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# KINETICS OF THIOLACTIC ACID OXIDATION BY DECAVANADATE AND $VO_2^+$ IN ACIDIC MEDIA

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**ABSTRACT.** The oxidation of thiolactic acid by decavanadate and $VO_2^+$ in aqueous acidic media, using perchloric acid, has been followed spectrophotometrically. A first-order dependence on decavanadate has been found for both the hydrolysis and the oxidation process as well as a first-order dependence on the substrate. The activation energy has been obtained. The oxidation by $VO_2^+$ under the conditions of comparable concentration with the substrate, has been approached by a stopped-flow technique. The reaction obeys an 1.5 order dependence on $VO_2^+$ ion, first-order in thiolactic acid and a complex (negative order) dependence on hydrogen ion concentration. The V(IV) intermediate valence state has been identified by ESR spectroscopy. Some suggestions on the mechanism were put on.

**Keywords*:*** decavanadate, thiolactic acid, kinetics, oxidation

## INTRODUCTION

In acidic medium, V(V) plays a role of an oxidizing agent relative to numerous inorganic or organic substances, and its ultimate valence state is V(III). Oxidation studies have been carried out on various compounds such as formic and malonic acids[1] glycollic acid[2], oxalic acid[3], mandelic acid[4], tartaric acid[5] and pinacol[6]. The oxidation of thiomalic acid (2-mercaptosuccinic acid)[7] has been approached using fast reaction techniques. In these oxidation reactions the mechanism postulated has involved the formation of a transient complex between the vanadium(V) and the organic substrate. No physical evidence for such complex was presented, with the exception of thiomalic acid oxidation where the spectrum of a purplish-brown colored intermediate has been recorded.

The difficulties arising in the oxidation with V(V) consist of the existence of numerous hydrolytic and acid-base equilibria involving this valence state, strongly depending on the solution pH, total V(V) concentration and ionic strength.

Monomeric species $VO_4^{3-}, HVO_4^{2-}, H_2VO_4^-, H_3VO_4$, and $VO_2^+$ or isopoly-vanadates $V_2O_7^{2-}, V_3O_9^{3-}, V_4O_{12}^{4-}, V_{10}O_{28}^{6-}, HV_{10}O_{28}^{5-}, H_2V_{10}O_{28}^{4-}$ are involved[8-14]. The decomposition and dissociation of decavanadate have been studied by spectrophotometrical means in basic[15,16], neutral and weakly basic[17] or acidic solutions[18-20], even from the kinetic point of view.

The purpose of this paper is to study the oxidation of thiolactic acid within the conditions where the main species is dacavanadate and/or vanadyl ion respectively and search for some reaction intermediates.

## EXPERIMENTAL

The chemicals used in this study were of reagent grade purity, purchased from commercial sources (Reanal Budapest, Merck, Fluka and Aldrich) and employed without further purification.

The preparation of the decavanadate stock solution has been made in the following manner: 0.0117 g of $NH_4VO_3$ were weighted and introduced to a 50 mL volumetric flask. It was dissolved into 10 mL NaOH 0.1 mol/L. Perchloric acid 0.24 mol/L was added to neutralize the solution and get to a pH value around 5.5, when made up to the mark. This solution contains $HV_{10}O_{28}^{5-}$ ion[10] in a concentration of $2x10^{-3}$ mol/L, expressed in monomer. The solution has an intense yellow colour and is stable up to 3 hr. The solution stability has been checked, by recording the UV/VIS spectra.

A similar procedure has been followed to prepare the $VO_2^+$ solution, but adding enough $HClO_4$ until a pH value in the range of 1.5 – 1.7 was reached. The solutions were used after the accomplishment of hydrolysis (1-2 hrs), when they become stable.

Thiolactic solution was prepared from a concentrated one of this acid and standardized by acid-base titration. It has been freshly prepared before each set of runs and used within a period of at most 3 hr.

