

OXIDATION OF 2-MERCAPTOPROPIONIC ACID BY HEXACYANOFERRATE-(III). MECHANISTIC INTERPRETATION ON THE BASIS OF ONE-PLUS RATE EQUATION

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One-plus rate equation is a useful tool in interpreting the reaction mechanism. The oxidation of 2-mercaptpropionic (thiolactic) acid by hexacyanoferrate-(III) has been undertaken as a kinetic study and has been found to obey such type of rate law. To suggest the reaction mechanism the inference of kinetic along with extra-kinetic proofs were taken into consideration. The reaction starts with the formation of an intermediate made up from one thiolactic acid and one hexacyanoferrate-(III) molecules, in a pre-equilibrium, followed by the electron-transfer process. The influences of the thiol compound and of the hydrogen ion have been deduced from the kinetic data. The paper discusses also some general and literature examples to illustrate the concepts in connection with network elucidation.

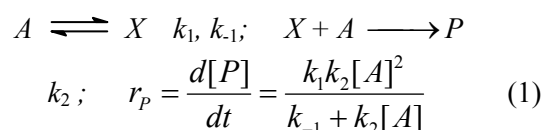
INTRODUCTION

At the very basis of chemical kinetics it is the knowledge of how the mechanics of any molecular event is reflected in the observable kinetic behaviour. Guidelines have been proposed within which a kineticist works in developing a reaction mechanism on the basis of the rate law that can be deduced from the kinetic measurements.¹⁻³ Extra-kinetic data as well as theoretical considerations will argue the given mechanism.^{4,5} Each kinetic study of a new reaction needs to measure reaction rates and compile an empirical power-law rate equation from extensive experimental results over a wide range of conditions. Unfortunately, most reactions of practical interest do not proceed by simple pathways. Therefore they do not always obey power-law rate equations and so have no exact and constant reaction orders. The larger the network, the harder is its elucidation. The rate equation of a multistep reaction with non-integer orders, especially with reverse steps, is complex and contains several terms in the denominator. They are obtained either from the steady-state or pre-equilibrium assumption. In all these cases, the number of phenomenological coefficients can be

reduced by one if both the numerator and the denominator are divided by one of the terms of the latter. The outcome is a one-plus rate equation, common in several fields of science. The traditional power-law with empirical fractional exponents cannot be expected to result from combinations of elementary steps. In contrast, one-plus rate equation can result from step combinations, contains integer (or at most integer multiple of 1/2) exponents, being more likely to reflect the true mechanism, and plays a key role in network elucidation.⁵ The phenomenological rate coefficients are combinations of elementary steps in the network.

This paper presents some literature examples to introduce the concepts, as well as the results obtained in our laboratory concerning the elucidation of the reaction mechanism on the basis of one-plus rate law.

The simplest example results from three elementary steps mechanism with X as an intermediate and an overall order between one and two.^{3,5}



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The rate law explains the fractional order. Dividing the numerator and denominator by the

$$\frac{d[P]}{dt} = \frac{k_a[A]^2}{1+k_b[A]}; \quad k_a = \frac{k_1k_2}{k_{-1}} \text{ and } k_b = \frac{k_2}{k_{-1}}; \quad \frac{[A]}{r_p} = \frac{k_b}{k_a} + \frac{1}{k_a} \frac{1}{[A]} \quad (2)$$

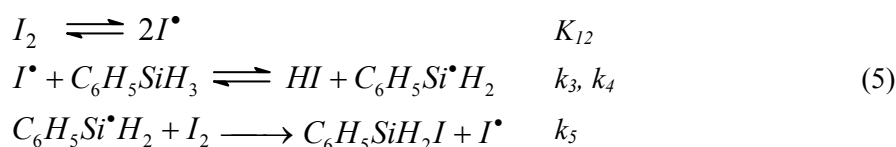
The number of rate coefficients has been reduced to two phenomenological ones (k_a and k_b). In order to determine these, a nonlinear regression can be used or the equation can be brought into a linear form and tested by linear regression or plotting.

