

*Dedicated to Professor Ionel Haiduc,
President of The Romanian Academy at his 70th anniversary*

ONE-PLUS RATE EQUATION, AN USEFUL TOOL TO ELUCIDATE THE REACTION MECHANISM

IOAN BALDEA, DANA - MARIA SABOU AND ALEXANDRA CSAVDARI*

ABSTRACT. One-plus rate equation rather than power rate equation is an useful tool in interpreting the reaction mechanism. Three systems, the oxidation of toluene and some substituted toluenes by Ce(IV), the oxidation of S-methylcysteine by chromate and the oxidation of thiamine by permanganate have been undertaken as kinetic studies and have been found to obey such type of rate laws. To suggest reaction mechanisms the inference of kinetic along with some extra-kinetic proofs were taken into consideration. The reactions start with the formation of intermediates made up from substrate and reactant as pre-equilibria, followed by electron-transfer processes. Various influence of hydrogen ion was deduced from the kinetic data. The paper also discusses general and literature examples to clear up the concepts in connection with network elucidation.

Key Words: one-plus rate law, chromate, permanganate, Ce(IV), toluene, xylene, S-methylcysteine, thiamine.

Introduction

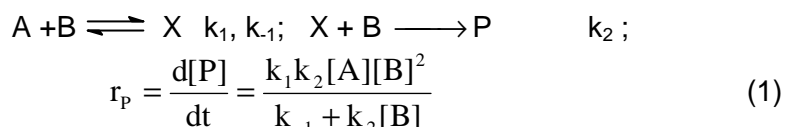
Guidelines have been proposed within which a kineticist works in developing a reaction mechanism on the basis of the rate law that can be deduced from the kinetic measurements¹⁻³. Extra-kinetic measurements as well as theoretical considerations will argue the postulated mechanism⁴⁻⁵.

The knowledge of how the changes of any molecular event are reflected in the observable kinetic behaviour is the very basis of chemical kinetics. Each kinetic study of a new reaction needs to measure reaction rates and compile *an empirical power-law rate equation* as complete as possible from extensive results over a wide range of experimental conditions. Most reactions of practical interest do not proceed by simple pathways. Therefore they do not obey always simple power-law rate equations and so have no exact and constant reaction orders. They are multistep reactions. The larger the network, the harder is its elucidation. Rate equation of a multistep reaction, especially with reverse steps is complex and contains more than one term in the denominator. The number of phenomenological rate coefficients can be reduced by one if numerator and denominator are divided by a term in the denominator. The outcome is an *one-*

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plus rate equation. The traditional power-law with empirical fractional exponents cannot be expected to result from combinations of elementary steps except for the case of simultaneous paths. In contrast, the one-plus rate equation can result from step combinations. It 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 the network elucidation⁵. The phenomenological rate coefficients are combinations of elementary steps in the network. This paper presents some results obtained in our laboratory as well as some literature examples to introduce the concepts concerning the elucidation of the reaction mechanism on the basis of one-plus rate law.

A straightforward example results from three elementary steps mechanism with X as an intermediate under steady-state conditions and an overall order between two and three^{3,5}:



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

$$\frac{d[P]}{dt} = \frac{k_a [A] [B]^2}{1 + k_b [B]} \quad \text{with} \quad k_a = \frac{k_1 k_2}{k_{-1}} \quad \text{and} \quad k_b = \frac{k_2}{k_{-1}} \quad (2)$$

The number of rate coefficients has been reduced to two phenomenological ones (k_a and k_b). The linear form is:

$$\frac{[A][B]}{r_p} = \frac{k_b}{k_a} + \frac{1}{k_a} \frac{1}{[B]} \quad (3)$$

Even more complicated rate laws can be deduced for other systems, with fractional order with respect to two participants like (4):

$$\frac{d[P]}{dt} = \frac{k_a [A][B]}{1 + k_b [A] + k_c [B]} \quad (4)$$

Such a case needs some series of measurements with variable concentration of A at several constant concentration of B taken in large excess. In order to determine the phenomenological rate coefficients a nonlinear regression can be used or the equation can be brought into a linear form and tested by linear regression or plotting. The linear form is obtained when double reciprocal is taken.

