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A COMPARATIVE STUDY ON THE OXIDATION OF HYDROXY- AND MERCAPTO- COMPOUNDS BY Cr(VI)

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ABSTRACT. Both, the thiols or mercapto-acids (RSH) and the alcohols or hydroxy-acids (ROH) are easily oxidised by various oxidising agents as Cr(VI), Mn(VII) $Fe(CN)_6^{3-}$, Ce(IV), etc. The importance of such a comparison of the two classes of compounds consists of the resemblance of –OH and –SH functions, as well as the involvement of such oxidation in many biological processes. Our comparative study is based on the literature data as well as our research in the field of oxidation of various thio-compounds as ethane thiol, mercaptoacetic acid, mercaptosuccinic acid, L(+)-cysteine, glutathione, thiophenol benzylmercaptane and alcohols or hydroxy-acids as benzyl alcohol, glycolic acid, lactic acid, malic acid, ascorbic acid by Cr(VI).

Kinetic rate laws are compared and mechanisms are discussed. There is some similar behaviour of two classes of compounds. Using Cr(VI) as oxidising agent, the rate laws, at acidity held constant are of the form:

$$-\frac{d[Cr(VI)]}{dt} = \frac{k'[ROH][Cr(VI)]}{1+K[ROH]} \quad \text{and}$$

$$-\frac{d[Cr(VI)]}{dt} = \frac{k'\{RSH]+k''[RSH]^2}{1+K[RSH]}[Cr(VI)]$$

Many differences were noticed. Generally, the oxidation of hydroxy-compound takes place at the carbon atom bearing the function and carbonyl products were obtained. On the contrary, thiols are oxidised at sulphur atom and disulphide products were obtained. However, the rate laws are similar. Generally, in the Cr(VI) oxidations, intermediate condensed compounds esters or thio-esters have been identified either directly by spectrophotometrical means, or indirectly by the inference on the rate law. With hydroxy-compounds the two-electronic charge transfer prevailed. With thio-compounds both mono- and two-electronic charge transfer takes place, depending on the nature of thiol. The involvement of free radicals has been also proved. Both classes of oxidation are strongly influenced by the acidity of the medium. Other medium effects were noticed.

INTRODUCTION

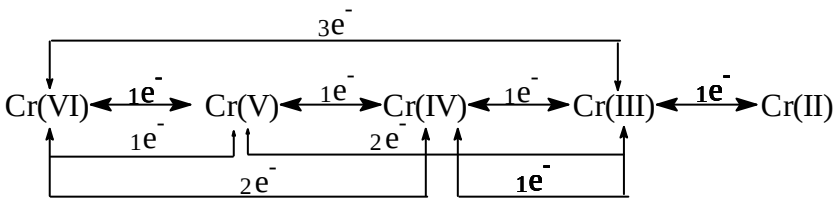
Oxidations by chromium (VI) have been extensively studied and documented. Some reactions of Cr(VI) include its usage in classical titrimetric analysis in determination of a number of metal ions or reducing agents as well as its usage in preparative organic chemistry [1]. The carcinogenic and mutagenic [2,3] nature of Cr(VI) ion and the fact it is a major industrial pollutant have stimulated intensive research in order to identify substances that effectively reduce Cr(VI) to a less harmful Cr(III) states under mild conditions [4-16]. Among these reducing agents there are alcohols, organic acids or bi-acids, ascorbic acid,

thiol compounds, hydroxy- and mercapto-acids. On the other hand, thiols are considered as the most active groups found in cells and are easily oxidised to less reactive disulphides. The thiol-disulphide interchange reaction is of the great importance in biochemistry [8,17].

That is why we have undertaken the study of oxidation reaction between Cr(VI) and various hydroxy- and thiol- compounds and a comparative discussion on rate laws and mechanisms seems to be quite interesting.

The first difference between the two related organic classes of compounds consists on the fact that when alcohols or hydroxy-acids are oxidised, the carbon atom bearing the function changes its oxidation state [4-7, 15, 16 18], while when thiols are oxidised, the sulphur atom involved in the function is the one to change the oxidation state [8-14, 17].

In order to present some reaction mechanisms, first we have to analyse the valence state of chromium, showed in the following scheme I. It indicates the ways of passing from Cr(VI) to the stable Cr(III) species. It includes one-, two-, or three- equivalent processes.



Scheme I

All the ways depicted in the scheme are involved in various oxidation reactions, including co-oxidations and induced reactions [18]. The development of techniques for detecting free radical intermediates or paramagnetic species and techniques of separating product complexes of Cr(III) have given illumination on some mechanistic aspects.