$$\frac{d[P]}{dt} = \frac{k_a[A][B]}{1+k_b[A]+k_c[B]}; \quad \frac{[B]}{r_p} = \frac{k_b}{k_a} + \frac{1+k_c[B]}{k_a} \frac{1}{[A]} \quad (3)$$

One literature example with the order as an integer multiple of 1/2 is the gas phase reaction between iodine and various silanes at 500-600 K yielding iodinated silanes and *HI*. It obeys a classical power rate law of 3/2 order, but the apparent $k_{3/2}$ depends upon the pressure and the

$$-\frac{d[I_2]}{dt} = \frac{k'[I_2]^{1/2}[C_6H_5SiH_3]}{1+k''[HI]/[I_2]} \quad (4)$$

The rate law resembles the classical case of hydrogen bromide formation,¹² and the mechanism is similar:



An inhibition process occurs (k_4). The rate-determining step involves an iodine atom and phenylsilane in the transition state of the process characterized by k_3 . The one-plus rate law similar to (4) deduced from the mechanism allows the identification of the phenomenological rate coefficients as combinations of rate constants of the elementary steps: $k' = k_3K_{I_2}^{1/2}$, and $k'' = k_4/k_5$. The dissociation pre-equilibrium (K_{I_2}) brings about the semi-integer overall order.

$$k_{obs} = \frac{k_a''[RSCH_3][H^+]}{1+k_b''[RSCH_3][H^+]}; \quad \text{linear form:} \quad \frac{1}{k_{obs}} = \frac{1}{k_a''} \frac{1}{[RSCH_3][H^+]} + \frac{k_b''}{k_a''} \quad (6)$$

A rate saturation effect appears. By considering the inference of the kinetic behaviour, the

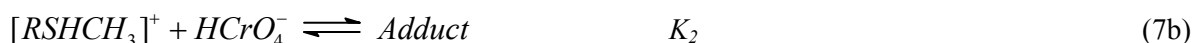
first term in the denominator, the rate law of the one-plus type is obtained:

More complex mechanisms lead to more complicated rate laws, exhibiting fractional order with respect to two participants, like (3). Here, series of measurements are required with variable concentration of A at several constant concentrations of B taken into large excess.

reaction product *HI*. In the case of phenylsilane,⁶ the rate law is of the form (4). This behaviour has been found with other silanes⁷⁻¹⁰ and toluene.¹¹ Such kinetics offers strong support for an atom abstraction chain mechanism.

The second example, based on literature survey and experimental studies of our group, concerns the oxidation of inorganic^{13,14} or organic thio-derivatives¹⁵⁻²⁰ by chromate. The formation of intermediates is a prominent feature of chromium-(VI) oxidations. Here we present the oxidation of S-methylcysteine (symbolized as *RSCH₃*) by chromate,²¹ where the combined dependence on substrate and hydrogen ion concentration upon the apparent first-order rate constant was found as:

following mechanism has been suggested:



The two coupled equilibria can also be written as an overall one, with $K = K_1K_2$.



The electron-transfer follows as rate-determining step and an S=O double bond is formed (9).



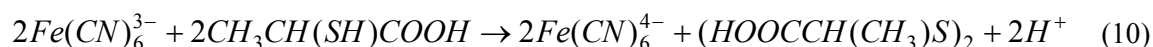
The next steps are fast, involving the formation of $Cr(V)$ that can also oxidize *S*-methylcysteine to sulfoxide.

Our experimental approach is concerned with a redox reaction in solution where 2-mercaptopropionic acid, as organic substrate, was oxidized by uniequivalent agent $[Fe(CN)_6]^{3-}$. Hexacyanoferrate-(III) is well-known as a selective one-electron outer-sphere oxidant, acting only upon the most easily oxidable substrates and frequently used as an interceptor for free radicals.²² The reduction potential of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple remains essentially constant around 0.41 V within the pH range 4 – 13, since neither the oxidized nor the reduced form are protonated,^{23,24} therefore, $[Fe(CN)_6]^{3-}$ is considered a mild oxidant. Only at higher acidities, due to the association with protons, species $H[Fe(CN)_6]^{2-}$, $H_2[Fe(CN)_6]^-$ and even $H_3[Fe(CN)_6]$ can be formed²⁵ and the potential increases from 0.56 to 0.93 V within 0.1 to 8.0 mol·dm⁻³ of H^+ concentration. The $[Fe(CN)_6]^{3-}$ ion is employed to oxidize a variety of organic substrates among which thiols, thiolacids and thioamides. The key step in the oxidation is an outer-sphere electron transfer, generally acknowl-

edged to proceed by the formation of a substrate-oxidant ion-pair or outer-sphere precursor complex, in a pre-equilibrium. Formation of such species is expected to bring about changes into the vibrational movements.²⁶

