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Kinetics of the Oxidation of Formazans. III. Oxidation by Copper(II) Ammine Complexes

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A study is reported of the oxidation of several formazans by copper(II) ammine complexes in 45.5 wt% ethanol-water mixtures at constant temperature (25±0.1°C) and at constant ionic strength (0.09 M *ammonium nitrate). The rate law found indicates that the mechanism for the initial stage of the oxidation is analogous to the complex formation reaction of copper(II) with 1,3-diphenyl-5-o-carboxyphenylformazan. The change in rate constant for the oxidation of 1,5-diphenyl-3-carboxyformazan on variation of the weight percentage of ethanol is consistent with this mechanism. A comparison between the oxidation of the formazans by hexacyanoferrate(III) and copper(II) revealed that in 45.5 wt% ethanol-water the ratio $k(Cu^{2+})/k(Fe(CN)_6^{3-})$ was nearly equal for the « red » formazans TPF and DPC_p—PF. The « yellow » formazans DPF and DPC—F have different values for this ratio.*

Introduction

In a preceding article the oxidation of several formazans by the hexacyanoferrate(III) anion under alkaline conditions has been reported.[1] In this article the results obtained in the outer sphere hexacyanoferrate(III) oxidations will be contrasted with the oxidations by copper(II). As copper(II) forms complexes[2-8] with the formazans under study it may be expected that the mechanism will be different in the sense that electron transfer between Cu^{2+} and the formazans is preceded by complex formation.

The copper(II) oxidations could be performed in the same medium as that employed for the hexacyanoferrate(III) oxidations, because the excess of ammonia keeps copper in solution.

Experimental Section

Reaction conditions, apparatus and chemicals used have been described in part I.[1] All solutions were intensively treated with nitrogen to prevent air oxidation of the formazans. The rate of the reaction was studied at constant temperature (25.0±0.1°C) and ionic strength: 0.09 *M* ammonium nitrate. All experiments have been performed with copper(II) in concentrations of $(1.8\text{-}10.8)\times 10^{-4}\,M$ in excess over the formazans $(1.8\text{-}3.6)\times 10^{-5}\,M$.

The formazans studied were:

1,5-diphenylformazan(DPF)
1,3,5-triphenylformazan(TPF)
1,5-diphenyl-3-carboxyformazan(DPF—C)
1,3-diphenyl-5-o-carboxyphenylformazan(DPC_o—PF)
1,3-diphenyl-5-p-carboxylphenylformazan(DPC_p—PF)

Results and Discussion

A logarithmic plot of the measured absorbance at the formazan maximum versus time showed straight lines in all cases. This results proves the reaction to be first order in the total formazan, indicated by FNH; in the following the same abbreviations and symbols as in part I[1] will be used. The pseudo first order constant k obtained from the logarithmic plots is proportional to the total copper(II) concentration $(Cu)_t$ (dropping ionic charges):

$$s = k' . (FNH) = k . (Cu)_t . (FNH) \qquad (1)$$

(s = reaction rate).

Results in k are given in Table I. For the analysis of the ammonia dependence of the rate constants the copper(II)-ammonia equilibria must be reckoned with. Following the analysis of the complex formation experiments in part II[8] of the present series, we may separate the contribution of each ammine complex:

$$s = \frac{(Cu)_t . (FNH) \sum_{n=0}^{6} k_n . (NH_3)^n}{S(NH_3)} \qquad (2)$$

with $(Cu)_t = (Cu) . S(NH_3)$, $S(NH_3) = \sum_{n=0}^{6} \beta_n . (NH_3)^n$ and $k_n = k_n{}^{\circ} . \beta_n$ (Cu) = concentration of the hexaquo ion; β_n and $k_n{}^{\circ}$ are the overall stability constant[9]

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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[3,10] 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. Combining the equations (1) and (2) gives:

$$k \,.\, S(NH_3) = \sum_{n=0}^{6} k_n \,.\, (NH_3)^n \qquad (3)$$

From the values in Table I $k \,.\, S(NH_3)$ in a first approximation is proportional to $(NH_3)^3$ with a slight increase on increasing (NH_3) for TPF and DPC_p–PF. Therefore the experimental values in Table I have been analysed in two different ways: 1) k_3 has been calculated using the equation:

$$k \,.\, S(NH_3) = k_3 \,.\, (NH_3)^3 \qquad (4)$$

2) values for k_3 and k_4 were obtained from applying a Polynomial Regression Program on an IBM 1130 computer on the equation (5):

$$k \,.\, S(NH_3) = k_3 \,.\, (NH_3)^3 + k_4 \,.\, (NH_3)^4 \qquad (5)$$

In Table I the experimental k values have been compared to the ones calculated in the two ways — 1) and 2) — indicated. It appears that only for DPC_p–PF and TPF the inclusion of the k_4 term (equation (5)) gives an substantially better fit then the k_3 term alone (equation (4)). Table II gives the resulting k_n^o values.