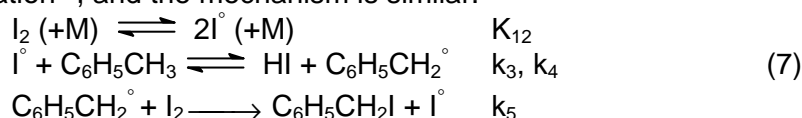
$$\frac{[B]}{r_p} = \frac{k_b}{k_a} + \frac{1 + k_c [B]}{k_a} \frac{1}{[A]}; \quad \text{Slope} = \frac{1 + k_c [B]}{k_a} \quad (5)$$

The first literature example with the order as an integer multiple of 1/2 is the gas phase reaction between iodine and various silanes⁶⁻¹⁰ and toluene¹¹ at 500-600K yielding iodinated compounds 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 reaction product HI. In the case of toluene¹¹, the rate law is of the form:

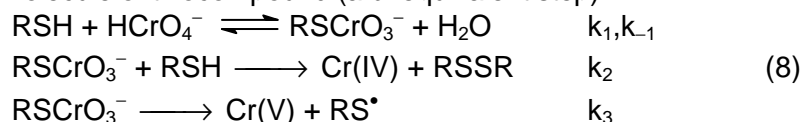
$$-\frac{d[I_2]}{dt} = k'[I_2]^{1/2}[C_6H_5CH_3]/(1 + k''[HI]/[I_2]) \quad (6)$$

Such kinetics offer strong support for an atomic abstraction chain mechanism. The rate law resembles the classical case of hydrogen bromide formation¹², and the mechanism is similar:

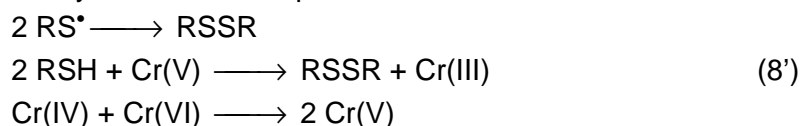


The one-plus rate law (6) can be deduced and the phenomenological rate coefficients are combinations of rate constants of the elementary steps in the above mechanism: $k' = k_3 K_{12}^{1/2}$ and $k'' = k_4 / k_5$. Here an inhibition process occurs (k_4). The rate-determining step is the one involving an iodine atom and toluene in transition state (k_3), and the dissociation pre-equilibrium (K_{12}) brings about the semi-integer overall order.

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. A general mechanism for the reaction of chromium(VI) with a thiol involves the formation of a chromium(VI) - thioester followed by a redox decomposition of this intermediate or its redox reaction with a second molecule of thiocompound (a bi-equivalent step).



They are followed by several fast steps:



These steps were considered on the basis of extra-kinetic proofs (free-radical and Cr(V) identification)^{13,15,20} and to justify the reaction stoichiometry. The two-step mechanism involving thioester formation and its subsequent reaction with a second molecule of thiol is consistent with the observed rate law for thiosulphate, cysteine, cysteine methyl ester, cysteamine, glutathione, mercaptoethanol, thioglycolic and thiomalic acids. The apparent first-order rate coefficient depends on substrate concentration, having a fractional order between one and two with respect to the substrate. The uniequivalent electron transfer within the condensed

species RSCrO_3^- is extremely slow and negligible in the rate law. When thioester is formed rapidly and in significant concentration in a pre-equilibrium, as found in almost all the cases, the fraction of Cr(VI) as condensed compound is $[\text{RSCrO}_3^-]/[\text{Cr}^{\text{VI}}]_t = K[\text{RSH}]/(1 + K[\text{RSH}])$. The one-plus type rate law is accordingly:

$$-\frac{d[\text{Cr}^{\text{VI}}]}{dt} = \frac{(k_1/k_{-1})k_2[\text{RSH}]^2}{1 + (k_1/k_{-1})[\text{RSH}]}[\text{Cr}^{\text{VI}}] = \frac{k_2K[\text{RSH}]^2}{1 + K[\text{RSH}]}[\text{Cr}^{\text{VI}}] \quad (9)$$

In such cases substantial spectral evidence has been found for the thioester formation^{18,19}.

On the other hand, there are instances where the dependence of the apparent first order rate constant on substrate concentration exhibits a sub-unitary order. It is the case of benzene thiol and α -toluenethiol in acetic acid¹⁹. Here the uniequivalent step prevails. In such situations the rate law is of the one-plus form:

$$-\frac{d[\text{Cr}^{\text{VI}}]}{dt} = \frac{k_3K[\text{RSH}]}{1 + K[\text{RSH}]}[\text{Cr}^{\text{VI}}] \quad (10)$$

Similar behaviour has been found in the case of chromate oxidation of secondary alcohols to ketones²⁰ or DL-methionine to corresponding sulfoxide²¹.

Our experimental approach concerns the oxidation of xylene by Ce(IV), the oxidation of S-Methylcysteine by chromate and the oxidation of thiamine by permanganate in acidic media.

