STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 1-2, 2000

THE EFFECT OF COPPER, LEAD AND IRON IONS ON THE OXIDATION OF MERCAPTOSUCCINIC ACID BY CHROMATE

ALEXANDRA RUSTOIU-CSAVDARI, IOAN BALDEA

"Babeş-Bolyai" University, Faculty of Chemistry and Chemical Engineering,
Department of Physical Chemistry, 11 Arany Janos Street,
3400 Cluj-Napoca, E-mail: arustoiu@chem.ubbcluj.ro

ABSTRACT. The effect of copper, lead and iron ions on the oxidation of mercaptosuccinic acid (thiomalic acid or TMA) by chromate in acidic media has been investigated in order to draw a conclusion about its potential use in kinetic analysis. Similar studies have been carried out for the oxidation of mercaptoacetic acid (thioglycolic acid or TGA), but only in the presence of lead. All ions increase the overall reaction rate: the Fe(II)-Fe(III) couple *via* an induction mechanism, while the Cu(I)-Cu(II) and Pb(II)-Pb(IV) couples *via* catalytic cycles. Reaction mechanisms have been proposed for all cases and "saturation" at high ion concentration has been explained. The effect of five other metal ions on both TMA and TGA oxidation has also been checked. Finally, the possible applications of both indicator reactions among kinetic methods of analysis are discussed and some recommendations are made.

Introduction

The reactions between some thiols and chromate in acidic media have been recently used as indicator reactions in kinetic methods of analysis. For example, the oxidation of thiosulfate has been proposed to determine Cu(II) [1,2], while the reactions of mercaptosuccinic acid (thiomalic acid or TMA) and mercaptoacetic acid (thioglycolic acid or TGA) may be used to determine both Cu(II) [3] and Pb(II) [4,5] in water samples. On the other hand, the oxidations of cysteine [6] and ethanethiol [7] are far to slow to be employed in such a way. All these methods relay on the catalytic effect of the metal ions in order to determine their concentration. Reaction rate (or some parameter related to it) against catalyst concentration graphs are used in calibration.

In order to elaborate a sensitive and selective catalytic method of analysis, the mechanism and kinetics of both catalyzed and uncatalyzed reaction paths have to be known. Therefore, the aim of this work was to elucidate the influence of copper, lead and iron ions on the reaction between thiomalic acid and chromate. The oxidation of thioglycolic acid (TGA) was investigated in more detail only in the presence of lead, since the effect of copper and iron is already known [8]. Experimental results for the reaction of TGA in the presence of Cu and Fe were compared with published ones.

Experimental

Reagents and solutions: Analytical grade reagents provided by *Reactivul* (Bucharest, Romania), *Reanal* (Budapest, Hungary), *Merck* (Darmstadt), *Fluka* (Buchs, Switzerland) and *Panreac* (Barcelona, Spain) were used without further purification. All solutions were prepared in demineralized and four times distilled water.

Stock solutions of 0.1 M perchloric acid as well as of $5x10^{-3}$ M $K_2Cr_2O_7$ were used to prepare the working solutions of $5x10^{-3}$ M and $2.64x10^{-4}$ M respectively. The 10^{-2} M working solutions of thiomalic and thioglycolic acids were prepared on a daily basis. Aqueous 10^{-2} M stock solutions of copper sulfate, iron nitrate and lead nitrate were prepared by dissolving the appropriate weighted amount in volumetric flasks of 100 ml. When necessary, 10^{-3} M and 10^{-4} M working solutions were prepared by means of dilution. Ionic strength was adjusted with 2.18 M natrium perchlorate.

The acids were standardized by the usual procedures. Concentration of each salt was determined by titrating the acid generated when 2 ml stock solution passed through a column of C-100H cationite resin (*Virolyte*, Victoria, Romania).

Instrumentation and procedure: A Jasco V-530 UV/VIS (*Jasco*, Japan) spectrophotometer with temperature controlled cell holders was employed to monitor the extent of the reaction. Temperature was kept constant with the aid of a Lauda-M12 (*Lauda*, Germany) precision circulation bath at 20.0 ± 0.1 ^{o}C. All solutions were thermostated prior to use and during the experiments in the same water-bath. Quartz cells of 5 cm path length were used at 345 nm. Data acquisition was performed automatically by means of a DTK personal computer.