RESULTS AND DISCUSSION

The stoichiometric ratio of reaction between 2-mercapto-propionic acid (abbreviated as RSH throughout the paper) and hexacyanoferrate-(III) has been proved by spectrophotometrical titration. Mixtures having increasing RSH:hexacyanoferrate-(III) molar ratios were allowed to react to completion in acidic media (for at least 10 half times). The remaining absorbance, due to unreacted Fe(III) species, was recorded at 420 nm. Its plot against the mixing ratio showed first a linear decrease up to a 1:1 ratio, where a sharp bent took place and constant and close to zero values described a horizontal line. It was an indication that corresponding disulphide was formed as the main product (eq. 10).



The kinetic approach employed pseudo-first-order conditions (excess concentrations of the organic substrate and the hydrogen ion) as well as a constant ionic strength of $\mu = 0.5$ mol·dm⁻³. Indeed, a plot obeying a semi-logarithmic equation has been found linear, except for the initial part. By excluding this initial period, the linearity was quite good (R^2 between 0.9980 and 0.9999). This implies first-order dependence with respect to the absorbing species (we count here the hexacyanoferrate-(III) and its outer-sphere ion-pair intermediate).

The intermediate formation - proposed as cause of the early non-linearity - receives some support from

spectral measurements recorded periodically with a typical reaction mixture. Since true isosbestic points are missing, an intermediate of some kind must be formed. If an inner-sphere species would have been created a shift of the 420 nm absorption band towards higher wavelength should be expected. Such a bathochromic shift is usually associated with the ligand-metal charge transfer when sulphur replaces oxygen or carbon as ligand in the complex.^{3,17-19} The absence of such shift proves the intermediate is of outer-sphere type. The final UV-Vis spectrum of the mixture coincides with that of the hexacyanoferrate-(II), proving it is the reduction product.

Our interest here lies on the influences exhibited by the thiolactic acid and hydrogen ion on the pseudo-first-order constant, describing the electron-transfer process. Such rate coefficients have been obtained from the linear part of semi-logarithmic plots of the type $\ln(A-A_\infty) = f(t)$. The intercept corresponds to $\ln(A_0 - A_\infty)$. By A , A_0 and A_∞ were symbolized the absorbance values recorded at 420 nm at various times of reaction, at the beginning and the end of the run, respectively.

Series of measurements have been performed, firstly at three constant acidities while varying RSH concentration and secondly at three excess concentrations of RSH, where the acidity was varied. Averages of the first-order observed rate coefficients are collected in table 1 (the number of replicate runs is given in parenthesis). However, further processing has been performed on the non-averaged k_{obs} values and has resulted in a complex behaviour.

Table 1

First order rate constants at 293.0 ± 0.1 K, $\mu = 0.5$ mol·dm⁻³ and at $2.22 \cdot 10^{-4}$ mol·dm⁻³ [Fe(CN)₆]³⁻, as a function of 2-mercapto-propionic acid concentration for three different excess concentrations of HClO₄ and as a function of [H⁺] for three different excess concentrations of the thiolactic acid