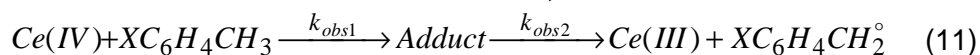
Experimental

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

The reactions were followed by spectrophotometrical means at appropriate wavelength, where the oxidant species exhibits a characteristic absorption band. A Jasco V-530 spectrophotometer (Japan), provided with a temperature jacket surrounding the cell holder and kinetic data acquisition has been used. Reactions were started directly in the spectrophotometer cell by injection of the reactant solution over the others, contained in the cell, and the absorbance was recorded as a function of time. The acidity and ionic strength were maintained constant by means of HClO_4 in excess and NaClO_4 . Temperature was controlled at a constant value by circulation of water from a Lauda M-20 thermostat through the cell-holder. Each reaction system has been studied in the presence of an excess of the organic substrate. The experimental details were presented elsewhere^{23,24}. At least three replicate runs were performed for each set of experimental conditions.

Oxidation of toluene and substituted toluenes by Ce(IV)

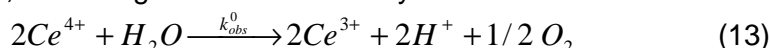
Preliminary investigations such as stoichiometric determination by spectrophotometrical titration²⁵ as well as spectra recorded immediately after mixing with solutions of increasing hydrocarbon concentration under conditions of very slow reaction, bring about arguments for the involvement of an intermediate. A small but systematic decrease of the intensity of Ce(IV) absorption band and the occurrence of an isosbestic point has been noticed (271, 275 and 276 nm in the case of toluene, *o*-xylene and *p*-xylene, respectively). Therefore, the reaction proceeds by consecutive steps, which under the excess concentration of substrate, is a first-order series



The further oxidation takes place and after hydrolysis the substituted benzyl alcohol is formed. The first stage could be attributed to the formation of an adduct between Ce(IV) and substituted toluene^{24,25}. The second stage is associated with the redox process consisting of an inner electron transfer within the complex, yielding a free radical and eventually the final products of the reaction. A first-order dependence on cerium has been found for both stages of the reaction. Indeed, the absorbance measurements ($A = f(t)$ curves) fitted a bi-exponential equation:

$$A - A_\infty = C_1 \exp(-k_{obs1}^0 \cdot t) + C_2 \exp(-k_{obs2}^0 \cdot t) \quad (12)$$

A and A_∞ stand for the absorbance at actual time and at the end of the reaction respectively. The parameters C_1 and C_2 are constants including the molar absorptivities and Ce(IV) initial concentration and k_{obs1}^0 and k_{obs2}^0 are apparent rate constants of the two consecutive steps. The apparent first-order rate constants were determined by means of this non-linear fitting. Several data are collected in table 1. Parallel to the oxidation of aromatic hydrocarbons, oxidation of water by Ce(IV) takes place in perchlorate media, according to the stoichiometry:



The kinetics of this reaction obeys a first-order dependence on Ce(IV) for the whole duration of the reaction. It has been deduced by the same procedure as for the overall process, described before. We determined the influence of different parameters on the oxidation of water and both water and substrate. Because the literature stipulates²⁶ and we have also found^{24,25}, Ce(III) diminishes the rate of the water oxidation reaction. Therefore, we introduced Ce(III) into the reaction mixture from the beginning in a ratio 1:1 ([Ce(IV)]:[Ce(III)]). The experimental curves for the water oxidation reaction were determined by a fitting method with the equation:

$$A - A_\infty = C_3 \exp(-k_{obs}^0 \cdot t) \quad (14)$$

The data were published previously²⁴. Here we are interested in the oxidation stage of the reaction and present data concerning the second stage. Several rate constants are presented in table 1. Once we had all the first-order rate constants, we proceeded by subtracting the rate constant of the oxidation of water, which is a simultaneous process having a linear kinetics, from the rate constants of the overall reaction as follows

$$k_{\text{obs}2} = k_{\text{obs}2}^0 - k_{\text{obs}}^0 \quad (15)$$

where $k_{\text{obs}2}$ is the observed first-order rate constants of the aromatic hydrocarbon oxidation reaction allowing for the water oxidation reaction, under the same acidity or ionic strength conditions employed.

