

Kinetics of the Oxidation of Formazans. I.
Hexacyanoferrate(III) Oxidations

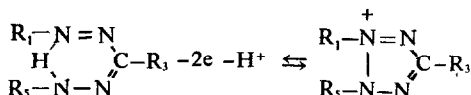
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A study is reported of the hexacyanoferrate(III) oxidations of several formazans in ammonia containing solutions. The reactions were performed in water as well as in ethanol (45.5 wt%) water mixtures at a temperature of 25°C and at an ionic strength of 0.09. With only one exception the reactions appeared to be first order in the formazan, hexacyanoferrate(III) and ammonia. Variation of the ammonium nitrate concentration at constant ionic strength revealed two competing reactions: oxidation by the $\text{Fe}(\text{CN})_6^{3-}$ and by the $\text{NH}_4\text{Fe}(\text{CN})_6^{2-}$ anion. The predominant reaction was found to be the oxidation of the formazan anion by the hexacyanoferrate(III) anion.

Introduction

Formazans¹ are compounds which contain the characteristic chain of atoms $-\text{N}=\text{N}-\text{C}=\text{N}-\text{NH}-$. They generally possess a good solubility in organic solvents as ethanol, acetone, benzene and chloroform. Their solutions show strong absorption bands in the visible and the ultraviolet. Formazans can have several possible structures due to geometrical isomerism.^{2,3} They behave as weak acids; unstable solid sodium and potassium salts have been isolated.^{4,5,6} Formazans form metal complexes⁷⁻¹² particularly of copper(II) and nickel(II) having the properties of chelates. Formazans can be oxidized by many oxidizing reagents to tetrazolium salts:¹³⁻¹⁶



In all work reported the oxidation of formazans has been used for preparative purposes; no detailed kinetic study of this oxidation has been published.

The aim of the present series is to determine the influence of complex formation on the oxidation of formazans. Complex formation has been proved to play an important part in many oxidations by metal ions.¹⁷⁻¹⁸ The effect mentioned will be studied by comparing on the one hand « outer sphere » and « inner sphere » oxidizing reagents and on the other hand formazans with an extra complex forming group (*in casu* $-\text{COOH}$) and simple compounds. In this part of the series the hexacyanoferrate(III) oxidations are reported. This ion appears to react chiefly via electron transfer,¹⁹ although there seem to be some indications that ligand replacement may occur in very special cases.²⁰ These oxidations have found to present enough specific difficulties not encountered in the metal ion oxidation to warrant a separate treatment. An extensive comparison between the two modes of oxidation will be presented in a following publication.

The following formazans have been studied: (referring to the above formula)

R ₁	R ₂	R ₃	
C ₆ H ₅	H	C ₆ H ₅	1,5-Diphenylformazan (DPF)
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	1,3,5-Triphenylformazan (TPF)
C ₆ H ₅	COOH	C ₆ H ₅	1,5-Diphenyl-3-carboxyformazan (DPF-C)
C ₆ H ₄ -o-COOH	C ₆ H ₅	C ₆ H ₅	1,3-Diphenyl-5-o-carboxyphenylformazan (DPC _o -PF)
C ₆ H ₄ -p-COOH	C ₆ H ₅	C ₆ H ₅	1,3-Diphenyl-5-p-carboxyphenylformazan (DPC _p -PF)

Experimental Section

Chemicals. TPF was obtained in *purum* quality from Fluka A.G.. Sodium hexacyanoferrate(III) was prepared by chlorine oxidation of a concentrated aqueous solution of sodium hexacyanoferrate(II) to which a few drops of 2N sodium hydroxide had been added. The reddish brown solution was poured into twenty times its volume of ethanol. The precipitate formed was filtered, washed with ethanol, dried and analysed. *Anal.* yielded: $\text{Fe}(\text{CN})_6^{3-}$ 66.56% (theor).