| 10 ² RSH (mol·dm ⁻³) | H ⁺ (mol·dm ⁻³) | | | 10 ² H ⁺ (mol·dm ⁻³) | RSH (mol·dm ⁻³) | | |
|--|--|--|--|---|--|--|--|
| | 0.32 | 0.10 | 0.032 | | 0.011 | 0.017 | 0.022 |
| | 10 ³ k _{obs} (s ⁻¹) | 10 ³ k _{obs} (s ⁻¹) | 10 ³ k _{obs} (s ⁻¹) | | 10 ³ k _{obs} (s ⁻¹) | 10 ³ k _{obs} (s ⁻¹) | 10 ³ k _{obs} (s ⁻¹) |
| 0.444 | | 0.36 (6) | 2.96 (3) | 15.8 | 0.94 (6) | 2.14 (3) | 2.87 (3) |
| 1.11 | | 2.29 (11) | 18.8 (11) | 12.6 | 1.45 (5) | 2.93 (3) | 4.48 (3) |
| 1.67 | | 4.42 (9) | 36.0 (6) | 10.0 | 2.29 (11) | 4.42 (9) | 7.41 (14) |
| 2.22 | | 7.41 (14) | 61.5 (7) | 7.94 | 3.66 (7) | 6.91 (3) | 10.3 (6) |
| 2.78 | 1.69 (4) | 11.7 (7) | 96.9 (6) | 6.31 | 5.10 (10) | 10.3 (3) | 15.2 (6) |
| 3.33 | 2.49 (5) | 16.8 (13) | 125 (5) | 5.01 | 8.08 (8) | 14.9 (4) | 22.0 (4) |
| 3.89 | 3.40 (4) | 22.6 (8) | 156 (7) | 3.98 | 13.8 (8) | 22.1 (3) | 37.4 (5) |
| 4.44 | 4.38 (5) | 28.4 (9) | 194 (6) | 3.16 | 18.8 (11) | 36.0 (6) | 61.5 (7) |
| 5.00 | 5.38 (5) | 35.9 (3) | 207 (5) | 2.51 | 30.2 (6) | 51.9 (4) | 84.3 (5) |
| 5.56 | 6.54 (7) | 48.4 (5) | 287 (8) | 2.00 | 42.4 (7) | 78.2 (3) | 121 (3) |
| | | | | 1.58 | 63.4 (9) | 114 (3) | 171 (7) |

The reaction order with respect to thiolactic acid was obtained from $\log - \log$ plots of the data, that were linear and of slopes systematically smaller than 2 (1.93, 1.89 and 1.74 for pH's 0.5, 1.0 and 1.5 respectively). The error of the slope was found less than 3 %. Furthermore, as thiolactic acid concentration is increased, a plot of k_{obs} vs. [RSH] is a curve within lower thiolactic acid concentration range, and tends to degenerate into a line of negative intercept at higher substrate concentration range. Therefore the observed dependence doubtlessly rules out the hypothesis of an integer second-order. This behaviour is rather consistent with a one-plus form of the rate equation. On this basis, the pseudo-first order rate coefficient dependence on [RSH] (at constant acid concentration) can be written as:

$$k_{obs} = \frac{k_a [RSH]^2}{1 + k_b [RSH]}; \quad (11)$$

with the linear form:

$$\frac{[RSH]}{k_{obs}} = \frac{k_b}{k_a} + \frac{1}{k_a} \frac{1}{[RSH]} \quad (12)$$

Figure 1 presents the linear dependence, for the three hydrogen ion concentrations used (0.32, 0.10 and 0.032 mol·dm⁻³, respectively) with good correlation coefficients: 0.9901, 0.9864 and 0.9853.

When the hydrogen ion concentration has been varied at constant thiolactic acid concentration, the corresponding $\log - \log$ plots lead to fractional negative order, between -1 and -2 (-1.85, -1.76 and -1.77, when RSH concentration was 0.011, 0.017 or 0.022 mol·dm⁻³ respectively). This can be interpreted again in the light of one-plus type dependence. Figure 2 shows the good linear plots ($R = 0.9691, 0.9810, 0.9800$) of the form $1/(k_{obs}[H^+]) = f([H^+])$ so-obtained, according to the equation:

