

A Kinetic Study of the Reaction between Iron(III) and Hydroxylamine in Strongly Acid Perchlorate Solutions

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The kinetics of the uncatalysed and copper ion catalysed reaction between iron(III) and hydroxylamine has been studied in strongly acid perchlorate solutions. The experimental rate laws have been found to be complicated, yielding little information about the detailed mechanisms of the reactions. The numerators have a common appearance with [Cu(II)] replacing one [Fe(III)] in the rate law of the catalysed reaction as compared with the uncatalysed reaction. This indicates that copper replaces iron in the rate-determining steps of the catalysed reaction. The first steps of both reactions seem to be the rapid formation of hydroxylamine complexes with Cu(II) and Fe(III), followed by the formation of a binuclear intermediate, or activated complex, containing two hydroxylamine bridges.

The reaction



has long been used for the quantitative determination of hydroxylamine.¹⁻⁴ The method consists of boiling the solution to be analysed with an excess of iron(III) solution for a few minutes and then titrating the cooled solution with potassium permanganate. The most serious source of error by this method seems to be the incompleteness of the reaction above before the titration is performed. For this reason it was considered necessary to have iron(III) present in large excess to increase the rate of reaction. Copper(II) catalyses the reaction and has been used with success at the analysis.⁵ The present paper is devoted to a study of the kinetics of the reaction both with and without copper(II) as a catalyst. Any previous studies of this topic do not seem to have been carried out, although it seems desirable to know the factors that influence the reaction rate of this reaction.

SYMBOLS AND NOTATIONS

$[\text{Fe(III)}]$	over-all concentration of iron(III).
$[\text{Fe(II)}]$	over-all concentration of iron(II).
$[\text{Cu(II)}]$	over-all concentration of copper(II).
$[\text{NH}_2\text{OH}]$	over-all concentration of hydroxylamine ($=[\text{NH}_3\text{OH}^+]$)
A	absorbance.
a	linear absorption coefficient ($a = A/l$; l = path length).
λ	wave length.

Index $_0$ denotes quantities at a moment immediately after mixing the reactant solutions, *i.e.* at the time $t=0$.

A, B, ... G, A', B', ... S' empirical constants containing rate constants together with constant concentration terms. The meaning of these constants will be explained further in connection with the equations in which they are used.

k_i rate constants.

EXPERIMENTAL

All the chemicals used were of analytical grade. The metal salts used were the perchlorates. The metal ion concentrations of the stock solutions were determined by standard methods: iron titrimetrically with permanganate (Fe(III) after quantitative reduction in a column of finely grained cadmium), copper gravimetrically. The stock solutions of Fe(II) contained 5–10 % Fe(III) and were slowly oxidized by dissolved oxygen. The values of $[\text{Fe(III)}]$ given in this paper represent the total concentration of Fe(III), *i.e.* also the amount contributed by the Fe(II) solution.

Hydroxylamine stock solutions were prepared and the purity of the preparations used was checked in the manner described in Ref. 6. A few measurements were performed with hydroxylamine solutions prepared from $(\text{NH}_2\text{OH})_2\text{SO}_4$ and with SO_4^{2-} removed by the addition of an equivalent amount of $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, filtering off the barium sulphate formed. The results of these measurements agreed within narrow limits with those obtained with $\text{NH}_2\text{OH} \cdot \text{HCl}$.

The temperature was $25.00 \pm 0.05^\circ\text{C}$; ionic strength 1.0–1.3 M; $[\text{H}^+] = 0.100$ M for those measurements where the effect of $[\text{H}^+]$ was not especially studied. The reaction rate was not sensitive to a change of the ionic strength from 1.0 M to 1.3 M, as was found by addition of the proper amounts of sodium perchlorate to the solutions.