Stock solution of $HClO_4$ 0.24 mol/L was obtained by dilution of a concentrated perchloric acid 70% (density 1.664 g/mL) and standardized by acid-base titration. $NaClO_4$ solution used for the adjustment of ionic strength was prepared from crystalline $NaClO_4 \cdot H_2O$ and standardized by acid-base titration after passing a known volume through a column with Vionit ionic resin in H-form.

Classic spectrophotometry was employed when the oxidant was $HV_{10}O_{28}^{5-}$. Kinetic measurements were performed, always under the conditions of pseudo-first-order using substrate excess, by means of an ABLE JASCO V-530 spectrophotometer, provided with a temperature jacket surrounding the cell holder. The cuvette jacket was connected to a LAUDA M-20 recirculatory water bath. Reaction mixtures were prepared directly in the quartz cell of the spectrophotometer with 5 cm path length. A rapid injecting of a measured amount of oxidant solution over the reaction mixture containing $HClO_4$, $NaClO_4$, and thiolactic acid in de-ionized tetra-distilled water at desired concentration started the reaction.

Either $HV_{10}O_{28}^{5-}$ or $VO_2^+$ exhibits an absorption peak around 280 nm, the first having a larger molar absorptivity. To avoid interference of thiolactic acid absorbing in the same range of spectrum at the concentration around 50 fold excess, the reaction was monitored at 340 nm.

When $VO_2^+$ was the oxidant, stopped-flow measurements were performed with a custom built multi-channel apparatus with photomultiplier detection. They used comparable concentrations of $VO_2^+$ and thiolactic acid, but excess of $H^+$.

To search for paramagnetic intermediate species, some ESR measurements were performed on a JEOL X-band type PE-3X ESR spectrometer, connected to 8-inch AEG-magnet at 100 kHz field modulation. Field measurements were achieved by an NMR-Gaussmeter, Drusch MNR-2. The spectrometer was set up with a flow system composed of two solution containers of approximately one liter each, connected to a quartz mixing cell, assuring the mixing of the reactants to occur immediately upon entrance to the microwave resonator.

## RESULTS AND DISCUSSIONS

*The stoichiometry* of the reaction has been considered 2 $CH_3CH(SH)COOH$ : 1 V(V), as Pickering and McAuley[7] determined for the oxidation of mercaptosuccinic acid. The products were disulphide and V(III). It was confirmed by an experimental spectrophotometrical titration.

*The oxidation by decavanadate.* Under the condition of a large excess of thiolactic acid (noted as RSH in the paper) the evolution of absorbance presents an exponential shape. Such a dependence is shown in figure 1. It should be mentioned that, at the acidity employed in the measurements, the acid hydrolysis of decavanadate takes pace along with the oxidation process. This is also shown in figure 1. As seen, the hydrolysis proceeds slower as compared to the oxidation. The acid hydrolysis obeys a first-order dependence on the coloured species (decavanadate) concentration.

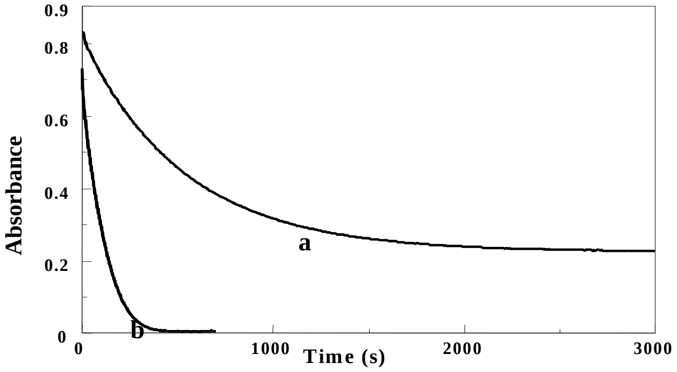


**Fig. 1.** *Absorbance against time dependence for the acid hydrolysis (curve a) and combined redox + hydrolysis (curve b). Conditions: [$HV_{10}O_{28}^{5-}$] = 2.22x$10^{-5}$ mol/L, [RSH] = 2.22x$10^{-2}$ mol/L, [$HClO_4$] = 3.16x$10^{-2}$ mol/L, $\mu$ = 0.5 mol/L and T = 293 K.*

