ and $k_{01}^{1,5}$ came out to be zero within the experimental error.

Rearrangement of Complex I

The rearrangement has been observed under a slight excess of formazan. The presence of complex II can then be neglected and also the oxidation of the formazan or the complex by copper(II) is excluded. Under the conditions employed the equilibrium between I and III lies completely on the side of the end product III, so no reverse reaction has to be taken into account. The reaction obeys a first-order rate law. In Figure 3 the observed rate constant is plotted as a function of the excess (over the 1:1 ratio) formazan concentration (Form_e) at fixed combinations of (NH₃) and (NH₄⁺).

From the plots it is clear that the rearrangement occurs via two independent pathways, according to:

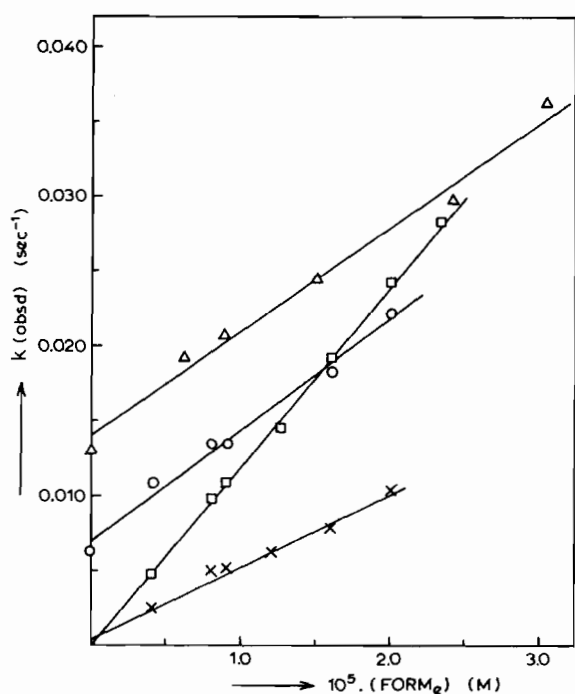


Figure 3. Observed rate constant for the reaction I \rightarrow III (see text) as a function of the excess formazan (over the copper/formazan 1:1 ratio). This excess is plotted as (FORM_e) ; measured at $16,650 \text{ cm}^{-1}$, $I = 0.10 \text{ M}$ and $t = 25.0^\circ \text{C}$. a (O): $(\text{NH}_3) = 0.36 \text{ M}$, $(\text{NH}_4^+) = 0.02 \text{ M}$; b (\square): $(\text{NH}_3) = 0.014 \text{ M}$, $(\text{NH}_4^+) = 0.02 \text{ M}$; c (\times): $(\text{NH}_3) = 0.014 \text{ M}$, $(\text{NH}_4^+) = 0.10 \text{ M}$ and d (Δ): $(\text{NH}_3) = 0.66 \text{ M}$, $(\text{NH}_4^+) = 0.02 \text{ M}$. In a, b and c a fixed copper(II) concentration of $3.53 \times 10^{-5} \text{ M}$ is used, in d the total formazan concentration is constant at $6.0 \times 10^{-5} \text{ M}$.

$$k_{(\text{obsd})} = b_1 + b_2 (\text{Form}_e) \quad (4)$$

The first term of equation (4) can be studied at equivalent concentrations of copper(II) and formazan. It was found that under these circumstances redox reactions were negligible by taking the ammonia concentration higher than 0.3 M . Table IV gives $k_{(\text{obsd})}$ as a function of the ammonia and the ammonium perchlorate concentrations. Inspection of the values in the Table suggests to express $k_{(\text{obsd})}$ (b_1 of equation (4)) as:

$$b_1 = b_1^0 + b_1^1 (\text{NH}_3)(\text{NH}_4^+) \quad (5)$$

A least-squares regression analysis on the values of Table IV then gives:

$$b_1^0 = 0.0005 \pm 0.003 \text{ sec}^{-1}, \quad b_1^1 = 0.86 \pm 0.03 \text{ M}^{-2} \text{ sec}^{-1}$$

From Table IV it is clear that the agreement between the observed b_1 values and those calculated from the parameter values given above is satisfactory.

Secondly, the medium dependence of the formazan dependent term of equation (4) has been studied at a constant excess formazan concentration of $9.0 \times 10^{-6} \text{ M}$ and a complex concentration of

TABLE IV. Formazan Independent Part of the Rate Constant for the Rearrangement Reaction I \rightarrow III as a Function of the Ammonia and the Ammonium Perchlorate Concentrations^a.