- (1) A. W. Nineham, *Chem. Rev.* 55 356 (1955).
- (2) I. Hauser, D. Jerchel and R. Kuhn, *Berichte* 82 515 (1949).
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- (4) E. Bamberger and P. de Gruyter, *J. Prakt. Chem.* 64, 199 (1901).
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- (17) W. F. Pickering and A. Mc Auley, *J. Chem. Soc. (A)* 1173 (1968).
- (18) M. M. Jones, D. O. Jonston and C. J. Barnett, *J. Inorg. Nucl. Chem.* 28, 1927 (1966).
- (19) K. B. Wiberg, H. Maltz and M. Okano, *Inorg. Chem.* 7, 830 (1968).
- (20) R. S. Murray, *Chem. Commun.* 824 (1968).

66.87%); Fe 17.86% (theor. 17.62%); N 27.17% (theor. 26.52%) DPF was synthesized according to von Pechman;²¹ DPF-C according to Bamberger;²² for DPC_o-PF the method of Wizinger⁸ was used. The same method was applied to the synthesis of DPC_p-PF, only 4-aminobenzoic acid was taken instead of 2-aminobenzoic acid. Analysis (in parentheses the calculated percentages):

	C	H
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%)

All other chemicals were reagent grade.

Reaction Conditions. Owing to the poor water solubility of the formazans used in the experiments it was necessary in most cases to use a mixture of water and ethanol up to 45.5 weight percents of ethanol. Whenever possible the experiments were also performed in water. As the reaction was found to liberate hydrogen ions, buffering of the solutions was inevitable: to this end a mixture of ammonia and ammonium nitrate was chosen. Excepting some special experiments the concentration of ammonium nitrate was kept constant at 0.09 M to ensure constant ionic strength. In order to get an idea of the ammonium nitrate influence on the reaction rate a second series of experiments was set up.

In these experiments the amount of ammonium nitrate was varied, while the ionic strength was kept constant by adding potassium or sodium nitrate. The whole set of experiments described were performed for each formazan at either one or two ionic strengths. The reaction conditions were chosen so that the oxidations could be followed photometrically and were finished in a reasonable time (up to one hour). This resulted in working under alkaline conditions ($8 < \text{pH} < 10$). A potassium hydroxide titration of the carboxylic formazans proved the carboxylic group to be completely dissociated under the experimental conditions.

The oxidations were performed in the following way: Solutions containing a constant concentration of the formazans (usually between 0.9×10^{-5} – 4.0×10^{-5} M) were treated with potassium hexacyanoferrate(III) in a ten to fifty fold excess at different ammonia concentrations. The varying concentrations were obtained by diluting more concentrated stock solutions of the formazans and of potassium hexacyanoferrate(III) that were made freshly every day to prevent air oxidation of the formazan²³ and hydrolysis of the ferrate(III).²⁴ The temperature was kept constant during the reactions (25.0 ± 0.1)°C. The decrease in concentration of the formazans was followed at 435 m μ for DPF, DPC_o-PF and DPF-C and at 485 m μ for TPF and DPC_p-PF. Because the hexacyanoferrate(III) also showed an appreciable absorption at the wavelength used for measuring the

formazan concentrations, the reference was made to contain a compensating quantity of hexacyanoferrate(III). In following the reactions use was made of an Optica CF 4 DR or a Zeiss PMQ II spectrophotometer, both equipped with thermostated stoppered 10 or 40 mm glass cells. The pH was measured with a E.I.L. 46A pH meter fitted with a GHS N 33 glass electrode and a RJ 23 calomel reference electrode.

Results and Discussion

Constant ammonium nitrate concentration. A logarithmic plot of the measured formazan absorbance (at 435 or 485 m μ) versus time showed straight lines in all cases. This result proves the reactions to be first order in the total formazan FNH. In the following concentrations are denoted by (---).