The semilogarithmic plots

$$\ln(A - A_\infty) = \ln(A_0 - A_\infty) - k_{obsd}^{h} t \tag{1}$$

were linear to more than 90 % of hydrolysis reaction. A, $A_0$ and $A_\infty$ stands for absorbance at the time t, at the beginning and at the end of the process respectively, and $k_{obsd}^{h}$ for the observed first-order rate constant of hydrolysis. It is in agreement with the data obtained by Clare and co-workers[18]. The same type of linear equation has been used for the sum hydrolysis + reduction by RSH process. It should be mentioned that the linear parts of such plots were only for at most 1-1,2 units of natural logarithm (about 40-50 % of reaction). Within this range of V(V) conversion, the correlation coefficients were in the range 0.9966 - 0.9998.

The reason for such a behaviour consists in the higher reactivity towards reduction of the smaller poly-oxovanadates or monomeric forms. Both hydrolysis and redox processes release fragments of higher reactivity, resulting a reaction rate increase. This work shows that the $VO_2^+$ ion reacts quite fast, requiring a stopped-flow device to monitor the reaction. In the same time this ion does not contribute significantly to the solution absorbance, due to its slow formation by hydrolysis and rapid consumption in redox reaction. By using the early part of the reaction it is to expect that decavanadate species $HV_{10}O_{28}^{5-}$ is the one involved. The fact the V(V) consumption by both hydrolysis and reduction by thiolactic acid proceeds faster that the hydrolysis itself indicates that polymeric vanadates accepts electrons, not only the monomeric V(V) species, generated by hydrolysis. Because the oxidation and hydrolysis take place simultaneously and obey first-order kinetics, one can distinguish them by making the differences between apparent first-order rate constants of the overall process and the hydrolysis one.

$$k_{obsd} = k_{overall} - k_{obsd}^{h} \tag{2}$$

$k_{obsd}$ represents the first-order rate constant for redox process only. Table 1 contains values of first-order rate constants under several experimental conditions.

As seen from the data presented in Table 1, the acid hydrolysis exhibits a linear dependence on the acidity. The same order has been determined previously by Clare and co-workers[18] at higher $H^+$ concentrations using nitric acid. Our results, when using $HClO_4$ as the hydrogen ion source, extend the first-order range towards lower acid concentrations.

Concerning the redox process, a first-order dependence on the thiolactic acid concentration has been noted as shown in figure 2a, while the effect of the acidity on the rate is more complex, as depicted in figure 2b.

**Table 1**

First order rate constants* for overall, hydrolysis and redox processes at various excesses of thiolactic acid and various perchloric acid concentration at ionic strength $\mu$ = 0.5 mol/L and T = 293 K, when $[HV_{10}O_{28}^{5-}]$ = $2.22\text{x}10^{-5}$ mol/L.

| $10^2[HClO_4]$ mol/L | $10^2$[RSH] mol/L | $10^3$ $k_{overall}$ ($s^{-1}$) | $10^3$ $k^h_{obsd}$ ($s^{-1}$) | $10^3$ $k_{obsd}$ ($s^{-1}$) |
|---|---|---|---|---|
| 1.00 | - | - | 0.475 | - |
| 1.59 | - | - | 0.854 | - |
| 2.51 | - | - | 1.42 | - |
| 3.16 | - | - | 1.80 | - |
| 5.01 | - | - | 3.06 | - |
| 7.94 | - | - | 5.04 | - |
| 10.00 | - | - | 6.63 | - |
| 1.59 | 2.22 | 12.23 | | 11.38 |
| 2.51 | 2.22 | 8.55 | | 7.13 |
| 3.16 | 2.22 | 7.96 | | 6.16 |
| 5.01 | 2.22 | 6.50 | | 3.44 |
| 7.94 | 2.22 | 7.70 | | 2.66 |
| 10.00 | 2.22 | 9.17 | | 2.54 |
| 3.16 | 0.556 | 2.80 | | 0.997 |
| 3.16 | 1.11 | 4.43 | | 2.63 |
| 3.16 | 3.33 | 12.23 | | 10.42 |
| 3.16 | 4.44 | 14.83 | | 13.02 |
| 3.16 | 5.56 | 18.28 | | 16.47 |

* The values in the table are means of at least 3 to 4 kinetic runs.