For a one-equivalent reducing agent, a step by step one-equivalent electron transfer reduces Cr(VI) to Cr(III). This route is not the usual one followed with the systems under discussion, with some exceptions. Chromium (VI) is known as a prevalent two-equivalent oxidising agent, and some complications arise, because more reaction routes are now opened. Some three-equivalent reductions of Cr(VI) were also observed, involving concerted action of two substrate molecules.

The variety of species of Cr(VI) in acidic solutions [19, 20] and the presumable passage of chromium through transient unstable species combine to give the system a considerable complexity.

Several groups all over the world dealt and are dealing with kinetic studies of Cr(VI) oxidation [5-18, 21-28] of hydroxyl and thiol compounds. Among them, a group in our laboratory has studied these classes of compounds [29-40].

The reactions under discussion have been found to proceed by inner-sphere mechanisms. It is well known that complexes of chromate of the dichromate, esteric or thioesteric type, stable or transient intermediate species are formed in acidic solutions. The condensation equilibrium of the form:

$$HCrO_4^- + H^+ + X^- \rightleftharpoons XCrO_3^- + H_2O \quad (1)$$

takes place with oxo-anions, halides or pseudo-halides, alcohols, diols, hydroxy-acids, thiols, mercapto-acids.

Table 1.

Equilibrium constants and the position of the charge-transfer ligand-Cr(VI) peak for various condensed compounds of Cr(VI) [33, 40, 42-44]

Compound	λ (nm)	K (M^{-1})
$HOCrO_3^-$	350	-
$O_3SOCrO_3^-$	350	4.1
$HO_2POCrO_3^-$	350	2.9
$CH_3COOCrO_3^-$	347	4.5
$O_2SOCrO_3^-$	350	36
$CH_3OCrO_3^-$	350	4.7
$C_2H_5OCrO_3^-$	358	6.9
$(SCN)OCrO_3^-$	380	9.2
$ClOCrO_3^-$	358	4.2
$O_3S\text{-}SCrO_3^-$	394	1.24×10^4
$Cys\text{-}SCrO_3^-$	426	1.48×10^3
$HOOCCH_2\text{-}SCrO_3^-$	425	1.1×10^3
$HOOCCH_2CH(COOH)\text{-}SCrO_3^-$	412	1.48×10^3
$C_2H_5\text{-}SCrO_3^-$	450	1.2×10^3
$Glu\text{-}SCrO_3^-$	428	1.44×10^3

Within the esteric type complexes, an oxygen atom plays the role of a bridge, and the species exhibits absorption spectra similar to the spectrum of $HCrO_4^-$ [41]. The position of the charge-transfer peak is not shifted significantly as compared to the one exhibited by $HCrO_4^-$. When another atom (Cl, S) is bound to Cr(VI), the charge-transfer peak is shifted towards red. Several data concerning the position of absorption band and formation constant are presented in table 1.

The table reveals that when a sulphur-chromium link is established, the formation constants are three to four orders of magnitude greater than those where an oxygen bridge is involved. On the other hand, the formation kinetics of the esteric or thioesteric type condensed compound has been measured for several cases, and rate laws have been found. The processes are faster than the subsequent redox ones. Therefore, it is undoubtedly established that such

condensed Cr(VI) intermediates are involved in the oxidation of alcohols, hydroxy-acids, thiols and mercapto-acids, they being able to provide low-energy routes for the electron transfer. As usually being the slowest one, electron transfer is rate determining step in most cases. Also, as seen, the complex formation, as well as its further decomposition, can depend on hydrogen ion concentration.

Table 2.

Comparison of the kinetic data on the formation of substrate-chromate complex and redox decomposition at 25°C for various compounds [30]

Substrate	Complex ($XCrO_3^-$)	10^{-3} K M^{-1}	k_f^0 $M^{-1}s^{-1}$	10^{-4} k_f^H $M^{-2}s^{-1}$	k^0 $M^{-1}s^{-1}$	10^{-2} k^H $M^{-2}s^{-1}$
$HCrO_4^-$	$Cr_2O_7^{2-}$	0.098	-	62	-	-
H_2PO_3	$HO_2POCrO_3^-$	0.008	-	50	-	-
$H_2S_2O_3^-$	$O_3SSCrO_3^-$	12.4	-	37	180	185
C_2H_2SH	$C_2H_5SCrO_3^-$	1.2	-	2.3	-	0.15
L-Cysteine	$CysSCrO_3^-$	1.48	2.1	0.014	7.7	0.007
		-	-	0.01	12.0	-
$CH_2(SH)COOH$	$RSCrO_3^-$	1.1	66.3	0.247	11.0	4.33
$HOOCCH_2CH$-(SH)-$COOH$	$RSCrO_3^-$	1.48	44.1	0.019	23.8	2.03

OXIDATION OF ALCOHOLS AND HYDROXY-ACIDS

The oxidation of alcohols yields aldehydes, ketones or other products when the cleavage of C-C bond takes place, depending on the nature of substrate and the concentration of reacting species [45, 46]. Westheimer reviewed chromate oxidation of alcohols concerning himself chiefly with the reaction mechanism [28, 47, 48]. The mechanism he elaborated for 2-propanol oxidation served as a model for the oxidation of various other substrates, and has been a focus for discussion and research.

$$HCrO_4^- + R_2CHOH \rightleftharpoons R_2CHOCrO_3^- + H_2O \qquad K \qquad (2)$$

$$R_2CHOCrO_3^- \longrightarrow R_2CO + Cr(IV) \qquad \text{r.d.s.} \quad k \qquad (3)$$

The fate of Cr(IV) species is questionable. Several paths are possible, involving subsequent reactions [49].