(NH_3) M	(NH_4^+) M	$k (= b_1)$ sec^{-1}	
		Obsd	Calc ^b
0.362	0.010	0.0028	0.0036
	0.020	0.0063	0.0067
	0.030	0.0082	0.0098
	0.050	0.0128	0.0161
	0.070	0.0220	0.0223
	0.100	0.0293	0.0316
0.662	0.010	0.0077	0.0062
	0.020	0.0132	0.0119
	0.050	0.0283	0.0289
	0.070	0.0363	0.0403
	0.100	0.0523	0.0574
1.33	0.010	0.0143	0.0119
	0.020	0.0270	0.0233
	0.030	0.0373	0.0347
	0.040	0.0490	0.0461
	0.050	0.0600	0.0575
	0.070	0.0817	0.0803

^a $(\text{FORM}_{\text{tot}}) = (\text{Cu}_{\text{tot}}) = 6.0 \times 10^{-5} \text{ M}$, $I = 0.10 \text{ M}$; $t = 25.0 \pm 0.1^\circ \text{C}$, in 50 wt % ethanol-water; measured at $16,130 \text{ cm}^{-1}$. ^bFrom equation (5) and the parameter values given in the text.

$5.2 \times 10^{-5} \text{ M}$. The observed pseudo first-order rate constant has been observed as a function of (NH_3) and (NH_4^+) (varied from 0.003 to 1.33 M and from 0.010 to 1.00 M , respectively up to a total of 52 independent rate measurements).

A first approximation to the equation to be used to express the medium dependence of the rate constants of Table V has been obtained by looking at the $k_{(\text{obsd})}$ values measured at pH values where the acid dissociation of the formazan can be neglected. After the subtraction of the formazan independent contribution b_1 of equation (5), the remaining part of the rate constant appeared to be inversely proportional to the ammonium ion concentration. In view of the mechanism, the most obvious way of explaining this term is to write it as

$$\frac{(\text{NH}_3)}{(\text{NH}_4^+)} \cdot \frac{1}{(\text{NH}_3)}$$

The factor $(\text{NH}_3)/(\text{NH}_4^+)$ suggests a formulation of the reaction analogous to the formation reaction, that is, involving the anion HF^- . The remaining factor $(\text{NH}_3)^{-1}$ can be explained as dissociation of one ammonia ligand from the complex I to add the formazan. On this basis a more general formula for

TABLE V. Rate Constant for the Rearrangement Reaction I \rightarrow III as a Function of the Medium^a.

(NH ₃) <i>M</i>	(NH ₄ ⁺) <i>M</i>	<i>k</i> sec ⁻¹	
		Obsd	Calc ^b
0.003	0.010	0.0155	0.0168
	0.035	0.0053	0.0061
	0.050	0.0052	0.0048
	0.100	0.0035	0.0034
0.102	0.010	0.0128	0.0130
	0.035	0.0090	0.0079
	0.050	0.0083	0.0081
	0.100	0.0113	0.0110
0.660	0.010	0.0133	0.0140
	0.035	0.0278	0.0260
	0.050	0.0390	0.0340
	0.100	0.0652	0.0619

^a(Complex I) = $5.2 \times 10^{-5} M$; (FORM_e) = $9.0 \times 10^{-6} M$, I = 0.10 *M*; *t* = 25.0 ± 0.1 °C, in 50 wt % ethanol-water; measured at 16,130 cm⁻¹. ^bCalculated from equation (6) and the parameter values given in the text.

*k*_(obsd) has been written in which it was assumed that the complex I, either directly or after splitting off ammonia, could react with the neutral and with the anion form (HF⁻) of the formazan.

After writing out the various contributions as was done for equation (1), *k*_(obsd) was found to follow the parameter equation:

$$k_{(obsd)} = \frac{b_2^0 + b_2^1(NH_3)^{-1} + b_2^2(NH_3)(NH_4^+)^{-1} + b_2^3(NH_4^+)^{-1}}{1 + b_2^4(NH_3)(NH_4^+)^{-1}} + b_1^1(NH_3)(NH_4^+) \quad (6)$$

Least-squares fitting of the observed rate constant to equation (6) gives: $b_1^1 = 0.894 M^{-2} sec^{-1}$, $b_2^2 = 0.352 \times 10^{-3} sec^{-1}$, $b_2^0 = 0.63 \times 10^{-4} sec^{-1}$, $b_2^3 = 0.154 \times 10^{-3} M sec^{-1}$, $b_2^1 = 0.45 \times 10^{-5} M sec^{-1}$, $b_2^4 = 0.0575$.

Table V gives a comparison between observed and calculated rate constants for a limited number of representative results.