The equation of the line at constant acidity is:

$$k_{obsd} = -(0.0007 \pm 0.0003) + (0.312 \pm 0.009)[RSH] \qquad (3)$$

confirming first-order dependence on RSH. The fig. 2b indicates a negative (–1) order with respect to hydrogen ion concentration. A plot of $1/k_{obsd}$ is quite linear. Therefore, the real rate constant ($s^{-1}$) can be computed as $k_{obsd}$[H+]/[RSH]. If some intermediate complex V-thiolactic acid is involved, through a V-S bond, as proved by McAuley[7], then the thiol function is involved and it should be acid dissociated before bonding or simultaneously with bonding, which is in accordance with a negative order on $H^+$.

Further experiments are needed to suggest a well argued reaction mechanism. It is obvious that some consecutive one-equivalent electron transfer steps are involved. The mixture change its colour to a pale-blue one, characteristic to V(IV) compounds. As presented in this paper, V(IV) has been identified by ESR studies.

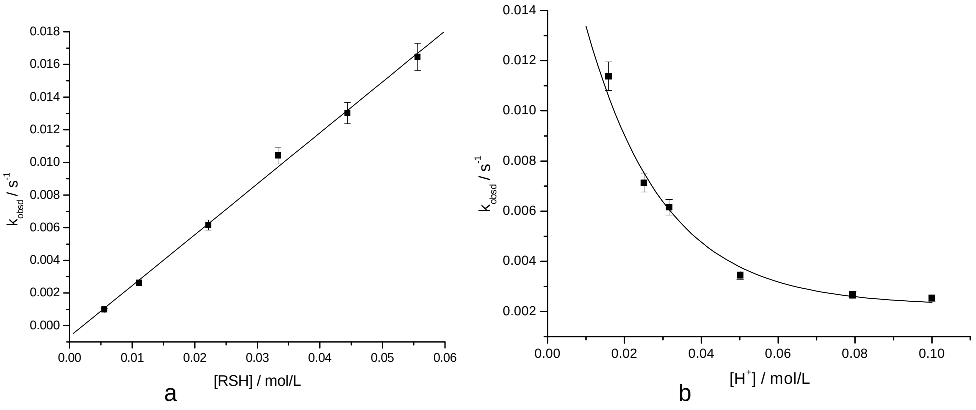


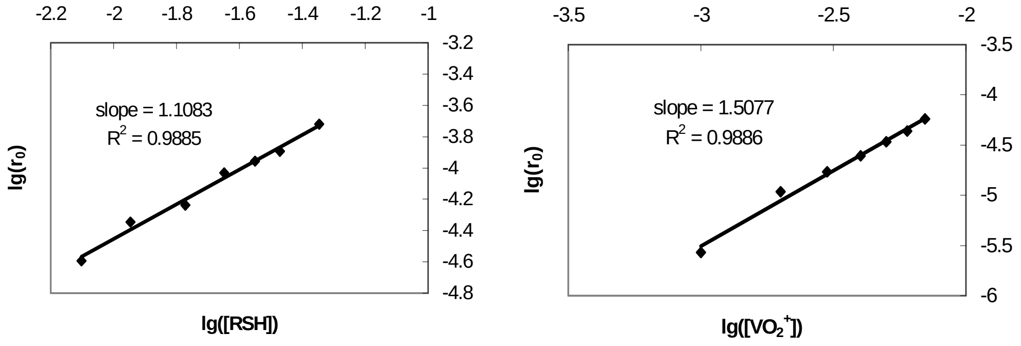
**Fig. 2.** *The effect of thiolactic acid (a), ($[H^+]$= 3.16x10$^{-2}$ mol/L) and $H^+$ (b) ($[RSH]$ = 2.22x10$^{-2}$ mol/L) on the reaction rate at T = 293 K.*