Table 1.
Apparent first-order rate coefficients of the oxidation reaction
as a function of toluene, *orto*- and *para*-xylene concentration:
[H⁺] = 1.0 mole.L⁻¹, [Ce(IV)] = 8.0.10⁻⁵ and μ = 3.0 and 40°C

Substrate S	10 ⁴ [S]	10 ⁴ k _{obs2} (s ⁻¹)
C ₆ H ₅ CH ₃	4.00	1.66
	6.00	2.32
	7.00	2.68
	8.00	2.92
	9.00	3.19
	10.00	3.42
<i>o</i> -CH ₃ C ₆ H ₄ CH ₃	4.00	0.23
	6.00	0.60
	7.00	0.78
	8.00	0.98
	9.00	1.10
	10.00	1.18
<i>p</i> -CH ₃ C ₆ H ₄ CH ₃	4.00	2.45
	6.00	3.22
	7.00	3.72
	8.00	4.01
	9.00	4.35
	10.00	4.64

The effect of aromatic hydrocarbon concentration, always in a large excess, upon the apparent rate constant at constant acidity is described with the best fit by equations:

$$r_2 = a \frac{[p-xylene]_0}{1 + b[p-xylene]_0} [Ce(IV)];$$

$$k_{\text{obs}2} = \frac{(13.8 \pm 0.5)[p-xylene]_0}{1 + (139 \pm 90)[p-xylene]_0} \quad (16)$$

$R^2 = 0.9800$, $\chi^2 = 7.50 \cdot 10^{-9}$ for $N = 18$. Similar equations have been deduced for toluene and *o*-xylene. We are interested here in the second stage that follows a one-plus pattern. It means an order between zero and one with respect to xylene and suggests also the involvement of an intermediate species. Even under high acid concentration, the hydrolysis of Ce(IV) ion takes place and complicates the kinetics. It is revealed from the influence of hydrogen ion concentration on the rate constant investigated in the limits presented in table 2.

Table 2.

Effect of hydrogen ion concentration on the apparent rate constant;
 $[\text{Ce(IV)}] = 8 \cdot 10^{-5} \text{ mol.L}^{-1}$; $[\text{Ce(III)}] = 8 \cdot 10^{-5} \text{ mole.L}^{-1}$; $[\text{xylene}] = 4.0 \cdot 10^{-4} \text{ mole.L}^{-1}$;
 $\mu = 3.0$ and temperature of 40°C

$[\text{H}^+]$ (mole.L ⁻¹)	Toluene	$10^4 \cdot k_{\text{obs2}} (\text{s}^{-1})$	
		<i>p</i> -Xylene	<i>o</i> -Xylene
0.25	0.19	1.46	0.15
0.5	0.38	2.28	0.28
1	0.63	3.16	0.56
1.5	0.96	4.07	0.77
2	1.26	5.08	1.03
2.5	1.51	5.98	1.25
3.0	1.78	6.15	1.43

The same behaviour was obtained with the other hydrocarbons. The data fit well with an equation of sub-unitary fractional order

$$k_{\text{obs2}} = \frac{a[\text{H}^+]}{b + c[\text{H}^+]} \quad (17)$$

The linear fit gave the slopes of 1.26, 1.64 and 0.141, the intercepts of 0.180, 0.177 and 0.136 with good correlation coefficients of 0.9982, 0.9993 and 0.9836 for toluene, *o*-xylene and *p*-xylene respectively.

The influence of ionic strength on the reaction rate suggests that like-charged species should be involved in the second stage of the reaction. In the case of *p*-xylene, for example:

$$\log k_{\text{obs2}} = -(5.68 \pm 0.06) + (3.43 \pm 0.12)(\sqrt{\mu}/(1 + \sqrt{\mu})) \quad (18)$$

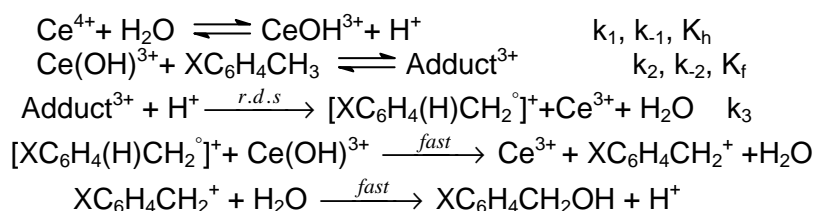
Activation parameters were determined for both stages of the reaction from the Arrhenius and from the Eyring plots. The values of activation energy and enthalpy for the first stage are quite small. The negative activation entropy is in agreement with the involvement of the adduct formation pre-equilibrium¹. Here we are interested in the second stage. Therefore, in table 3 we present the activation parameters. Activation enthalpy is greater for xylene oxidation as compared to toluene oxidation.

Table 3.
Activation parameters for the redox stage of the
aromatic hydrocarbons oxidation.

Substrate	E _a (kJ/mole)	ΔH [‡] (kJ/mole)	ΔS [‡] (J/Kmole)	ΔG [‡] (kJ/mole)
Toluene	48.2±4.7	45.7±4.7	-170.1±6.2	99.0±6.8
p-xylene	73.2±5.6	70.64±5.7	-92.6±7.2	99.6±7.0
o-xylene	87.0±4.9	84.4±4.9	-55.6±3.8	101.8±6.2

The step of electron-transfer needs a little bit higher activation energy. The entropy modification in this stage is also negative, suggesting a bimolecular process, namely proton assisted formation of Ce(III) and uni-equivalent oxidized product. On the other hand, an isokinetic temperature seems to appear that is equivalent to a linear correlation between ΔH[‡] and ΔS[‡] (almost the same value of ΔG[‡]). This is a strong proof for a common oxidation mechanism of the three aromatic hydrocarbons.