The values obtained for the parameters b_2^0 and b_2^1 are comparatively small, so that the terms in equation (6) containing these parameters give no appreciable contribution to the overall value of the rate constant. These contributions (stemming from the neutral form of the formazan) can consequently be neglected. It is easy to see that $b_2^4 = K_{H_2F}$, for which the values 0.043 and 0.045 have been obtained earlier. For b_1^1 the value $0.86 M^{-2} sec^{-1}$ was obtained earlier. Again the agreement is satisfactory.

The results obtained may be summarized in expressing the rate rearrangement as:

$$-\frac{d(I)}{dt} = \frac{d(III)}{dt} = k_{13}^{1,0}(HF^-)(I) + k_{13}^{1,1}(NH_3)^{-1}(HF^-)(I) + k_{13}^{2,1}(NH_3)(NH_4^+)(I) \quad (7)$$

with

$$k_{13}^{1,0} = b_2^2(K_{H_2F})^{-1}(FORM_e)^{-1} = 900 M^{-1} sec^{-1}$$

$$k_{13}^{1,1} = b_2^3(K_{H_2F})^{-1}(FORM_e)^{-1} = 400 sec^{-1}$$

$$k_{13}^{2,1} = 0.89 M^{-2} sec^{-1}$$

Rearrangement of Complex II

Complex II is formed when the amount of copper (II) is in excess over the metal/ligand 1:1 ratio. Under this condition oxidation of the complexes may occur. We have found however that, if the ammonia concentration is over 0.3 *M*, complex II rearranges to III before appreciable oxidation occurs. Figure 4 gives

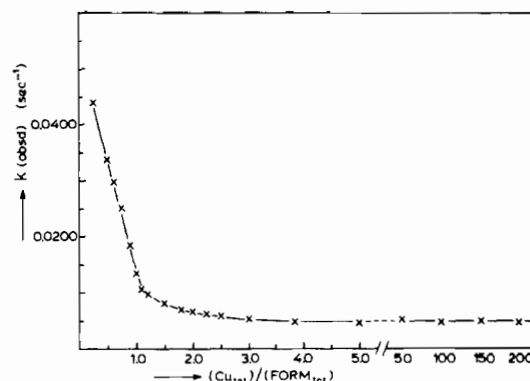


Figure 4. Observed rate constant for the formation of complex III (see text) as a function of the copper/formazan mol ratio. Results obtained at 16,130 cm⁻¹, (NH₃) = 0.66 *M*, (NH₄⁺) = 0.02 *M*, I = 0.10 *M* and *t* = 25.0 °C; the total formazan concentration is constant ($6.0 \times 10^{-5} M$), while the concentration of copper(II) perchlorate varies.

the observed pseudo first-order rate constant as a function of the ratio of the total concentrations of copper (II) and formazan. Up to the value 1 for this ratio, the plot obeys equation (4), the rearrangement of complex I. When the ratio is higher than 1 the rate decreases slowly to a constant value which remains unaltered up to a 200 fold excess of copper. This constant value of the rate constant can only be interpreted as the rate of rearrangement of complex II. This reaction has been found to obey a rate law similar to the rearrangement of I:

$$k_{(obsd)} = c_1 + c_2(NH_3)(NH_4^+) \quad (8)$$

The measured values of the first-order rate constant are in Table VI. Regression analysis using equation

TABLE VI. Rate Constant for the Rearrangement II \rightarrow III (see text) as a Function of the Ammonia and the Ammonium Perchlorate Concentration^a.

(NH ₃) <i>M</i>	(NH ₄ ⁺) <i>M</i>	<i>k</i> sec ⁻¹	
		Obsd	Calc ^b
0.660	0.100	0.0230	0.0226
0.660	0.050	0.0097	0.0113
0.660	0.010	0.0025	0.0023
0.362	0.020	0.0027	0.0025
0.660	0.020	0.0043	0.0046
1.33	0.020	0.0103	0.0091

^a(FORM_{tot}) = 6.0×10^{-5} M; (Cu_{tot}) = 3.0×10^{-4} M; I = 0.10 M; *t* = 25.0 ± 0.1 °C, in 50 wt % ethanol-water; measured at $16,130$ cm⁻¹. ^bCalculated from equation (8) and the parameter values given in the text.

(8) gives $c_1 = 0.000 \pm 0.001$ sec⁻¹, $c_2 = 0.342 \pm 0.02$ M⁻² sec⁻¹.