An attempt to determine activation parameters has also been made. Measurements at three different temperatures (293, 303 and 313 K) have been carried out, studying both the hydrolysis and the redox processes, when the experimental activation energies $E_a^h$ = 61.0 kJ/mol and respectively $E_a^{redox}$ = 34.0 kJ/mol for the two reactions have been computed. Even if few, these measurements are quite reliable, as the value obtained for $E_a^h$ is similar to the one given by Clare at al[18] in nitric acid (75 kJ/mol) and other pH range (other prevalent equilibria).

*Oxidation by $VO_2^+$.* Oscillograph traces, obtained by means of a stopped-flow device, showing the disappearance of $VO_2^+$ ion, were recorded under various concentration of $VO_2^+$, RSH and $H^+$, the last in the concentration range where vanadium $VO_2^+$ was the predominant species. The reaction has accomplished within 1- 1.5 seconds.

Reaction orders were determined combining the isolation and the initial rate methods, by varying one after the other the concentration of one reactant while keeping the concentration of the other constant, as well as solution pH (1.5) and ionic strength (0.1 mol/L). By calculation of the initial reaction rate, the reaction order with respect to the species whose concentration was varied, has been determined from the classic double logarithmic plot. Such plots are exemplified in figure 3, for the two main reactants.

For $VO_2^+$ concentration ranging from 5x10$^{-4}$ mol/L to 3.5x10$^{-3}$ mol/L at constant concentration of thiolactic acid (1.13x10$^{-2}$ mol/L) the method leads to an order of 1.5. Analogously a first-order dependence was found for thiolactic acid (2.5x10$^{-3}$ - 2.25x10$^{-2}$ mol/L) at constant concentration of $VO_2^+$ (2.5x10$^{-3}$ mol/L).



a b

**Fig. 3.** *Double logarithmic plots giving the reaction orders on RSH (a) and $VO_2^+$ (b).*

Investigating the effect of $H^+$ upon the reaction rate proved more troublesome, which owes to the very narrow range of pH's usable in the investigations: 1.5-1.7. This limitation has two causes, the lower limit being that the construction of the stopped-flow apparatus does not allow for more acidic solutions, while the incomplete hydrolysis of the polymeric structure of the oxovanadate compound at higher pH's provided the upper limit. Nevertheless a clear trend towards decreasing rates with increasing pH was seen, allowing to estimate the reaction order on $H^+$ as being -1. The value is the same as in the case of decavanadate oxidation.

The influence of the ionic strength of the solution upon the reaction was also investigated, using constant concentrations of the reactants at pH 1.5, while varying ionic strength between 0.1 and 1 mol/L. It was found that the redox process suffers no effect of the ionic strength at pH 1.5, as the classical plot $\lg k_{obs}$ versus $\mu^{1/2}$ shows no trend.

It should be mentioned, at this point, that the information so far achieved was found not satisfactory to describe the full mechanism of the reaction. That is because one or more further steps are known from the presence of some intermediates, which have been investigated by other means.

*ESR investigations on the $VO_2^+$/thiolactic acid system.* The first ESR measurements were performed in continuous flow, when the attempts to identify paramagnetic species in the reaction of $VO_2^+$ ($2.5 \times 10^{-3}$ mol/L) with thiolactic acid ($7.5 \times 10^{-3}$ mol/L), at pH 1.5 and ionic strength 0.1 showed the presence of free V(IV), in moderate concentrations, at some stage of the reaction. This complies with results reported in literature[22,23]. Figure 4 shows the intensity of ESR signal of V(IV) at different elapsed-time.