A reaction mechanism can be suggested, based on kinetic and extra-kinetic data. It involves the formation of an adduct between toluene and the hydroxo-complex of Ce(IV), followed by the inner electron transfer. This rate-determining step also involves a proton, to stabilise the formed free radical. It is difficult to assign the position of this hydrogen ion. It can be bound either to the nucleus (π electron system conjugated with the free electron on methylene group), or to the side group²⁷. A proton stabilized free radical has been suggested by Baciocchi and co-workers²⁸. The subsequent steps - the oxidation to carbenium ion and its hydrolysis - are very rapid and leads finally to the major oxidation product, which is benzyl or methylbenzyl alcohol. It is presented in the scheme below:



The electron transfer takes place as proton assisted. To get more arguments to the suggested mechanism, we followed the oxidation reaction of substituted toluene, and checked whether a Hammett correlation holds. As presented before, the apparent first-order rate constant of the second stage (allowing for water oxidation) was calculated for nine compounds. Data are presented in table 4. The Hammett equation, by using the data in the table is

$$\lg \frac{k_{\text{obsd 2 X}}}{k_{\text{onsd 2 H}}} = -(0.06 \pm 0.1) - (1.25 \pm 0.05)\sigma \quad (19)$$

with $R = 0.9849$. It suggests a common mechanism. As the equation stipulates, the electron-releasing substituents increase the oxidation reaction rate, while the electron-withdrawing substituents have the opposite effect.

Table 4.

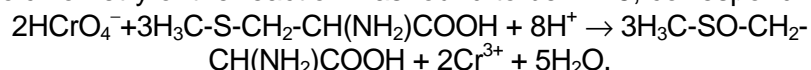
Observed first-order rate constants (allowing for water oxidation) for the oxidation process (k_{obs2}) and substituent constants at $[\text{Ce(IV)}]_0 = [\text{Ce(III)}]_0 = 8 \cdot 10^{-5} \text{ mole.L}^{-1}$; $[\text{p-xylene}] = 1.0 \cdot 10^{-3} \text{ mole.L}^{-1}$; $\mu = 2.0$ and temperature of 40°C ^{29,30}

Substrate	σ	$10^4 k_{\text{obs2}} (\text{s}^{-1})$
<i>p</i> -Xylene	-0.31	6.52
<i>m</i> -Xylene	-0.07	2.74
Toluene	0.0	3.32
<i>p</i> -Chloro-toluene	0.11	2.18
<i>p</i> -Bromo-toluene	0.15	2.04
<i>p</i> -Toluenesulphonic acid	0.32	0.85
<i>m</i> -Chloro-toluene	0.37	0.67
<i>m</i> -Nitrotoluene	0.71	0.39
<i>p</i> -Nitrotoluene	0.78	0.28

The rate determining step involves charge separation that may proceed easily with electron donating substituents on the aromatic ring. The reaction constant, negative and relative close to unity, suggests a free radical mechanism³¹. The $\rho = -1.25$ is in agreement with the one of the oxidation in acetic acid as solvent, with perchloric acid addition, of $\rho = -1.7$ ³². Here, because of lower dielectric constant as compared to water solution, the field effects are more important and a higher reaction constant value should be expected³¹.

Oxidation of s-methylcysteine by chromate

The stoichiometry of the reaction was found to be 1:1.5, corresponding to



This ratio has been established by colorimetric measurements at 350 nm. At excess concentrations of S- methylcysteine over 1.5 (abbreviated as MC) all amount of oxidizing agent Cr(VI) is completely consumed in the process and final absorbance remains small and constant. This implies that the oxidised product is the corresponding sulfoxide. Even with strong oxidizing agents such as peroxyanions, peroxydisulfate and peroxydihosphate, the oxidation product was sulfoxide in the case of alkyl aryl sulphide³³ or diphenylsulfide³⁴.

The kinetic measurements were made at various concentrations of S- methyl-cysteine always in large excesses, at constant acidity, and also at various HClO_4 concentrations (at constant excess of substrate). Under the pseudo-first-order conditions studied, apparent first-order kinetics has

been obtained. Plots of $\ln(A - A_\infty)$ versus time were linear over large degree of reaction with very good correlation coefficients (0.9900 - 0.9990), confirming the first-order dependence with respect to the oxidizing agent. Pseudo-first order rate coefficients were calculated from such plots.