During all experiments, the colored species Cr(VI) was the limiting component. The reaction was initiated directly in the cell, by the rapid injection of 4 ml of the chromate solution into a mixture of 12 ml containing all the other reagents. Simultaneously, the automated data acquisition was started and values of the absorbance were recorded, depending on the needs of experiments, every 1 to 5 sec. The mixing time of reagents did not exceed 0.5 sec. The order of adding the solutions into the cell prior the addition of chromate, did not affect the results. Each kinetic run was carried out for aproximately four half-lives. The final value of the absorbance, A_∞, was considered to be the smallest achieved value after 8 to 10 half-lives. Three to five replicate runs were carried out under identical experimental conditions.

Results and discussions

The uncatalyzed oxidation of TMA [9], TGA [10] thiosulfate [11] as well as of other nine biological and non-biological thiols [12] by chromate in acidic media has already been investigated. When the substrate is in excess, a disulfide is the main reaction product in all cases:

$$6\ RSH + 2\ HCrO_4^- + 8\ H^+ \rightarrow 3\ R_2S_2 + 2\ Cr(III) + 8\ H_2O \qquad (1)$$

RSH stands for the thiol, while R_2S_2 stands for $S_2(CH(COOH)\text{-}CH_2\text{-}COOH)_2$ in the case of TMA and for $S_2(CH_2\text{-}COOH)_2$ in the case of TGA, respectively. The reaction starts with a rapid equilibrium to form a relatively stable thioester $RSCrO_3^-$. This will further yield the products in some rate determining steps.

$$RSH + HCrO_4^- \Leftrightarrow RSCrO_3^- + H_2O \qquad K_f \qquad \text{(rapid)} \quad (2)$$

$$RSCrO_3^- + RSH \rightarrow R_2S_2 + Cr(IV) \qquad k_{ox} \qquad (\textbf{slow}) \quad (3)$$

$RSCrO_3^-$ stands for $HOOC\text{-}CH_2\text{-}CH(COOH)\text{-}SCrO_3^-$ in the case of TMA and for $HOOC\text{-}CH_2\text{-}SCrO_3^-$ in the case of TGA, respectively. The rates of processes (2) and (3) are described by the following laws:

$$rate_f = \left\{k_f^0 + k_f^H [H^+]\right\}[RSH][HCrO_4^-] \qquad (4)$$

and $$rate_{ox} = \left\{k_{ox}^0 + k_{ox}^H [H^+]\right\}[RSH][HCrO_4^-] \qquad (5)$$

respectively. k_f^0 and k_{ox}^0 stand for second order rate coefficients of the uncatalyzed paths of reactions (2) and (3) respectively, while k_f^H and k_{ox}^H stand for third order, H^+ catalyzed paths of the same processes. Their values, along with the equilibrium constant K_f of reaction (2), are given in Table 1 for both TMA [9] and TGA [10].

Table 1

Individual rate coefficients - oxidation of TMA and TGA by chromate at 25.0 ± 0.1 °C. Literature data.

Parameter	Substrate	
	TMA	**TGA**
k_f^0 ($M^{-1}s^{-1}$)	44.1 ± 0.3	66.3 ± 1.2
k_f^H ($M^{-2}s^{-1}$)	(1.92±0.01) x 10^2	(2.47 ± 0.05) x 10^3
K_f (M^{-1})	(1.48 ± 0.07) x 10^3	(1.10 ± 0.15) x 10^3
k_{ox}^0 ($M^{-1}s^{-1}$)	23.8 ± 0.03	11.7 ± 0.70
k_{ox}^H ($M^{-2}s^{-1}$)	(2.03 ± 0.13) x 10^2	(4.33 ± 0.06) x 10^2
Ionic strength (M)	0.5	0.2

It may be concluded from Table 1 that only the formation of the thioester of thiomalic acid occurs somewhat slower than that of thioglycolic acid. Otherwise, the rates of TMA and TGA oxidation are comparable under identical experimental conditions.