$$\frac{1}{k_{obs}[H^+]} = \frac{k_b'}{k_a'} + \frac{1}{k_a'} [H^+] \quad (13)$$

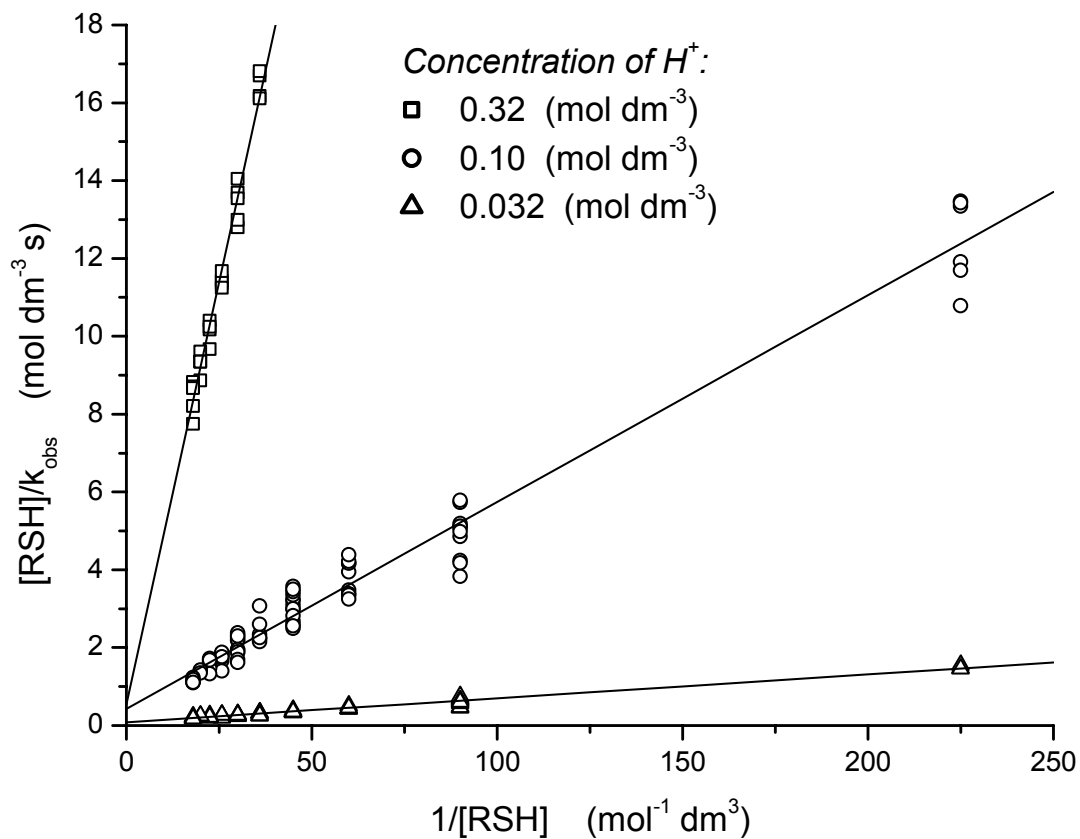


Fig. 1 – Linear plot of one-plus form at three constant $[H^+]$ and variable $[RSH]$.