The apparent first-order rate coefficient depends upon the substrate and mineral acid concentration. By increasing the concentration of the substrate at constant acidity, increased first-order rate constants were found with a slight tendency of levelling off, as depicted in figure 1.

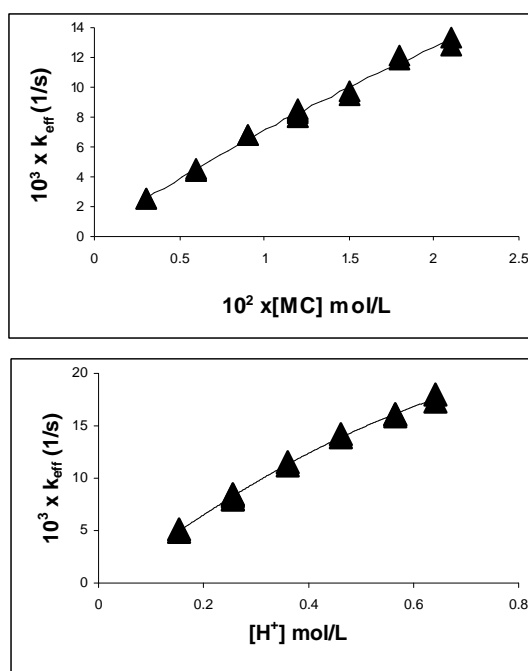


Figure1. Dependence of apparent first-order rate constant on S-methylcysteine ($[H^+] = 0.26$), and perchloric acid ($[MC] = 0.012$) at 60°C and ionic strength of 0.7

This behaviour can be rationalised by the rate equation (similar to 10):

$$-\frac{d[Cr^{VI}]}{dt} = \frac{k_a[MC]}{1 + k_b[MC]}[HCrO_4^-]; \quad \frac{1}{k_{obs}} = (1.62 \pm 0.34) + (1.47 \pm 0.05) \frac{1}{[MC]}$$

R=0.9976 (20)

$$-\frac{d[Cr^{VI}]}{dt} = \frac{k'_a[H^+]}{1 + k'_b[H^+]}[HCrO_4^-]; \quad \frac{1}{k_{obs}} = (29.0 \pm 5.5) + (9.45 \pm 0.34) \frac{1}{[H^+]}$$

R=0.9960 (20')

which is of the one-plus form. The combined dependence on both the substrate and hydrogen ion concentration concerning the apparent first-order rate constant and its linear form are as follows:

$$k_{obs} = \frac{k_a''[MC][H^+]}{1 + k_b''[MC][H^+]} \quad \frac{1}{k_{obs}} = \frac{1}{k_a''} \frac{1}{[MC][H^+]} + \frac{k_b''}{k_a''} \quad (21)$$

By considering the inference of the kinetic behaviour, the following mechanism can be suggested:

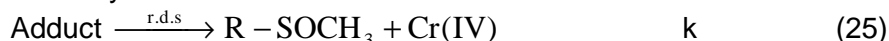
- The pre-equilibria involving the adduct intermediate could be either



We symbolize here S-methylcysteine by $R-SCH_3$ to show the two possibilities of protonation in forming the adduct intermediate. The two coupled equilibria can be written as an overall one, with $K = K_1' K_2'$ (or $K_1'' K_2''$).



- It is followed by the electron transfer and the formation of a S-O double bond



The process continues by rapid steps of the type (8), given in the literature cited example, with the formation of Cr(V). It also can oxidize S-methylcysteine to sulfoxide. The rate law deduced by this reaction scheme is of the form (21) in which third-order rate constant $k_a'' = kK = (2.8 \pm 0.1) \text{ L}^2\text{mole}^{-2}\text{s}^{-1}$ and $k_b'' = K = (29.0 \pm 7.5) \text{ L}^2\text{mole}^{-2}$ and first-order rate constant for electron transfer $k = (9.7 \pm 2.8) \cdot 10^{-2} \text{ s}^{-1}$ were computed.

The oxidation of thiamine (vitamin B 1) by permanganate

The anti-oxidant character of Vitamin B1 is well known. In order to set up a kinetic method of analysis for Vitamin B1, we have studied the kinetics of its oxidation by permanganate in acidic media³⁵. The stoichiometry of the process was determined at constant acidity of 0.2 mole.L^{-1} using various molar ratios. The remaining absorbance, after the reaction achieved completion, is presented in figure 2.