The effect of Fe(II)-Fe(III) and Cu(I)-Cu(II) redox couples on the oxidation of TGA by chromate in acidic media was previously reported by Bâldea [8]. He observed that the reaction rate increased in the presence of small amounts of either iron or copper ions. However, concentrations of 10^{-6} mole/l copper bring about the same effect as a one order of magnitude higher iron ion content. Bâldea explained the rate enhancement by iron *via* an induction mechanism: Fe(II) reduces Cr(VI) to Cr(V) which is a better and faster oxidant of the substrate than $HCrO_4^-$ itself. On the other hand, a catalytic cycle was proposed for copper. Under excess of RSH, Cu(II) traps the substrate as a ligand in Cu(II)-complexes, in ratios 1:1 and 1:2 copper-ligand. These react more easily with chromate to yield the main reaction product. The released Cu(I) will regenerate the catalyst by oxidation with Cr(VI) to form Cu(II) and Cr(V).

According to the rate law (5), under the excess of thiol and constant hydrogen ion concentration, the slow stage (3) obeys a first order rate law with respect to the colored Cr(VI) species. Hence, it can be written as follows:

$$r = -\frac{d[RSCrO_3^-]}{dt} = k_{obsd}\,[Cr(VI)] \qquad (6)$$

where k_{obsd} is a pseudo-first-order rate constant. First order kinetics is proved by the linear dependence, in terms of absorbance, of the semilogarithmic plots of the equation below.

$$\ln(A - A_\infty) = \ln(A - A_\infty) - k_{obsd}\,t \qquad (7)$$

A, A_0 and A_∞ stand for the absorbance at any reaction time *t*, initial absorbance and the value of A at completion, respectively.

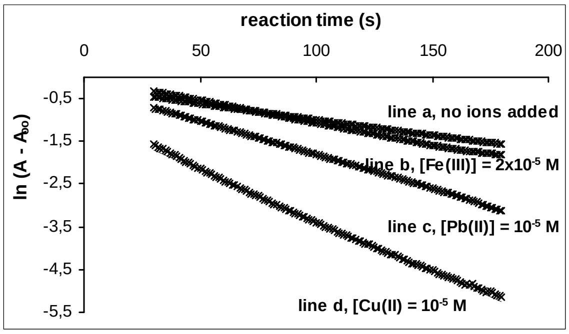

Fig. 1. Oxidation of TMA: semilogarithmic plots to determine k_{obsd} in the absence (line *a*) and presence (lines *b,c* and *d*) of metalic ions; 20.0 ± 0.1 °C, 10^{-3} M TMA, 2.2×10^{-4} M $HClO_4$, 6.6×10^{-5} M Cr(VI), ionic strength of 0.15 M.

Figure 1 refers to the oxidation of thiomalic acid. It shows that points lie on lines for more than 90 % of reaction completion, both in the absence (line *a*) and in the presence (lines *b, c* and *d*) of small amounts of iron, lead or copper ions. This proves that pseudo-first order kinetics is preserved in the presence of the metal ions. The slopes give the values of the rate coefficients k_{obsd}. The higher slopes of lines *b,c* and *d* as compared to the one of line *a*, reveal a rate enhacement by even very small amounts of the above listed ions. Similar conclusions were drawn for the oxidation of thioglycolic acid in the presence of small amounts of lead.

The dependence of k_{obsd} versus total copper, lead and iron concentration is presented in Figure 2 for the oxidation of TMA. It is obvious that in the range of small ion concentrations k_{obsd} may be expressed as:

$$k_{obsd} = k_0 + k_{ion}[ion] \tag{8}$$

where k_0 and k_{ion} stand for the contributions of a pseudo-first and a -second order reaction path, respectively. Under the same experimental conditions, but an ionic strength of 0.2 M, similar results were obtained for TGA. However, preliminary experiments proved that the ionic strength does not affect reaction rates of neither TMA or TGA oxidation.