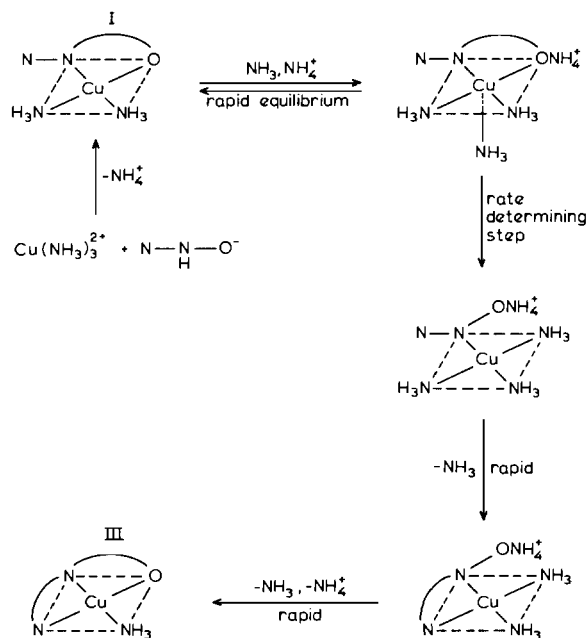
The first term of equation (8) can thus be neglected in the mechanism.

Conclusion

Of the complexes occurring in the reaction scheme given in the first subsection of the preceding section, only compound III can be isolated. Of this compound the structure is known, as outlined above. The structure of the other complexes however may be inferred from the kinetic results. We have found that complex I is formed in the reaction between Cu(NH₃)₃²⁺ and the formazan phenoxide anion. The fact that this form is the reactive species makes it reasonable to assume that in complex I the phenolic oxygen is bound to copper. During complex formation a second proton splits off. This suggests that the resulting amide nitrogen also functions as a donor atom. Complex I can then still function as a ligand for a second copper(II) metal ion to form complex II, suggesting that the formazan is bicoordinated in complex I. We may then formulate the rearrangement I \rightarrow III as the coordination of the third donor atom of the formazan. The complicated medium dependence of the reaction excludes the direct combination of the last donor atom. In fact the medium dependence of the formazan independent rearrangement is exactly the same as found for the decomposition of the ammine [1-(2-carboxyphenyl)-3,5-diphenylformazanato] copper(II) complex [4] (the corrected [5] formula is used here).

We propose to adopt a similar mechanism here, which means that the rate determining step is breaking of the Cu–O bond in a reactive intermediate, formed from I by coordination of an extra ammonia

ligand to the central ion of complex I and simultaneous addition of an ammonium ion at the negative (oxygen donor atom) side of the ligand. The Cu–O bond is then labilized by the pentaammine effect [12] and the positive ion associated with the oxygen donor atom. Then in a rapid subsequent reaction the ligand will first coordinate via two nitrogen atoms, after which the oxygen will re-coordinate. Indeed in a constructed molecular model the last mentioned coordination sequence (N, N, O) seemed to be less hindered than the sequence (O, N, N). The proposed mechanism is pictured in the following scheme:



In this scheme the formazan is represented by its donor atoms.

A similar mechanism must be assumed for the reaction II \rightarrow III, as the rate constant for this reaction obeys the same rate equation as the formazan independent path of the reaction I \rightarrow III. The second, formazan dependent, route of the reaction I \rightarrow III can easily be accommodated to the proposed mechanism. This reaction route has already been formulated as coordination of the formazan anion to complex I at the side vacated by a leaving ammonia molecule. A more exact analysis has also revealed a second reaction route of coordination of an extra formazan anion to the complex without splitting off ammonia. The originally bound formazan can then leave. If the entering ligand attacks with its oxygen donor atom, the only result is ligand exchange in I. A first coordination step via nitrogen, however, is also possible and can result in the stable product III. This mechanism is reinforced by the fact that the analogous carboxyphenylformazan directly forms a stable product, the structure of which is analogous to

III [5]. This product is formed at a rate similar to the one of the present reaction [4].

If this proposition is accepted, the difference between both systems lies in the presence of a comparatively stable intermediate I in the case of the hydroxyphenyl ligand, probably as a result of the possibility that a stable five-membered ring can be formed in I. It is then easy to accept that for the carboxyphenyl ligand coordination of the carboxy group will not result in ring closure (this possibility is mechanistically excluded by the principle of microscopic reversibility [4, 10]).

Summing up the conclusions reached we may say that, especially for more complicated multidentate ligands as the formazans are, the successive addition of the donor atoms forms a complicated pattern, in which ring closure is not automatically a fast consecutive reaction to the coordination of the first donor atom. This possibility of ring closure as the rate determining step is receiving increasing attention [13].

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