Defining the rate of a reaction as:

$$s = -\frac{d(\text{FNH})}{dt} \quad (1)$$

this result means

$$s = k' \cdot (\text{FNH}) \quad (2)$$

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

$$k' = k \cdot (\text{NH}_3) \cdot (\text{Fe}(\text{CN})_6^{3-})_t \quad (3)$$

Experimental results are in Table I; the average k values and the concentration ranges used in Table II. The most simple explanation of the (NH_3) dependence of the reaction rates is that the hexacyanoferrate(III) ion oxidizes the weakly acidic formazans as the anions FN^- (of which only a negligible amount can be present¹). In this case the oxidation of the « neutral » formazans is negligible, since no (NH_3) independent term is observed. The term « neutral » only refers to the dissociation of the imino group, the carboxylic acid group being completely dissociated (see Experimental). This interpretation requires the acid dissociation to be rapid compared with the oxidation of the anion. The very rapid proton exchange between the terminal nitrogen atoms in the formazans points in this direction.²⁵

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

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

Consequently this formazan is only oxidized in the « neutral » form. For DPF-C the percentage of ethanol was varied between 0 and 45.5 wt%. Results in k' are in Table III.

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(22) E. Bamberger and E. W. Wheelwright, *J. Prakt. Chem.* 65, 125 (1902).

(23) P. Krumholtz and H. Watzek, *Monatshft* 70, 437 (1937).

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(25) H. Zollinger, B. L. Kaul and P. B. Fischer, *Helv. Chim. Acta* 51, 1449 (1968).

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

DPF ^a **	0.9	1.35	1.80	TPF ^a	8.0	12.0	16.0	20.0
114	119.6	115.4	113.7	483	3.63	3.68	3.67	3.70
152	119.6	113.3	117.4	604	3.60	3.57	3.59	3.69
229	119.6	117.3	118.6	724	3.46	3.48	3.45	3.53
305	112.5	111.9	111.0	966	3.71	3.52	3.46	3.58
DPF-C ^a	4.32	5.76	7.20	DPF-C ^b	4.32	5.76	7.20	
381	10.63	10.98	10.94	3.8	4094	3661	3924	
305	10.69	10.53	10.56	5.7	3238	3339	3404	
228	11.18	11.40	10.79	7.6	3451	3461	3458	
191	11.15	10.84	11.31	11.4	3401	3296	—	
DPC _p -PF ^a	6.0	10.0	14.0	DPC _p -PF ^b	4.0	6.0	8.0	
477	2.42	2.39	2.33	1.91	1370	1461	1431	
286	2.17	2.30	2.26	0.76	1539	1513	1433	
DPC _o -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* has been given as a function of: horizontally $(\text{Fe}(\text{CN})_6^{3-})$ 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.

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

Formazan	(FNH) [*]	$(\text{Fe}(\text{CN})_6^{3-})^{**}$	$(\text{NH}_3)^{***}$	Solvent ^{****}	<i>k</i>
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 -PF	4.0	6.0–14.0	286–477	^a	2.3 ± 0.1
DPC _p -PF	4.0	4.0–8.0	0.76–1.91	^b	1450 ± 50
DPC _o -PF	4.0	10.0–30.0	66–328	^b	18.3 ± 0.9

* (FNH) in units $10^{-5} M$. ** $(\text{Fe}(\text{CN})_6^{3-})$ in units $10^{-4} M$. *** (NH_3) in units $10^{-3} M$. **** ^a 45.5 wt% ethanol in water; ^b water.

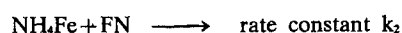
Table III. Rate constants (in units $\text{sec}^{-1} M^{-2}$) for the DPF-C- $\text{Fe}(\text{CN})_6^{3-}$ reaction as a function of the percentage of ethanol, at constant ammonia, ammonium nitrate and hexacyanoferrate(III) concentrations.

%	<i>k</i>	%	<i>k</i>
0	3381	22.1	188
4.0	1836	29.1	54
6.6	1194	45.5	11
14.0	512		

Variation of the ammonium nitrate concentration.