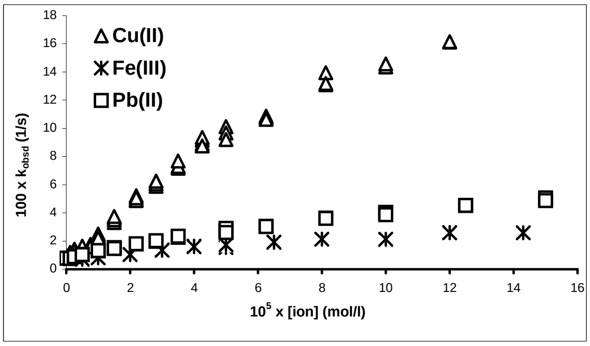

Fig. 2. Oxidation of TMA: the dependence k_{obsd} *vs* total ion concentration. Experimental conditions of Figure 1.

The values we found for k_0 and k_{ion} are given in Table 2 for both substrates. For TGA computed values on the base of literature data [8] are also given. It may be observed that although the overall reaction rates of TMA and TGA oxidation are comparable, the latter occurs somewhat slower under the same experimental circumstances, regardless of the absence or presence of any metallic ions. Further, for all metal species, k_{obsd} levels off towards higher concentrations. Therefore, the following dependence was assumed:

$$k_{ion} = k_{obsd} - k_0 = \frac{a[ion]}{1 + b[ion]} \tag{9}$$

where ***a*** and ***b*** are some constants. The equation above can also be written in its linear form:

$$\frac{1}{k_{ion}} = \frac{b}{a} + \frac{1}{a} * \frac{1}{[ion]} \qquad (10)$$

Table 2

k_0 and k_{ion} values for TMA and TGA oxidation at 20.0 ± 0.1 °C, 10^{-3} M RSH, $2.2x10^{-4}$ M $HClO_4$, $6.6x10^{-5}$ M Cr(VI), ionic strength of 0.15 M (TMA) and 0.2 M (TGA).

Parameter	**Substrate**		
	TMA	**TGA**	
k_0 (s^{-1})	(7.85 ± 0.54)x10^{-3}	(4.25 ± 0.16)x10^{-3}	** 6.63x10^{-2}*
k_{ion} ($M^{-1}s^{-1}$)	**Pb:** (4.44 ± 0.23)x10^{2}	**Pb:** (3.85 ± 0.19)x10^{2}	* ---
	Cu: (1.96 ± 0.06)x10^{3}	**Cu:** (2.39 ± 0.24)x10^{2}	** **Cu:** 2.82x10^{4}*
	Fe: (2.09± 0.75)x10^{2}	**Fe:** 1.80x10^{2}	** **Fe:** 2.55x10^{3}*

** Computed values on the base of literature data [8] at 25.0 ± 0.1 °C, $4x10^{-3}$ M TGA, $1x10^{-2}$ M H^+, $4x10^{-4}$ M Cr(VI), ionic strength of 0.2 M.*

According to relationship (10), the plot of $1/k_{ion}$ *vs* 1/[ion] should give a straight line. From its slope and intercept, the values of ***a*** and ***b*** may be obtained.

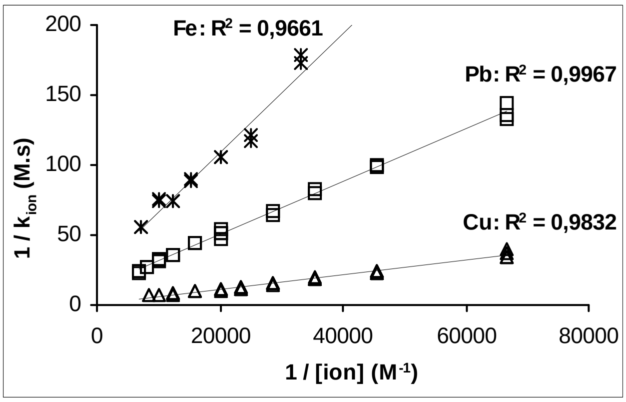

Fig. 3. Oxidation of TMA: the dependence of the inverse of k_{ion} on the inverse of the total ion concentration.