The kinetic measurements were carried out spectrophotometrically by a Zeiss PMQ II Spectralphotometer at the wave length 300 nm. This wave length is at the base of the strong absorption band of iron(III) in the ultraviolet region of the spectrum. The

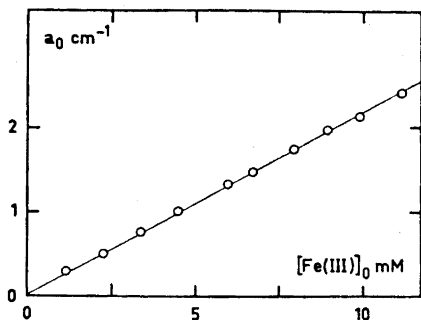


Fig. 1. Uncatalysed reaction. a_0 versus $[\text{Fe(III)}]_0$. $[\text{Fe(II)}]_0 = 0.46$ mM; $[\text{NH}_2\text{OH}]_0 = 20.00$ mM; $\lambda = 300$ nm.

absorbing species are Fe^{3+} , FeOH^{2+} , and FeCl^{2+} . Despite the fact that the absorbance is the sum of three terms, Lambert-Beer's law is obeyed, as can be seen from Fig. 1 which shows the initial absorbances obtained for different values of $[\text{Fe(III)}]_0$, while $[\text{NH}_2\text{OH}]_0$, $[\text{Cl}^-]$, and $[\text{H}^+]$ are kept constant. The rate laws were determined by the method of initial rates. By systematically changing the concentrations of all the relevant components it was possible to determine the complicated rate laws with a high degree of reliability. The reaction rates were evaluated graphically.

MEASUREMENTS AND RESULTS

Stoichiometry. The stoichiometry of the reaction seems to be well established by the use of the reaction for analytical purposes. The demand that Fe(III) should be in at least 3-fold excess at the analysis seems to be due to the fact that under these conditions the reaction between Fe(III) and NH_2OH is sufficiently rapid to be complete before the titration with permanganate. Thus, there is no reason to believe that the stoichiometry would be other than $\Delta[\text{Fe(III)}]/\Delta[\text{NH}_2\text{OH}] = 2/1$.

Rate laws. Preliminary measurements indicated that both the uncatalysed and the copper-catalysed reactions were inhibited by Fe(II). Therefore, the measurements were generally carried out in the presence of added Fe(II). The inhibition was strongest in the uncatalysed reaction, making the precision of the initial rates very poor in the absence of added Fe(II). Even with Fe(II)

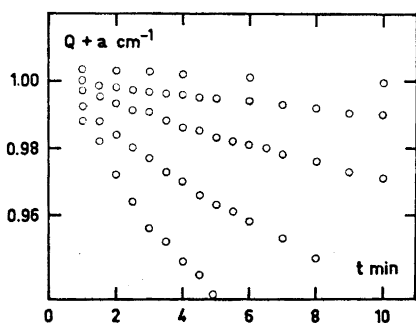


Fig. 2. Uncatalysed reaction. A few kinetic runs with $[\text{Fe(II)}]_0 = 0.46$ mM; $[\text{NH}_2\text{OH}]_0 = 20.00$ mM, while $[\text{Fe(III)}]_0$ from top to bottom is 1.14, 2.25, 4.44, 6.66, and 8.88 mM. Q is an arbitrary constant used to obtain roughly equal initial absorbances.

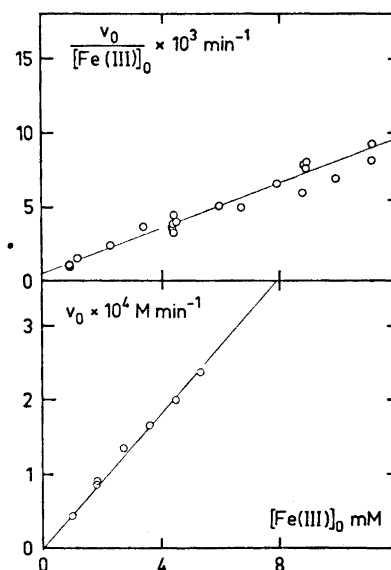


Fig. 3. Dependence of the initial rate on $[\text{Fe(III)}]_0$. Top: Uncatalysed reaction; $[\text{Fe(II)}]_0 = 0.46$ mM; $[\text{NH}_2\text{OH}]_0 = 20.00$ mM. Bottom: Catalysed reaction; $[\text{Fe(II)}]_0 = 1.80$ mM; $[\text{Cu(II)}] = 1.91$ mM; $[\text{NH}_2\text{OH}]_0 = 20.00$ mM.