I.
$$Cr(IV) + Cr(VI) \rightleftharpoons 2Cr(V) \qquad (4)$$

$$Cr(V) + R_2CHOH \longrightarrow Cr(III) + R_2C=O \qquad (5)$$

II.
$$Cr(IV) + R_2CHOH \longrightarrow Cr(II) + R_2CO \qquad (6)$$

$$Cr(II) + Cr(VI) \longrightarrow Cr(III) + Cr(V) \qquad (7)$$

Mechanism I was favoured by Westheimer. The path II has been dismissed from the very beginning, because Cr(II) is such a powerful reducing agent that it has not been a likely species in the system. However, the interest in it has been recently renewed by some studies like the one on Cr(VI) oxidation of 2(2-hydroxyethyl)pyridine in aqueous acidic media [50].

Chromium (V) behaves like chromate itself and oxidises R_2CHOH in a two-equivalent step [27].

III. $$Cr(IV) + R_2CHOH \longrightarrow Cr(III) + R_2\dot{C}HO \quad (8)$$

$$R_2\dot{C}HO + Cr(VI) \longrightarrow R_2CO + Cr(V) \quad (9)$$

$$Cr(V) + R_2CHOH \longrightarrow Cr(III) + R_2CO \quad (5)$$

The failure to detect free radicals in the early studies had the result that path III has been firstly ruled-out.

However, the oxidation of cyclobutanol [26, 51-54] or even i-propanol made Roček and co-workers to conclude that the organic substrate reduces Cr(IV) in one-equivalent step instead of reacting with Cr(VI) to generate Cr(V). It favours the route III. On the other hand, Wiberg and Mukherjee [55] followed the rate of acetone formation at the oxidation of 2-propanol, relative to the growth and decay of Cr(V) EPR signal in acetic acid solutions, giving support to the route III. In the mechanism I two equivalents of Cr(V) are formed for one acetone molecule, while in the mechanism three, the reciprocal is valid in the early stages of the process. The analysis showed the ratio corresponds to route III. The overall stoichiometry is 1,5 : 1 i-propanol : Cr(VI).

More recently, proofs like the initiation of polymerisation or EPR measurements have undoubtedly proved the existence of free radicals in numerous systems, giving further support to mechanism III. Numerous alcohols or α-hydroxy-acids are reported in the literature to undergo such reaction pathways [15, 36, 56-59].

As we have already mentioned, in some cases Cr(VI) seems to behave different than the usual bi-electronic way towards hydroxylic substrates.

Such an example is the oxidation of ascorbic acid, for which Dixon and co-workers [60] have given a mechanism involving mono-electronic steps only, contrary to those bi-electronic of type III given in previous studies [15, 36]. The conclusion was reached based on the fact that Mn(II) and I^- used to trap the Cr(IV) and Cr(V) intermediates respectively, had no influence either in the mechanism or the stoichiometry. It was confirmed by some theoretical studies [61, 62] using molecular orbital calculations. The rate-determining step is assumed to be the formation of ester intermediate.

Another case is the Oswal and Bakore interpretation of malonic acid oxidation by Cr(VI), either uncatalysed or catalysed by Mn(II) [63]. In this reaction the one-electron decomposition of the intermediate substrate-Cr(VI) complex, giving Cr(V) and free radical, is believed to be rate-determining. Cr(V) reacts further in a bi-electronic path.

A number of Cr(VI) oxidations of alcohols with oxalic acid and α-hydroxy-acids [64-67], as well as oxidations of polyfunctional organic compounds like several α-hydroxy-acids [68-70] or polyhydroxylic compounds like glycerol [71] have been found to proceed by an one-step rate-determining three-electron transfer, leading directly to Cr(III). The free radical formed in the process reduces mono-electronically another Cr(VI) molecule, forming Cr(V). The behaviour of Cr(V) is similar to the usual one of Cr(VI), leading to Cr(III) in a one-step bi-electron transfer.