Figure 3 presents the plots of equation (10) for the oxidation of TMA. For all the studied ions, points lie on lines with good or satisfactory correlation coefficients. Similar results were obtained for the oxidation of TGA. The constants ***a*** and ***b*** are given in Table 3 for both substrates, along with the values obtained on the base of literature data [8] for TGA.

Table 3

The constants ***a*** and ***b*** for TMA and TGA oxidation. Experimental conditions of Table 2.

Parameter	**Substrate**					
	TMA			**TGA**		
	Cu	**Pb**	**Fe**	**Cu**	**Pb**	**Fe**
a ($M^{-2}s^{-1}$)	1965	542	227	488 * *64350*	480 * ---	315 * *3235*
b (M^{-1})	2413	7113	5033	6946 * *303730*	2139 * ---	20268 * *15872*

** Computed values on the base of literature data [8].*

Based on Figures 2 and 3 as well as on data in Tables 2 and 3, it may be concluded that the effect of Cu(I)-Cu(II) and Fe(II)-Fe(III) redox couples on the oxidation of TMA by Cr(VI) is similar to that on the oxidation of TGA. Moreover, our findings for TGA oxidation are in agreement with those published by Baldea. Therefore, a rate enhancement *via* an induction mechanism for iron and *via* a catalytic cycle for copper may be assumed for the reaction of thiomalic acid.

Hence, the following sequence of steps is believed to concur processes (2) and (3) in the presence of iron:

$Fe(II) + HCrO_4^{-} \Leftrightarrow Fe(III) + HCrO_4^{2-}$ K_1 (rapid) (11)

$RSH + HCrO_4^{2-} \Leftrightarrow RSCrO_3^{2-} + H_2O$ K_f' (rapid) (12)

$RSCrO_3^{2-} + RSH \rightarrow R_2S_2 + Cr(IV)$ k_{ox}' (**slow**) (13)

In step (11) Fe(II) reduces chromate to Cr(V) in $HCrO_4^{2-}$. This is a better oxidant of the substrate than Cr(VI). An equilibrium has been considered for process (11) because the standard reduction potentials of the Cr(VI)/Cr(V) and Fe(III)/Fe(II) redox couples are comparable [8]. Equilibrium (12), in which $HCrO_4^{2-}$ combines with an TMA molecule to form a Cr(V)-S bonding, has been assumed by analogy with process (2) and the general tendency of all $H_nMO_4^{-}$ type acids to form poly- or heteropoly-compounds. Step (13), which yields the main reaction product, is slow within the sequence (11)-(13), but faster than step (3). Thus, the overall reaction rate (6) will increase. Steps (11)-(13) are consistent with an induction mechanism.

Parallel to processes (2)-(3) and (11)-(13), the reactions below may also occur. These are consistent with rate a enhancement *via* a catalytic cycle [13].

$Fe(III) + HCrO_4^{-} \Leftrightarrow FeCrO_4^{+} + H^{+}$ K_2 (14)

$Fe(III) + RSH \Leftrightarrow FeSR^{2+} + H^{+}$ K_3 (15)

$FeSR^{2+} + RSH \Leftrightarrow Fe(SR)_2^{+} + H^{+}$ K_4 (16)

$Fe(II) + HCrO_4^{2-} \rightarrow Fe(III) + Cr(IV)$ (17)

$Fe(SR)_2^+ + FeSR^{2+} + H^+ \rightarrow 2\ Fe(II) + RSH + R_2S_2$ (**slow**) (18)

$Fe(II) + Cr(IV) \rightarrow Fe(III) + Cr(III)$ (19)

$RSH + Cr(IV) \rightarrow RS\bullet + Cr(III)$ (20)

$2\ RS\bullet \rightarrow R_2S_2$ (21)

All processes are faster than (3) or (13). Some regenerate Fe(II) or yield Cr(IV), which further may oxidize the substrate. The species RS• stands for a thiyl radical. The concentration of $FeCrO_4^+$ from equilibrium (14), which will cause an inhibitory effect, is extremely low (K_2 = 1.4 [14]) under the employed experimental conditions (both $[HCrO_4^-]$ and [Fe(III)] are small). Although the oxidation of Fe(II) by Cr(V) in step (17) is considered to be rate determining in the overall process of Fe(II) oxidation by Cr(VI) [14], within this context it is considered to proceed fast.