It is known^{26,27,28} 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.^{29,30,31} The metal ion may act as an actual bridge for electron transfer²⁹ or simply as a means of bringing to-

gether the two negatively charged ions (*in casu* FN^- and $\text{Fe}(\text{CN})_6^{3-}$). 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^{32,33,34} between K^+ and $\text{Fe}(\text{CN})_6^{3-}$ and in all probability not between Na^+ and $\text{Fe}(\text{CN})_6^{3-}$.²⁶ 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'* with varying (NH_4^+) at constant ionic strength (addition of Na^+ or K^+) and constant pH (figure 1) proves the effect of ion pairing on the oxidation rates in the $\text{NH}_4^+ - \text{Fe}(\text{CN})_6^{3-}$ system to be approximately the same as it is in the $\text{K}^+ - \text{Fe}(\text{CN})_6^{3-}$ system. These results mean that in the oxidation of the anion FN^- two competing reactions must be considered:



- (26) J. H. Swinehart, *J. Inorg. Nucl. Chem.* 29, 2313 (1967).
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 (31) M. Shporer, G. Ron, A. Loewenstein and G. Navon, *Inorg. Chem.* 4, 361 (1965).

- (32) G. S. Hartley and G. W. Donaldson, *Trans. Far. Soc.* 33, 457 (1937).
 (33) C. B. Monk, *J. Chem. Soc.* 423 (1949).
 (34) J. C. James and C. B. Monk, *Trans. Far. Soc.* 46, 1041 (1950).

Here and in the following ionic charges will be dropped. $\text{Fe} = \text{Fe}(\text{CN})_6^{3-}$. The rate constant of equation (3) can now be decomposed as follows:

$$k' \cdot (\text{FNH}) = k_1 \cdot (\text{Fe}) \cdot (\text{FN}) + k_2 \cdot (\text{NH}_4\text{Fe}) \cdot (\text{FN}) \quad (4)$$

Defining the concentration constants:

$$\alpha = \frac{(\text{FN}) \cdot (\text{NH}_4)}{(\text{FNH}) \cdot (\text{NH}_3)} ; \quad \beta = \frac{(\text{NH}_4\text{Fe})}{(\text{NH}_4) \cdot (\text{Fe})}$$

and the pseudo constant

$$\alpha' = \frac{(\text{FN})}{(\text{FNH})} \quad (5)$$

then when working at constant ionic strength and constant $\frac{(\text{NH}_3)}{(\text{NH}_4)}$ (adjusted by fixing the pH) and varying (NH_4) , k of equation (4) can be expressed as:

$$\frac{k'}{(\text{Fe})_t} = k^* = \frac{k_1 \cdot \alpha' + k_2 \cdot \alpha' \cdot \beta \cdot (\text{NH}_4)}{1 + \beta \cdot (\text{NH}_4)} \quad (6)$$

When (NH_4) is very small, the amount of NH_4Fe is negligible compared with $(\text{Fe})_t$ and equation (6) reduces to:

$$k^* = k_1' + (k_2' - k_1') \cdot \beta \cdot (\text{NH}_4) \quad (7)$$

with $k_1' = k_1 \cdot \alpha'$ and $k_2' = k_2 \cdot \alpha' \cdot \beta$.

Indeed plots of k' versus (NH_4) (of which figure 1 gives a representative one for TPF) approach straight lines at low (NH_4) . From these plots k_1' and $(k_2' - k_1') \cdot \beta$ can be obtained. At higher (NH_4) the plot deviates from the initial straight line; in this case we get from (6):

$$\frac{k^* - k_1'}{(\text{NH}_4)} = k_2' - k^* \cdot \beta \quad (8)$$

Plotting the left hand term of (8) versus k^* gives β .

In this way values of $\frac{k_1'}{k_2'} = \frac{k_1}{k_2 \cdot \beta}$ and of β have been obtained for three formazans at different ionic strengths. Experimental conditions and results are in Table IV.

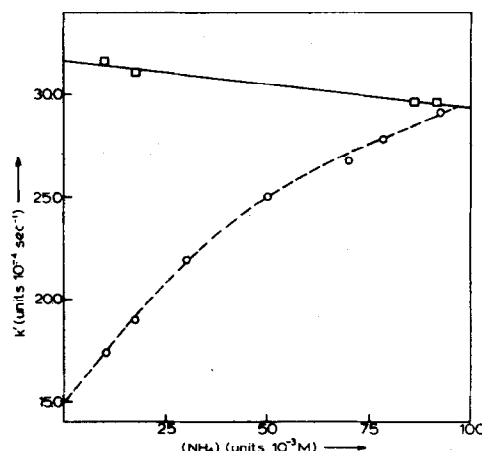


Figure 1. Reaction rate k' for the hexacyanoferrate(III) oxidation of TPF ($3.6 \times 10^{-5} M$) as a function of (NH_4) in 45.5 wt% ethanol water mixtures. The quotient of the ammonia concentration and the ammonium nitrate concentrations is 6.42.