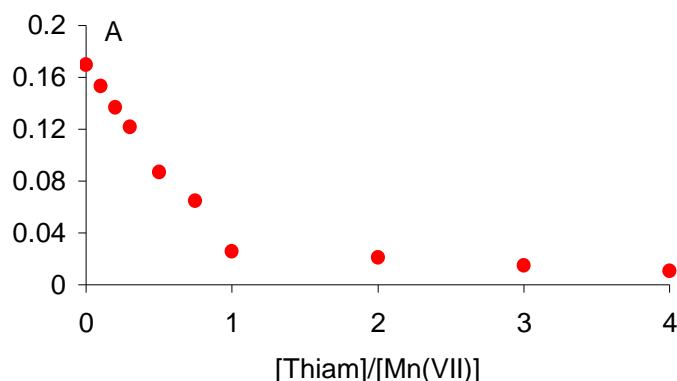
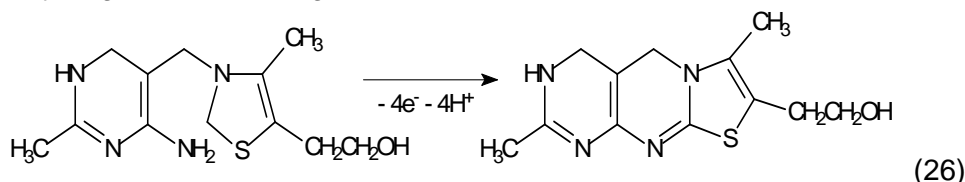


Figure 2. The left absorbance after the reaction has been accomplished at various molar ratios in the initial reaction mixture

It reveals an obvious change of the slope at the ratio 1.2 Thiamine:1 MnO_4^- confirming a process that involves four electrons. It corresponds to dehydrogenation and ring closure.



Kinetic measurements were made by spectrophotometrical means, following the absorbance of permanganate at 525 nm. The absorbance evolution can be described by an exponential, except for a small initial part where a salient decrease of it takes place. We have exploited the exponential dependence for the determination of first-order rate coefficient, as the slope of the line of $\ln(A - A_\infty)$ versus time. The results of at least three replicate runs are presented as means in table 5. The apparent first-order rate constants are dependent on both the substrate and the acid concentration. An increase of the rate coefficient has been found for the two influences but not strictly proportional. A slight tendency of levelling off appears in both cases. Indeed, if the initial rate as the decrease of absorbance against time was measured from the slope of the absorbance curve (within less than 5% of reaction) at various initial concentration of thiamine, the behaviour presented in figure 3 has been obtained.

It can be described by an equation of the one-plus rate law form at constant HClO_4 concentration of 0.2:

$$r_0 = \frac{k_a [\text{Thiam}]}{1 + k_b [\text{Thiam}]} [\text{MnO}_4^-]; \quad r_0 = \frac{(25.9 \pm 1.1) [\text{Thiam}]}{1 + (181 \pm 13) [\text{Thiam}]} [\text{MnO}_4^-] \quad (27)$$

Table 5.

The effect of thiamine concentration at constant $[\text{H}^+] = 0.1$ and of the acid at constant $[\text{Thiam}] = 8.1 \cdot 10^{-3}$, at 25°C and ionic strength of 0.5

$10^3 [\text{Thiam}] \text{ mol.L}^{-1}$	$10^2 k_{\text{obs}} (\text{s}^{-1})$	$[\text{H}^+] \text{ mol.L}^{-1}$	$10^2 k_{\text{obs}} (\text{s}^{-1})$
0.81	2.18	0.10	2.18
1.40	3.90	0.15	3.10
1.70	4.50	0.20	3.92
2.10	5.62	0.25	4.08
2.70	6.63	0.30	5.60
3.30	8.21	0.35	6.44
4.10	9.63	0.50	9.81
4.90	10.8		
5.30	11.5		
5.70	12.2		
6.20	13.0		

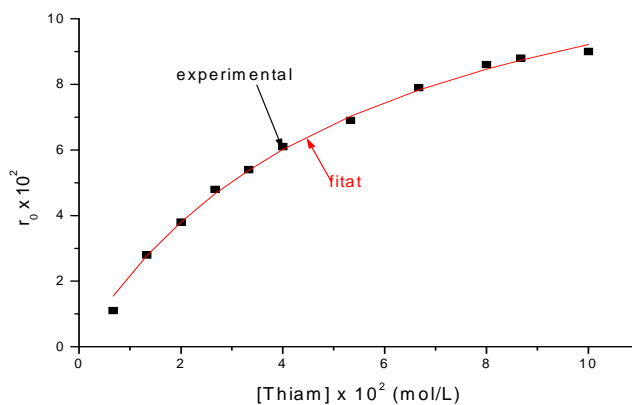


Figure 3. Dependence of the initial rate with thiamine concentration at 25°C and ionic strength of 2.00