The idea of comparing the results with those obtained for the oxidation of thiolactic acid by Cr(VI) urged us to search for organic radicals in the studied reaction[24]. However, no such species could be observed, due to either experimental limitations - such as the incapability of setting a sufficiently slow flow - or to reaction it self – the radical is formed in very low "teady-state" concentrations (has a too short life time).

With identical experimental setup - only differing by the application of stopped-flow in contrast to the previous continuos one - kinetic curves were obtained, directly from the plotter of the spectrometer console. That was achieved by positioning at a constant magnetic field corresponding to that found in the field sweep experiments, and monitoring the evolution of the signal in time (in the units of ”mm per second”). The curves obtained this way were then scanned and digitized, in order to be transferred to simple ASCII format for later use in computer simulations. Good, reproducible kinetic curves were produced, but this part of the study is still in its early stages.

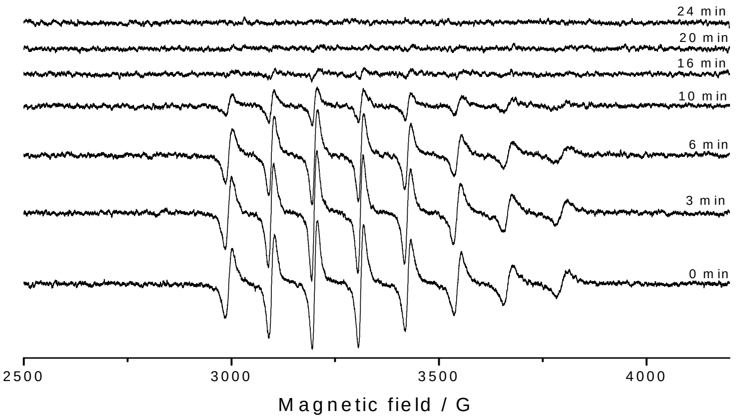


**Fig. 4.** ESR spectrum of free V(IV) and its evolution in time.

## CONCLUSIONS

Although more data are needed to infer a certain and complete reaction scheme, there are several obvious findings as the rate law, the electron transfer with polyoxo-vanadate (before a more reactive monomer is separated), the involvement of V(IV) that reacts not too fast, small or lack of any effect of ionic strength. They argued the supposition that successive and parallel steps are involved: the formation of a 1:1 complex with a S-V bond along with a binuclear 1:2 RSH:V(V) complex, where the substrate is a bridge, the formation of V(IV) in one-equivalent electron transfer that needs the formation of a thiyl radical, further oxidation by V(IV). The assumption of the binuclear intermediate also finds support in the work of Kiss at al.[25] who concluded that bidentate mercaptocarboxylates were formed $COO^-$-V or $S^-$-V coordinated mono or bis complexes.

On the base of these findings, the following mechanism can be assumed when having $VO_2^+$ as oxidizing agent:

$$VO_2^+ + RSH \overset{K_{a1}}{\rightleftharpoons} VO_2 - SR + H^+ \tag{4}$$

$$VO_2 - SR \xrightarrow{k_1} V(IV) + RS\bullet \tag{5}$$

$$2\,VO_2^+ + RSH \overset{K_{a2}}{\rightleftharpoons} VO_2 - SR'COO - VO_2 + 2\,H^+ \tag{6}$$

$$VO_2 - SR'COO - VO_2 \xrightarrow{k_2} V(IV) + RS\bullet \tag{7}$$

$$V(IV) + RSH \xrightarrow{k_3} V(III) + RS\bullet + H^+ \tag{8}$$

$$2\,RS\bullet \xrightarrow{fast} RSSR \tag{9}$$

Further ESR studies will bring information on $k_3$.

When the oxidant is $HV_{10}O_{28}^{5-}$, a similar mechanism can be assumed. In the first step an adduct is formed, which reacts further to yield V(IV), thiyl free radical and a cluster having one vanadium unit less. Here, the volume of the V(V) species should make difficult the formation of the 1:2 intermediate complex. However, the fact that only first-order in polyoxo-vanadate has been found, does not rule out the binding of the substrate by thiol and carboxylic function to two neighboring $VO_4$ units in the cluster.

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