added, the reproducibility was poor. The studies of the copper-catalysed reaction were carried out at so high $[\text{Cu(II)}]$ ($[\text{Cu(II)}] > 0.5 \text{ mM}$) that the uncatalysed reaction was negligible.

By determining the initial rates at concentrations of the components which were systematically changed, the following relationships were obtained.

Uncatalysed reaction:

$$-\left(\frac{\Delta[\text{Fe(III)}]}{\Delta t}\right) = v = A[\text{Fe(III)}]^2, \quad ([\text{NH}_2\text{OH}], [\text{Fe(II)}] = \text{constant}) \quad (1)$$

$$1/v = B + C[\text{Fe(II)}]^2, \quad ([\text{Fe(III)}], [\text{NH}_2\text{OH}] = \text{constant}) \quad (2)$$

$$\frac{[\text{NH}_2\text{OH}]}{v} = D + \frac{E}{[\text{NH}_2\text{OH}]}, \quad ([\text{Fe(III)}], [\text{Fe(II)}] = \text{constant}) \quad (3)$$

$$D = \text{constant} \quad ([\text{Fe(III)}] = \text{constant}) \quad (4)$$

$$E = F[\text{Fe(II)}]^2 \quad ([\text{Fe(III)}] = \text{constant}) \quad (5)$$

$$v = \frac{G}{[\text{H}^+]^2} \quad ([\text{Fe(III)}], [\text{Fe(II)}], [\text{NH}_2\text{OH}] = \text{constant}) \quad (6)$$

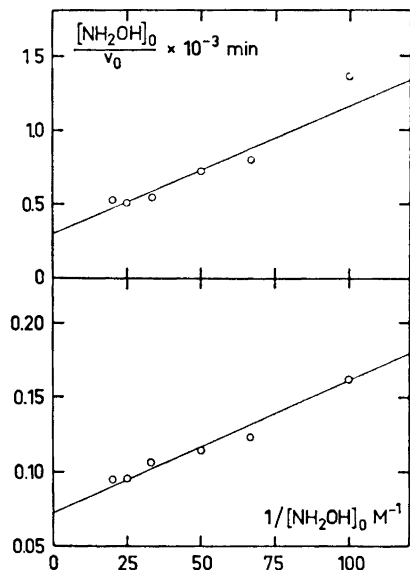


Fig. 4. $[\text{NH}_2\text{OH}]_0/v_0$ versus $1/[\text{NH}_2\text{OH}]_0$. Top: Uncatalysed reaction; $[\text{Fe(III)}]_0 = 4.34 \text{ mM}$; $[\text{Fe(II)}]_0 = 0.261 \text{ mM}$. Bottom: Catalysed reaction; $[\text{Fe(III)}]_0 = 4.58 \text{ mM}$; $[\text{Fe(II)}]_0 = 2.66 \text{ mM}$; $[\text{Cu(II)}] = 1.90 \text{ mM}$.

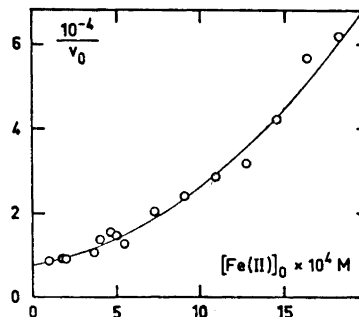


Fig. 5. Uncatalysed reaction. $1/v_0$ versus $[\text{Fe(II)}]_0$. $[\text{Fe(III)}]_0 = 8.88 \text{ mM}$; $[\text{NH}_2\text{OH}]_0 = 20.00 \text{ mM}$.