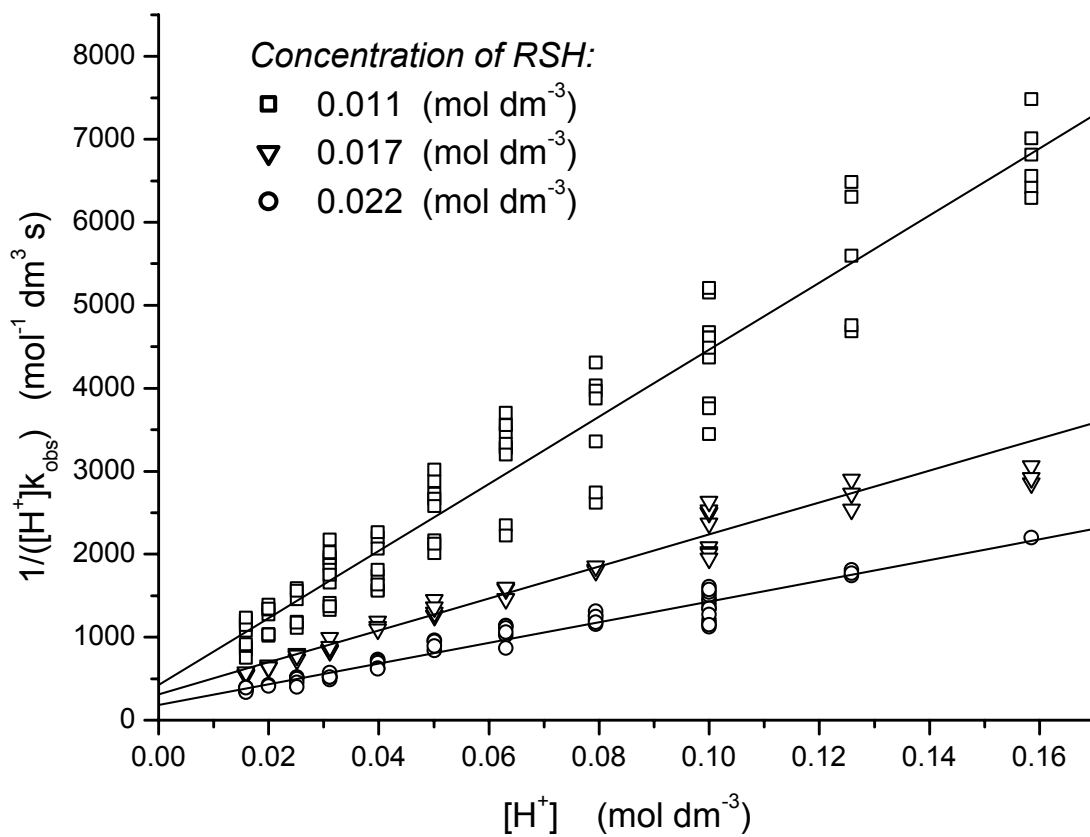


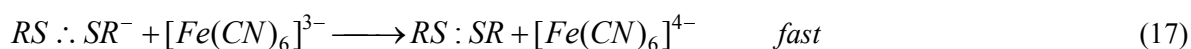
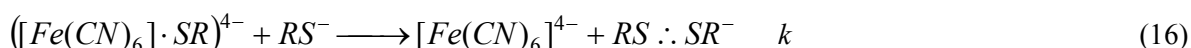
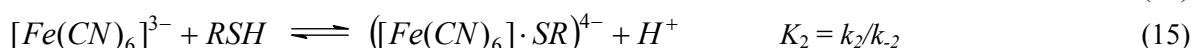
Fig. 2 – Linear dependence of one-plus form at three constant $[RSH]$ and variable $[H^+]$.

The apparent activation energy has been obtained from the temperature dependence of the observed first-order rate constant measured in the interval 283-333 K (with 0.032 mol·dm⁻³ H⁺ and 0.011 mol·dm⁻³ RSH). A value of 10.1±0.7 kJ·mol⁻¹ has been calculated from an Arrhenius plot (R = 0.9918 with averaged rate coefficients). Such an abnormally low value for redox reactions in solution suggests the involvement of an exothermal

pre-equilibrium. Similar values were found with N-acetylcysteine and 3-mercaptopropionic acid.²⁷

Additional tests aimed to prove the involvement of free radicals in the reaction by initiating the polymerization of ethylacrylate. Some polymer was formed, even in experiments at concentration level as low as in the kinetic measurements.

All the experimental facts guide us to consider the following reaction mechanism:



The oxidizing agent does not associate a proton under acid conditions employed.²⁸ Reactive species is the outer-sphere complex $([Fe(CN)_6] \cdot SR)^{4-}$, which undergoes the electron transfer assisted by a newly dissociated thiolactic acid at thiol group to form a disulphide ion-radical $RS \cdot SR^-$. The disulphide radical, having a sulphur-sulphur three electron bond, with the third electron in an anti-bonding orbital, has been identified and characterized in several cases and proved to be more stable than a thiyl radical.²⁹ Such a species has been suggested in the case of cysteine and related thiols.²⁷ It reacts fast with hexacyanoferrate-(III) to generate the final oxidation product, disulphide.