Table I. Reaction conditions and experimental* and calculated** rate constants (sec^{-1} M^{-1}) for the formazan-copper(II) ammine oxidations in 0,09 M ammonium nitrate

	k exp.			k calc(3)**	k calc(4)**
TPF [a]***	5.4	8.1	10.8		
144	4.40	4.30	4.38	6.32	4.43
216	3.67	3.49	3.56	4.21	3.49
310	2.91	2.80	2.82	2.89	2.87
432	2.46	2.38	2.35	2.03	2.45
DPC_p–PF [a]	4.0	6.0	8.0		
201	2.55	2.59	2.68	3.49	2.65
306	2.28	2.14	2.18	2.24	2.19
400	—	1.95	1.95	1.68	1.96
471	1.69	1.71	1.66	1.47	1.73
DPF [a]	5.4	8.1	10.6		
155	5.32	5.27	5.29	5.71	5.66
216	3.84	3.86	3.75	3.81	3.81
310	2.59	2.62	2.59	2.62	2.65
432	1.90	1.89	1.84	1.83	1.89
DPF–C [a]	2.7	3.3	4.05		
150	33.70	—	33.20	34.13	33.29
224	22.67	21.97	22.67	22.80	22.50
299	17.44	16.21	17.09	16.89	16.87
499	11.33	10.94	11.03	10.91	12,07
DPF–C [b]	1.8	2.7	3.6		
297	73.89	74.44	—	78.24	73.79
446	50.39	49.26	49.17	50.53	49.49
595	37.22	35.19	37.56	36.61	37.10
744	30.56	29.58	29.17	28.28	29.62

* For each formazan k has been given as a function of: horizontally (Cu^{2+}) in units 10^{-4} M and vertically (NH_3) in units 10^{-3} M. ** The number in breakets — (3) or (4) — refers to the use of equations 3 and 4 respectively. *** [a] The formazan is dissolved in 45.5 wt% ethanol in 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 has been done before[1] for the hexacyanoferrate(III) oxidation. For this formazan the weight percentage of ethanol has been varied between 0 and 45.5 wt%, keeping the ammonia and the copper(II) concentration constant. Results are in Table III.

Table II. Rate constants k_3^o and k_4^o (sec^{-1} M^{-1}) for the oxidation of formazans by copper ammine complexes

Formazan*	k_3^o	k_4^o	$k_3^o/k(Fe(CN)_6^{3-})$
TPF [a]	50±3	1.8±0.1	14
DPC_p–PF [a]	30±2	1.6±0.1	13
DPF [a]	100±4	—	0.9
DPF–C [a]	620±15	—	57
DPF–C [b]	2870±120	—	0.9

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

Table III. Rate constants (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
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) and nickel(II) to the reaction mixture did not alter the rate of the reactions, when a correction was made for the consumption of ammonia by the metal ions.

Conclusion

The absence of a spectral indication[3,10] 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 alter the rate of the oxidation, establish that no appreciable quantity of the metal formazan complex is present under the experimental conditions. On the other hand DPC_o–PF[8] in exception to the other formazans under study, rapidly forms complexes. The complex formation of DPC_o–PF has been studied in detail[8] and it has been found that this formazan reacts with the triammine complexes of nickel(II) and copper(II). A reaction obeying the same rate law has now been found to govern the redox kinetics of the Cu^{2+}–DPF and Cu^{2+}–DPF–C systems. (For TPF and DPC_p–PF the fourth cop-

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per(II) ammonia complex too was found to contribute to the reaction rates). This may be taken as a strong indication that at least in the initial stage the mechanism is the same for complex formation and oxidation, or, in other words, that complex formation between Cu^{2+} and the formazans determines the oxidation rates. At this time it is not yet possible to say where the complex forming mechanism elaborated for the Cu^{2+} and Ni^{2+}–DPC_o–PF systems breaks off and electron transfer occurs; for DPC_o–PF, where no oxidation, but only complex formation is observed, M–O bonding seems to prevent this electron transfer process to occur. For reasons of anology it may be assumed that in the rate determining step of the redox reactions the formazan reacts with the triamminecopper(II) and the tetramminecopper(II) complex as the neutral molecule; this in contradiction to the hexacyanoferrate(III)-formazan reactions, for which indications have been found that the anion is the reactive species.[1]

This discrepancy about the nature of the reacting formazan species is confirmed by the small change in rate constant in going from water to 45.5 wt% ethanol-water for DPC–C (Table III). If the reaction did involve a change of charge the effect would have been much greater,[11] as indeed it is the case for the hexacyanoferrate(III) oxidation, where k changes by a factor 300 (Table III of ref. 1).

The rate constants found in this work for the copper(II) oxidations of the formazans may be compared with those found[1] earlier[1] for the hexacyanoferrate(III) oxidations. This can only be done for the medium 45.5 wt% ethanol-water. In the hexacyanoferrate(III) oxidations a significant difference was found[1] between the two « red » (closed form) formazans TPF and DPC_p–PF and the « yellow » (open form) formazan DPF. It was suggested earlier[1] to explain this difference from the greater acid strength of the « yellow » form. In the copper(II) oxidations however the three formazans mentioned are oxidized at about the same rate; this may be explained from the fact that in the copper(II) oxidations the undissociated formazan reacts, so that the acid strength is no longer relevant.

If we accept the above interpretation DPF–C is oxidized by Cu^{2+} at a much greater rate then could be expected from the hexacyanoferrate(III) oxidations. (Compare the ratio $k_3^o/k(Fe(CN)_6^{3-})$ in Table II). This may be due to the COO^--group favouring complex formation. Ring formation may in this case differ from the Cu^{2+}–DPC_o–PF mechanism.

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