The constants A, B, C, D, E, F, and G are empirical constants. The constants D and E represent, *e.g.*, the intercept and the slope, respectively, of the straight lines obtained, when $[\text{NH}_2\text{OH}]/v$ was plotted versus $1/[\text{NH}_2\text{OH}]$ at constant

values of [Fe(III)] and [Fe(II)]. Eqn. (4) shows that D is independent of [Fe(II)], whereas eqn. (5) shows that E is proportional to [Fe(II)]². The corresponding graphs are shown in Figs. 2–5. The quantities D and E are shown in Table 1. Eqn. (2) might include a term in [Fe(II)] but the experimental error

Table 1. Experimental values of the quantities D and E. [Fe(III)]₀ = 4.34 ± 0.02 mM.

[Fe(II)] ₀ mM	D	E
0.087	337 ± 63	0.29 ± 0.66
0.174	440 ± 150	2.52 ± 1.65
0.261	309 ± 194	8.50 ± 2.22
0.348	393 ± 315	13.74 ± 3.42
0.443	517 ± 333	16.20 ± 3.61

is much higher than the value of the coefficient. The value of D might likewise increase somewhat with [Fe(II)]. The precision is, however, too poor to permit any sure decision as to whether this increase is significant. The equations above can be summarized in the experimental rate law (disregarding the dependence on [H⁺]).

$$v = \frac{k_1[\text{Fe(III)}]^2[\text{NH}_2\text{OH}]^2}{[\text{NH}_2\text{OH}] + k_2[\text{Fe(II)}]^2} \quad (7)$$

The meaning of the empirical constants A, B ... can be realised by a comparison of eqns. (1)–(6) with eqn. (7). It is seen that the empirical constants throughout represent combinations of rate constants and constant concentration terms.

Copper catalysed reaction:

$$v = A'[\text{Fe(III)}], ([\text{Fe(II)}], [\text{Cu(II)}], [\text{NH}_2\text{OH}] = \text{constant}) \quad (8)$$

$$\frac{[\text{Cu(II)}]}{v} = B' + C'[\text{Cu(II)}], ([\text{Fe(III)}], [\text{Fe(II)}], [\text{NH}_2\text{OH}] = \text{constant}) \quad (9)$$

$$B' = D'/[\text{NH}_2\text{OH}] + E'/[\text{NH}_2\text{OH}]^2, ([\text{Fe(III)}], [\text{Fe(II)}] = \text{constant}) \quad (10)$$

$$B' = F' + G'[\text{Fe(II)}], ([\text{Fe(III)}], [\text{NH}_2\text{OH}] = \text{constant}) \quad (11)$$

$$\frac{[\text{NH}_2\text{OH}]}{v} = M' + \frac{N'}{[\text{NH}_2\text{OH}]}, ([\text{Fe(III)}], [\text{Fe(II)}], [\text{Cu(II)}] = \text{constant}) \quad (12)$$

$$M' = P' + Q'[\text{Fe(II)}], ([\text{Fe(III)}], [\text{Cu(II)}] = \text{constant}) \quad (13)$$

$$N' = R'[\text{Fe(II)}], ([\text{Fe(III)}], [\text{Cu(II)}] = \text{constant}) \quad (14)$$

$$v = \frac{S'}{[\text{H}^+]^2} ([\text{Fe(III)}], [\text{Fe(II)}], [\text{Cu(II)}], [\text{NH}_2\text{OH}] = \text{constant}) \quad (15)$$

The graphs corresponding to some of these equations are shown in Figs. 3, 4, 6, and 7. The quantities B', C', M', and N' are shown in Tables 2 and 3. These equations can be summarized in the experimental rate law (disregarding the dependence on [H⁺])