The rate law has been deduced from this mechanism, employing the pre-equilibrium assumption with the electron-transfer step (16) as rate determining. In addition, since both hexacyanoferrate-(III) and the outer-sphere intermediate absorb at 420 nm, the total *Fe(III)* concentration ($[Fe(III)]_{total} = [Fe(CN)_6]^{3-}_{free} + ([Fe(CN)_6] \cdot SR)^{4-}$) must be used. Expressing $([Fe(CN)_6] \cdot SR)^{4-}$ from equilibrium (15) and $[RS^-]$ from equilibrium (14), and inserting into the rate law of the slow step (16), the result is equation (18). This is of the one-plus form and explains the dependence on both $[RSH]$ and $[H^+]$, in an obvious agreement with the experimental findings:

$$-\frac{d[Fe(III)]_{total}}{dt} = \frac{2kK_1K_2[RSH]^2/[H^+]}{[H^+]\{1 + K_2[RSH]/[H^+]\}}[Fe(III)]_{total} \quad (18)$$

The stoichiometric factor of 2 accounts for the consumption of a second $Fe(CN)_6^{3-}$ molecule in

the fast step (17). The linear form of the observed pseudo-first order rate coefficient k_{obs} is:

$$\frac{[RSH]}{k_{obs}[H^+]} = \frac{1}{2kK_1} + \frac{1}{2kK_1K_2} \frac{[H^+]}{[RSH]} \quad (19)$$

By using all the data collected in our measurements we have obtained a linear dependence as described by equation (19), with a

relatively good correlation coefficient, R = 0.9734 (figure 3 and eq. 20).

$$\frac{[RSH]}{k_{obs}[H^+]} = (4.9 \pm 0.4) + (4.95 \pm 0.07) \frac{[H^+]}{[RSH]} \quad (20)$$

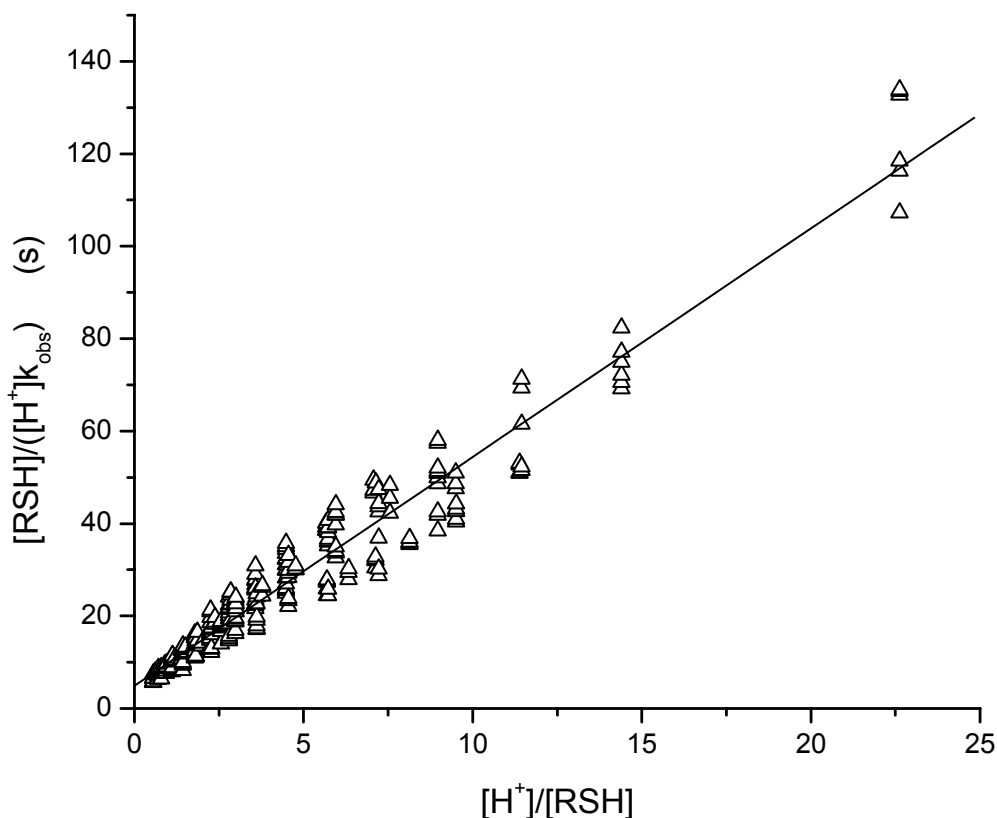


Fig. 3 – Plot of eq. (19) deduced from the mechanism.