Under the excess of RSH and higher iron concentrations, equilibria (15) and (16) are shifted to the right; so that more Fe(III) is trapped in some complexes and less will be able to follow the sequence (11)-(13). Therefore, the contributions in the total reaction rate of the inductive and catalytic paths are modified. This explains the curvature of the k_{obsd} *vs* total iron concentration in Figure 2.

The above inductive mechanism was proposed by Baldea [8] for the oxidation of thioglycolic acid, by taking into account the individual mechanisms of the TGA-Cr(VI), TGA-Fe(III) and Fe(II)-Cr(VI) reactions.

The reaction mechanism of thiomalic acid oxidation by chromate in the presence of copper ions relies on the formation of some copper-thiol complexes [15,16]. Thus, the sequence of steps below is considered to occur in parallel with processes (2) and (3):

$Cu(II) + RSH \Leftrightarrow Cu^{II}SR^+ + H^+$ K_5 (22)

$Cu^{II}SR^+ + RSH \Leftrightarrow Cu^{II}(SR)_2 + H^+$ K_6 (23)

$Cu(I) + RSH \Leftrightarrow Cu^{I}SR + H^+$ K_7 (24)

$Cu^{I}SR + RSH \Leftrightarrow Cu^{I}(SR)_2^- + H^+$ K_8 (25)

$Cu^{I}SR + HCrO_4^- \rightarrow Cu^{II}SR^+ + HCrO_4^{2-}$ (26)

$Cu^{II}(SR)_2 + Cu^{II}SR^+ \rightarrow 2\ Cu(I) + R_2S_2 + RS^-$(**slow**) (27)

$Cu(I) + HCrO_4^- \rightarrow Cu(II) + HCrO_4^{2-}$ (28)

Rapid equilibria (22)-(25) yield the above mentioned complexes. When RSH is in excess, Cu(I)-thiol complexes will be mainly formed in Cu:RSH ratios of 1:1 and 1:2 [15,16]. Process (27) is similar to (18). It is (27) rate determining, but still much faster than step (3), (13) or (18). The catalytic cycle is closed and Cu(II) is regenerated by means of reaction (28). It may be compared with the similar process for iron in step (11). Instead, because the standard reduction potential of the Cu(II)/Cu(I) couple is far below the one of Cr(VI)/Cr(V) [8], process (28) is far from equilibrium. This is why, a catalytic cycle and not an induction mechanism was proposed to explain the rate enhancement by copper ions. Cr(V) obtained in (26) or (28) may further be involved in steps like (12) and (13). However, these will have a negligible contribution to the overall reaction rate because (27) is faster than (13), k_{obsd} values for copper laying higher in Figure 2 than those for iron. The sequence above is completed by fast steps (20) and (21). The tendency to level off, of the k_{obsd} *vs* [Cu] plot in Figure 2, is explained in a similar way to that of iron: in excess of RSH and higher copper content more chelate complex $Cu^{I}(SR)_2^{-}$ will form. It is more stable against oxidation by chromate, hence it will remove part of copper from the catalytic cycle.

Because the oxidation of thiomalic acid in the presence of lead resembles that in the presence of copper (significantly higher reaction rate as compared to that of iron, curvature of the k_{obsd} versus total ion concentration plots in Figure 2), a similar catalytic cycle has been assumed to explain the rate enhancement. Thus, the following reaction path was assumed to occur in parallel with (2) and (3):

$$Pb(II) + RSH \Leftrightarrow Pb^{II}SR^{+} + H^{+} \qquad K_9 \qquad (29)$$

$$Pb^{II}SR^{+} + RSH \Leftrightarrow Pb^{II}(SR)_2 + H^{+} \qquad K_{10} \qquad (30)$$

$$Pb^{II}SR^{+} + HCrO_4^{-} \rightarrow Pb^{IV}SR^{3+} + Cr(IV) \qquad (\textbf{slow}) \quad (31)$$

$$Pb^{IV}SR^{3+} + RSH \rightarrow Pb(II) + R_2S_2 + H^{+} \qquad (32)$$

$$Pb^{IV}SR^{3+} + Pb^{II}(SR)_2 \rightarrow 2\,Pb(II) + R_2S_2 + RS^{-} \qquad (33)$$