The tendency of levelling off of the observed first- order rate coefficient in table 5 can be described by a linear double reciprocal plot with the equations:

a) at constant perchloric acid concentration:

$$k_{\text{obs}}^{-1} = (3.50 \pm 0.06) \cdot 10^{-2} [\text{Thiam}]^{-1} + (1.8 \pm 0.3); \quad R = 0.9988, \quad (28)$$

b) at constant thiamine concentration:

$$k_{\text{obs}}^{-1} = (4.36 \pm 0.13) \cdot [\text{H}^+]^{-1} + (3.0 \pm 0.7) \quad R = 0.9978 \quad (29)$$

The combined dependence on both the substrate and hydrogen ion concentration, concerning the apparent first-order rate constant, is of the one-plus form, which can be transposed into a linear equation.

$$k_{\text{obs}} = \frac{k_a' [\text{Thiam}][\text{H}^+]}{1 + k_b' [\text{Thiam}][\text{H}^+]} \quad \frac{1}{k_{\text{obs}}} = \frac{1}{k_a'} \frac{1}{[\text{Thiam}][\text{H}^+]} + \frac{k_b'}{k_a'} \quad (30)$$

The line is presented in figure 4 and has a good correlation coefficient of $R = 0.9959$.

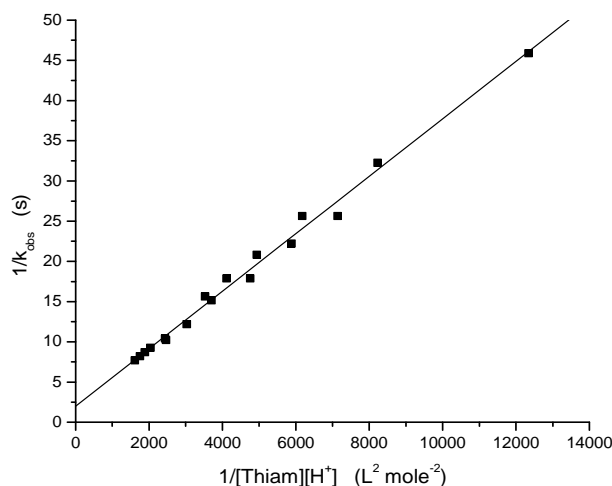
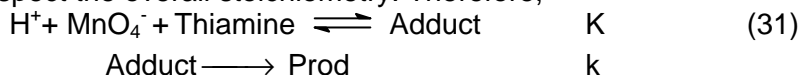


Figure 4. The double reciprocal plot of equation (30)

From the parameters of the line we obtained the following figures:
 $1/k_a' = (3.57 \pm 0.09) \cdot 10^{-3} \text{ mole}^2 \text{ L}^{-2} \text{ s}$ and $k_b' / k_a' = (2.0 \pm 0.5) \text{ s}$.

The steep decrease of the absorbance at 525 nm immediately after mixing as well as the rate law expression lead to the conclusion of a two step mechanism involving a pre-equilibrium followed by the rate determining step with the stoichiometry of transition state (1 Thiamine:1 MnO_4^- : 1 H^+). It is difficult to predict the change in oxidation state of manganese in this step. The reaction continues with complete reduction of the manganese intermediate valence states to Mn(II) in this strong acid medium, to respect the overall stoichiometry. Therefore,



From this two step mechanism, following the disappearance of the $[\text{Mn(VII)}]_t$, measured by the absorbance, the rate law deduced has the expression

$$k_{\text{obs}} = \frac{kK[\text{Thiam}][\text{H}^+]}{1 + K[\text{Thiam}][\text{H}^+]} \quad (32)$$

which is of the form (10). From the parameters of the linear equation (30), the rate constant of third order is $kK = (2.80 \pm 0.07) \cdot 10^2 \text{ L}^2 \cdot \text{mole}^{-2} \cdot \text{s}^{-1}$, $k = 0.50 \pm 0.16 \text{ s}^{-1}$ and $K = (5.6 \pm 1.6) \cdot 10^2 \text{ L}^{-2} \cdot \text{mole}^2$.

Conclusions

As presented for the studied reactions, the experimental kinetic data obey one-plus rate laws, with integer exponents. In each case a pre-equilibrium involving the oxidant and the organic substrate is present. In acidic media, the involvement of hydrogen ion is quite different for the three reactions approached. Phenomenological rate coefficients and some intermediate formation constants could be calculated. The data fit well with the rate law deduced from the reaction schemes of two steps, the pre-equilibrium and the rate determining electron transfer, thus supporting the suggested mechanisms. Extra kinetic proofs (stoichiometry, the absorbance evolution at the start of the processes) also account for the suggested reaction networks.

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