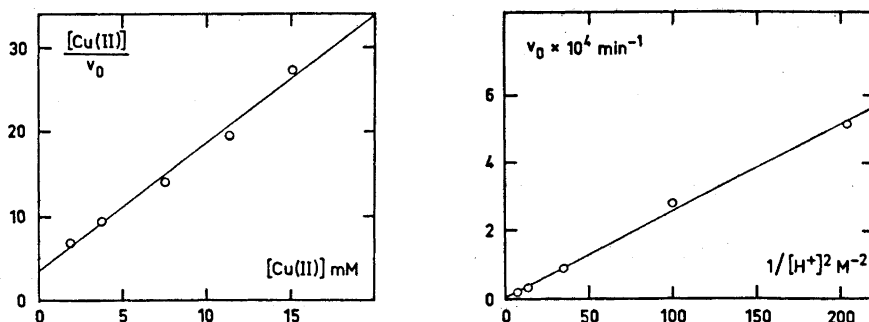


Fig. 6. Catalysed reaction. $[\text{Cu(II)}]/v_0$ versus $[\text{Cu(II)}]$. $[\text{Fe(III)}]_0 = 4.64 \text{ mM}$; $[\text{Fe(II)}]_0 = 1.73 \text{ mM}$; $[\text{NH}_2\text{OH}]_0 = 20.00 \text{ mM}$.

Fig. 7. Catalysed reaction. v_0 versus $1/[\text{H}^+]^2$. $[\text{Fe(III)}]_0 = 4.56 \text{ mM}$; $[\text{Fe(II)}]_0 = 1.69 \text{ mM}$; $[\text{Cu(II)}] = 1.90 \text{ mM}$; $[\text{NH}_2\text{OH}]_0 = 20.00 \text{ mM}$.

Table 2. Experimental values of the quantities B' and C'. $[\text{Fe(III)}]_0 = 4.61 \pm 0.14 \text{ mM}$.

$[\text{NH}_2\text{OH}]_0$ mM	$[\text{Fe(II)}]_0$ mM	B'	C'
5.00	1.73	55.9 ± 14.1	4.90 ± 1.51
7.50		23.4 ± 3.3	3.30 ± 0.65
10.00		11.9 ± 7.6	2.62 ± 0.78
12.50		11.3 ± 3.8	1.86 ± 0.40
15.00		5.28 ± 2.98	2.02 ± 0.32
17.50		4.68 ± 4.94	1.83 ± 0.52
20.00		3.47 ± 1.69	1.51 ± 0.18
	0.85	3.31 ± 0.42	1.22 ± 0.03
	1.69	3.98 ± 2.49	1.45 ± 0.21
	2.69	7.12 ± 2.31	1.28 ± 0.18
	3.59	8.53 ± 3.92	1.38 ± 0.30
	4.46	12.68 ± 2.66	1.20 ± 0.21

Table 3. Experimental values of the quantities M' and N'. $[\text{Fe(III)}]_0 = 4.64 \pm 0.12 \text{ mM}$.

$[\text{Fe(II)}]_0$ mM	$[\text{Cu(II)}]_0$ mM	M'	N'
1.73	1.90	52.9 ± 11.1	0.491 ± 0.120
	3.80	34.1 ± 8.7	0.337 ± 0.081
	7.60	26.4 ± 4.5	0.185 ± 0.041
	11.40	27.9 ± 3.5	0.087 ± 0.029
	15.10	25.9 ± 6.2	0.087 ± 0.045
0.87	1.90	47.6 ± 8.9	0.429 ± 0.084
1.74		64.1 ± 20.5	0.78 ± 0.22
2.66		72.3 ± 10.1	0.89 ± 0.12
3.54		79.4 ± 11.9	1.37 ± 0.15
4.43		89.3 ± 25.5	1.85 ± 0.45
5.59		106 ± 41	2.52 ± 0.45
7.45		127 ± 15	3.14 ± 0.19
9.32		141 ± 67	3.83 ± 1.19

$$v = \frac{k_3[\text{Fe(III)}][\text{Cu(II)}][\text{NH}_2\text{OH}]^2}{[\text{Fe(II)}][\text{NH}_2\text{OH}] + k_4[\text{Cu(II)}][\text{NH}_2\text{OH}] + k_5[\text{Fe(II)}]} \quad (16)$$