Mchrotra [17] and Begley [18] proved that Pb(II) can form lead-thiol complexes in Pb:RSH ratios of 1:2. Přibil [19] also mentions that some thiols, such as thioglycolic acid, bind lead. Therefore, rapid equilibria (29) and (30) were assumed. Rate determining would be the two-equivalent electron transfer within the lead-thiol complex, that is step (31). This may be slow within the cycle (29)-(33), but it is faster than (3), (13) or (18) and slower than (27) (see the plots in Figure 2). Regeneration of the catalyst may also occur rapidly in (33), which could also involve a two-equivalent process with the formation of RS^{+}. RS^{+} reacts immediately with RS^{-} to yield R_2S_2. Process (33) is similar to (27) and (18). The sequence is completed by reactions (20) and (21). An analog catalytic cycle has been assumed for the oxidation of thioglycolic acid in the presence of lead.

Another slow electron transfer process - slower than (31) - involves $Pb^{II}(SR)_2$ and chromate. We suppose, by similarity with copper, that the complex $Pb^{II}(SR)_2$ is more resistant to oxidation by chromate than $Pb^{II}SR^{+}$. Hence, at higher ion concentrations more lead will be bound in this form and thus removed from further catalytic action. This could explain the shape of the k_{obsd} *vs* [Pb] plot in Figure 2.

The curvature of the k_{obsd} plots can be also explained, for all studied ions, on the base of equation (9) and the values of constants ***a*** and ***b*** given in Table 3. At small ion concentrations (of the order of magnitude of 10^{-6} M), the second term of the sum (1 + b[ion]) is negligible; hence rate enhancement depends linearly on [ion]. When the latter is increased, its significance in the sum will also increase and the plots of k_{obsd} will level off.

The weaker effects of iron and copper on TGA oxidation are probably due to the fact that TGA is indicated as masking agent for iron in acidic media [19] as well as for copper in alkaline [20] or weak acid media [19]. With iron an intensely red complex is formed, while the complexes of copper may be colorless – in alkaline – or red – in weak acid media. This is consistent with our experimental observations: values of absorbance (including A_∞) were somewhat higher when kinetic runs were carried out in the presence of iron or copper.

Both Figure 2 and Table 2 reveal the fact that, under the same experimental conditions, copper achieves the best rate enhancement of TMA oxidation. Lead and iron follow it. On the other hand, lead ions affect the most significantly the rate of TGA oxidation. Their catalytic effect is even stronger than that of copper ions, while rate enhancement by iron is barely sensed. These findings led to the conclusion that the $Cu^{I}(SR)_2^-$ complex of TGA is more stable against oxidation by chromate than the complex of TMA. The same is applicable for the $Pb^{II}(SR)_2$ complexes, although rate enhancements by lead are almost identical for both substrates.

Thus, from analytical point of view, the use of TMA oxidation in kinetic determination of Cu(II) is rather indicated than that of TGA oxidation, provided the effects of lead and iron can be suppressed. This was already achieved in the presence of pyrophosphate [3,19]. If only the effect of iron ions is masked, for example with the aid of 1,10-phenantroline [19], both substrate oxidations are recommended as indicator reactions for the joint analysis of Cu(II)-Pb(II) mixtures. However, the concentration of lead in the reaction mixture should not exceed $5x10^{-4}$ M. Otherwise, precipitates will form with the thiols.

The effect of several other ions on the oxidation of TMA and TGA by chromate has been investigated, under the same experimental condition as employed for copper, lead and iron. Comments on the obtained results, along with the concentration limits C_{lim} at which their presence in the reaction mixture is sensed *via* kinetic measurements, are given in Table 4.

Table 4

Effect of various metal ions on the rates of TMA and TGA oxidation. Experimental conditions are the same as listed for Figure 1.