Solid line: $(\text{K}_3[\text{Fe}(\text{CN})_6]) = 12 \times 10^{-4} M$; $(\text{K}) + (\text{NH}_4) = 0.1 M$

Dotted line: $(\text{Na}_3[\text{Fe}(\text{CN})_6]) = 12 \times 10^{-4} M$; $(\text{Na}) + (\text{NH}_4) = 0.1 M$

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 in the redox reactions (Table II). In ethanol (45.5 wt%) water mixtures DPF, DPF-C and DPC_o-PF had an absorption maximum between 435 and 455 m μ ; TPF and DPC_p-PF had one at 485 m μ . In water only the absorption maximum of DPC_p-PF changed to 435 m μ , the other maxima remained constant.

Conclusion

A comparison of the results in Tables II and III shows large differences in rates between the various formazans and between water and water-ethanol mixtures as solvents. The effect of ethanol addition on the rates may be explained from the corresponding change in dielectric constant. Table III indeed shows a smooth change. The ionic strength is too high³⁵ to connect this behaviour with the supposed reaction mechanism. The rate constants for the different formazans can only be compared in ethanol (45.5 wt%) containing mixtures, wherein all formazans could be

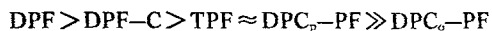
Table IV. Rate constants and reaction conditions* for experiments with variation of the ammonium nitrate concentration.

Formazan	Ionic Strength	$\frac{(\text{NH}_3)}{(\text{NH}_4)}$	k_1'	$(k_2' - k_1') \cdot \beta$	β	$\frac{k_2}{k_1}$
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; $(\text{FNH}) = 3.6 \times 10^{-5} M$; $(\text{Na}_3[\text{Fe}(\text{CN})_6]) = 12.0 \times 10^{-4} M$.

(35) A. A. Frost and R. G. Pearson, « Kinetics and Mechanism », John Wiley and Sons, New York, 1961.

dissolved. Here k increases in the order:



The rate constants for the first four formazans are all of the same order, while the rate constant for $\text{DPC}_o\text{-PF}$ is extremely small as compared to them, and also independent of the ammonia concentration. This means that under these circumstances no oxidation of the $\text{DPC}_o\text{-PF}$ anion is observed. The analogous para substituted $\text{DPC}_p\text{-PF}$ however is oxidized as the anion with $k=2.33$, comparable with k for TPF (3.60), this effect therefore may be ascribed to a steric ortho effect: internal proton bridging between the terminal N atom and the anionic ortho-carboxylic group in the formazan. This will depress the N-H dissociation constant and so the rate of the pH dependent part of the oxidation (see equation (3)). It can also explain the fact that $\text{DPC}_o\text{-PF}$ is in the yellow, while $\text{DPC}_p\text{-PF}$ is in the red form (see the following).

Something more can be said about the sequence of the first four constants. As is known formazans show^{2,3} geometrical isomerism; two of the four 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 already the names suggest, the 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 then be concluded that DPF, DPF-C and $\text{DPC}_o\text{-PF}$ are in the yellow form and TPF and $\text{DPC}_p\text{-PF}$ are in the red form under the conditions used in the experiments. Thus comparing DPF and TPF there seem to be some indications that the yellow form is somewhat more easily oxidized than the red form. Since oxidation is proceeded by acid dissociation the reason for the observed difference may also be that the red form is a weaker acid on account of its proton bridging capacity.

The ratio $\frac{k_2}{k_1}$ is greater than one for all formazans. As discussed earlier this enhancing effect of a cation on an anion-anion reaction may be expected.

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

The rate constants obtained in this paper 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.

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