The meaning of the empirical constants A' , B' ... is evident from a comparison of eqns. (8)–(15) with eqn. (16). The following values of the constants or quotients between constants were calculated from the experimental values of B , C , D , E , B' , C' , M' , and N' : $k_1 = 126 \pm 52 \text{ M}^{-2} \text{ min}^{-1}$; $k_2/k_1 = 1800 \pm 600 \text{ M min}$; $k_3 = 10.9 \pm 3.8 \text{ M}^{-1} \text{ min}^{-1}$; $k_4/k_3 = 0.125 \pm 0.040 \text{ M min}$; $k_5/k_3 = (3.69 \pm 0.23) \times 10^{-3} \text{ M}^2 \text{ min}$. The error limits represent three standard deviations.

DISCUSSION

The experimentally determined rate laws of both the reactions are very complicated. It therefore seems difficult to draw any reliable conclusions concerning the mechanisms from either of them.

The numerators of both rate laws have a common appearance, where the rate law of the catalysed reaction contains $[\text{Cu(II)}]$ instead of one $[\text{Fe(III)}]$ in the rate law of the uncatalysed reaction. This indicates that Cu(II) replaces Fe(III) in the rate-determining step(s) of the catalysed reaction. The first step of both reactions seems to be the rapid formation of complexes between Cu(II) and Fe(III) , respectively, and hydroxylamine, followed by the formation of a binuclear intermediate, or activated complex, containing two hydroxylamine bridges. The catalytic effect of Cu(II) can then be explained by the greater strength of the $\text{Cu(II)} - \text{NH}_2\text{OH}$ complexes. The existence of rather strong copper complexes with hydroxylamine has been reported by Szilard,⁷ whereas the corresponding iron(III) complexes are unknown (and probably very weak). The concentrations of the hydroxylamine complexes of Cu(II) , Fe(III) , and Fe(II) are, however, also very small because the concentration of free NH_2OH is exceedingly small at the hydrogen ion concentrations applied in the study ($[\text{H}^+] > 0.050 \text{ M}$), the dominating hydroxylamine species being NH_3OH^+ .

The strong $[\text{H}^+]$ -dependence can be explained by a loss of two protons from two NH_3OH^+ ions in the formation of the two complexes mentioned above.

The existence of a term in $[\text{Fe(II)}]^2$ in the denominator of eqn. (7) makes it uncertain whether this equation represents the "true" rate law. An experimental rate law of this kind could be obtained from a "true" rate law of the form

$$v = \frac{P}{[\text{Fe(II)}] + Q[\text{NH}_2\text{OH}]} + \frac{R}{1 + S[\text{Fe(II)}]} \quad (17)$$

which can be transformed to

$$v = \frac{P + (PS + R)[\text{Fe(II)}] + QR[\text{NH}_2\text{OH}]}{Q[\text{NH}_2\text{OH}] + [\text{Fe(II)}] + QS[\text{Fe(II)}][\text{NH}_2\text{OH}] + [\text{Fe(II)}]^2} \quad (18)$$

The quantities P and R do not represent true constants but probably have the form $k_i[\text{Fe(III)}]^2[\text{NH}_2\text{OH}]^2$. By neglecting the proper terms, eqn. (18) can be made analogous to eqn. (7). A corresponding situation might be the case for the catalysed reaction.

From the analytical point of view it might be noted that the inhibition by the product Fe(II) is more marked with the uncatalysed reaction. With the catalysed reaction it can be made negligible by having Cu(II) in large excess.

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