Ion	C_{lim} (M)	Comments
Cd(II)	10^{-4}	Increases rate for both TMA and TGA; If [Cd(II)] > $5x10^{-4}$ M, precipitates will form.
Ni(II)	$5x10^{-4}$	Increases rate for TMA
	10^{-4}	Increases rate for TGA
Co(II)	10^{-3}	Decreases slightly the rate for TMA
		Increases significantly the rate for TGA
Zn(II)	$5x10^{-4}$	Increases rate for both TMA and TGA
Mn(II)	---	Does not affect reaction rates

Oxidation of the two substrates behaves similarly in the presence of all, but Co(II), ions listed above. However, these species affect reaction rates only when present in a relatively high concentration. Thus, it is unlikely that any kinetic method will be developed for their analysis, on the base of indicator reaction (1).

REFERENCES

1. A. Rustoiu-Csavdari, I. Bâldea, *Proceedings of the 2nd International Conference of the Chemical Societies of the South-Eastern European Countries On Chemical Sciences for Sustainable Development*, Chalkidiki, Greece, **2000**, PO 658.
2. A. Rustoiu-Csavdari, I. Bâldea, L. Copolovici, D. M hai, *Lucrările celei de a XI-a Conferință Internațională de Chimie şi Inginerie Chimică,* Bucureşti, România, **1999**.
3. D. Mihai, *Kinetic Determination of Cu(II) by its Catalytic Effect on the Oxidation Reaction of Mercaptosuccinic Acid by Chromate (Advanced Studies Thesis)*, Babeş-Bolyai University, Cluj-Napoca, Romania, **2000**; A. Rustoiu – Csavdari, I. Bâldea, D. Mihai, *unpublished work*.
4. A. Rustoiu-Csavdari, I. Bâldea, C. Călin, *Proceedings of the 6th International Symposium On Kinetics in Analytical Chemistry, KAC'98*, Kassandra, Greece, **1998**, p. 39.
5. A. Rustoiu-Csavdari, I. Bâldea, M. Stan, *Chem. Bull. "Politehnica" Univ. (Timişoara)*, **1998**, *43(57),* 143.
6. I. Bâldea, G. Niac, *Studia Univ. Babeş-Bolyai, Chem.,* **1986**, *31(2)*, 41.
7. G. Niac, S. Schön, I. Bâldea, *Studia Univ. Babeş-Bolyai, Chem.,* **1986**, *31(2)*, 31.
8. I. Bâldea, *Studia Univ. Babeş-Bolyai, Chem.,* **1989**, *34(1)*, 80.
9. I. Bâldea, *Studia Univ. Babeş-Bolyai, Chem.,* **1994**, *39(1-2),* 138.
10. I. Bâldea, *Studia Univ. Babeş-Bolyai, Chem.,* **1987**, *32(2),* 42.
11. I. Bâldea, G. Niac, *Inorg. Chem.,* **1968**, *7*, 1232; I. Bâldea, G. Niac, *Inorg. Chem.,* **1970**, *9*, 110.
12. J. F. Perez – Benito, N. Saiz, E. Amat, *J. Mol. Catal., A-Chem.,* **1998**, *135*, 1.
13. D. L. Leussing, I. M. Kolthoff, *J. Amer. Chem. Soc*., **1953**, *75*, 3904, D. L. Leussing, L. Newman, *J. Amer. Chem. Soc*., **1955**, *78*, 552.
14. J. H. Espenson, E. L. King, *J. Amer. Chem. Soc*., **1963**, *85*, 3328.
15. A. McAuley, *Coordin. Chem. Rev.,* **1970**, *5*, 245.
16. I. M. Klotz, G. H. Czertinki, A. A. Fies, *J. Amer. Chem. Soc*., **1958**, *80*, 2920.
17. R. C. Mchrotra, *J. Organometallic Research*, **1986**, *283*, 185.
18. M. G. Begley, C. gaffney, P. G. Harrison, A. Steel, *J. Organometallic Research*, **1985**, *289*, 281.
19. R. Přibil, *Applied Complexonometry*, Pergamon Press, Oxford, **1982**, pgs. 72, 113 and 149.
20. R. Přibil, V. Vesely, *Talanta*, **1961**, *8*, 880.