From the parameters of the linear regression we were able to compute $K_2 = 0.99 \pm 0.09$ and $2kK_1 = 0.20 \pm 0.02 \text{ s}^{-1}$. The specified error is the standard error of the parameter. An estimate of k , based on the acid dissociation of the thiol group ($\text{pK}_a = 10.24$),³⁰ leads to a value of $(1.8 \pm 0.2) \cdot 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, close to diffusion limit, also arguing for the low apparent activation energy.

The agreement between the mechanism based rate equation and the experimental one, as well as the low apparent activation energy, prove that the

reaction network we have advanced seems very probable.

However, from a kinetic point of view, it is difficult to ascertain the rate determining step. For further clarification, the steady-state approximation was considered for the outer-sphere complex $[\text{Fe}(\text{CN})_6 \cdot \text{SR}]^{4-}$ and the disulphide ion-radical $\text{RS} \cdot \cdot \text{SR}^-$. Under this assumption, the forward step (15) is rate-determining and the total $\text{Fe}(\text{III})$ concentration is practically equal to that of hexacyanoferrate-III. The rate law takes the following form:

$$\frac{d[\text{Fe}(\text{CN})_6^{4-}]}{dt} = -\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2kk_2K_1[\text{RSH}]^2}{k_{-2}[\text{H}^+]^2 + kK_1[\text{RSH}]}[\text{Fe}(\text{CN})_6^{3-}] \quad (21)$$

The plot of the corresponding linearized expression for k_{obs} (eq. 22):

$$\frac{[\text{RSH}]}{k_{\text{obs}}} = \frac{1}{2k_2} + \frac{k_{-2}}{2kk_2K_1} \frac{[\text{H}^+]^2}{[\text{RSH}]} \quad (22)$$

was found to be inconsistent with the experimental data, as it appears rather curved towards higher abscissa values.

Therefore, we consider the pre-equilibrium approximation valid and the electron-transfer (16),

with its substantial modification of structure, the slower step in comparison with the formation of an “ion-pair” or outer-sphere complex.

EXPERIMENTAL

The chemicals in the study were of guaranteed reagent grade purity, purchased from commercial sources (Merck, Fluka, and Reanal Budapest) and used without further purification. Solutions were prepared in demineralised and four-distilled water.

The reaction was followed by spectrophotometrical means at 420 nm, where hexacyanoferrate(III) exhibits a characteristic absorption band. A Jasco V-530 spectrophotometer (Japan), provided with a temperature jacket surrounding the cell holder and with kinetic data acquisition has been used. Reactions were started directly in the spectrophotometer cell by injection of the oxidizing agent solution over the others, contained in the cell, and the absorbance was recorded as a function of time. Mixing time does not exceed 0.5 seconds. The acidity and ionic strength were maintained constant by means of HClO₄ in excess and NaClO₄, respectively. The temperature was controlled at a constant value by circulation of water through the cell-holder from a Lauda M-20 thermostat. Each reaction system has been studied in the presence of an excess of the organic substrate. The experimental details were presented elsewhere.^{19,31} At least three replicate runs were performed for each set of experimental conditions.

CONCLUSIONS

As presented by the studied reaction, the experimental kinetic data obey a one-plus rate law, with integer exponents. The involvement of a pre-equilibrium rather than the steady-state of an outer-sphere complex between the oxidant and the organic substrate is considered from the kinetic behaviour. The electron-transfer, with major change in structure, is the rate-determining step. In acidic media, hydrogen ions inhibit the hexacyanoferrate(III) reaction. Phenomenological rate coefficients and the intermediate formation equilibrium constant could be calculated.

The data fit well with the rate law deduced from the reaction scheme under the pre-equilibrium assumption, thus supporting the suggested mechanism. Extra kinetic proofs (stoichiometry, absorption spectra and free radical presence) also account for the reaction network.

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