The suggested mechanism is:

$$Cr(VI) + 2S \longrightarrow CrS_2 \longrightarrow Cr(III) + P + \dot{R} \qquad (10)$$

$$\dot{R} + Cr(VI) \longrightarrow Cr(V) + P \qquad \text{fast} \qquad (11)$$

$$Cr(V) + S \longrightarrow Cr(III) + P \qquad (12)$$

where S stands for substrate, P for product and R• for free radical.

It is believed that at large substrate concentrations, the rate laws second order in substrate (first order in each of the two different substrates in the case of co-oxidations, and first order in polyolic substrates) support the presumption of a one-step three-electron reduction of Cr(VI).

At low substrate concentrations, the reaction order in substrate is only half of the value found at high concentrations (one for one substrate and zero for the second one in co-oxidations). It shows that the process (10) may require two steps: a slow bi-electronic one giving Cr(IV), followed by a fast, mono-electronic one to give Cr(III) and R•. Therefore, the three-electronic mechanism is again reduced to a bi-electronic one of type III.

For the general case of bi-electronic mechanisms, and under the excess concentration of hydroxy-compound (which is the most common setting for experimental measurements), rate laws of the following form:

$$-\frac{d[Cr(VI)]}{dt} = \frac{a[ROH]}{1 + b[ROH]}[Cr(VI)]_t; \qquad (13)$$

$$k_{obs}^{redox} = \frac{a[ROH]}{1 + b[ROH]} \qquad (14)$$

prove themselves to be valid when the redox step is rate determining. A first-order dependence on Cr(VI) total concentration is shown, while the reaction order for the substrate can range between 0 and 1. Depending on the value of parameter b, the zero order is reached when the hydroxy-compound is taken in very large excess. However, under usual experimental conditions a first-order dependence on substrate concentration is also found. The fact is not surprising, Cr(VI) having a strong tendency to behave in a bi-electronic way and hydroxy compounds being well-known as bi-electronic substrates.

There are several situations where not the redox step, but the formation of the intermediate complex is rate determining. For such cases, the global rate law is much simpler:

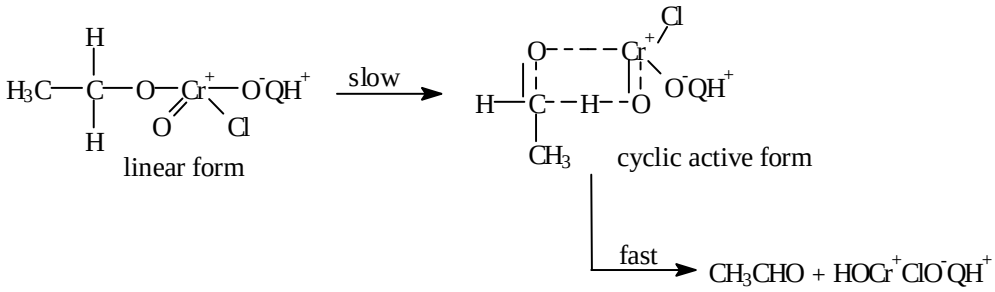
$$-\frac{d[Cr(VI)]}{dt} = k_1[ROH][Cr(VI)] \quad (15)$$

namely first order in both substrate and oxidant concentrations.

If the substrate is in excess, the observed first-order constant is of the form:

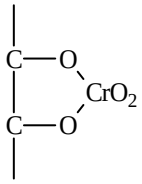
$$k_{obs} = k_1[ROH] \quad (16)$$

The process becomes more complex when the intermediate formation proceeds in more than one step. Such examples are the oxidations of primary alcohols by quinolinium chlorochromate [72], where the redox active form of the intermediate complex is not the linear one initially formed in the equilibrium reaction between ROH and Cr(VI), but the one subsequently formed in a slow, rate determining cyclization step. The cyclic intermediate undergoes a further fast decomposition yielding Cr(IV) and products.



(17)

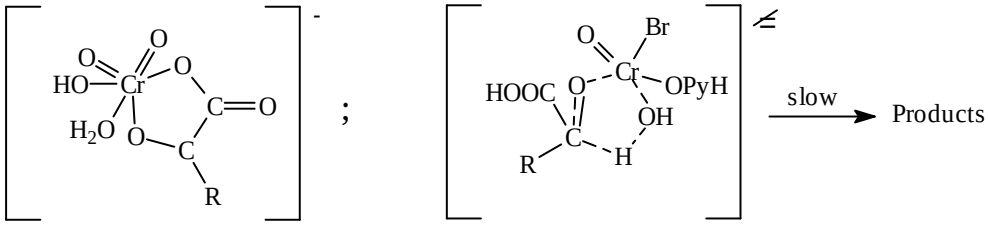
The cyclic intermediates are a common feature of the inner-sphere oxidation reactions of many hydroxy-compounds. Glycol oxidations proceed, for example, through condensed intermediate species of the form [73]:



In the case of α-hydroxy-acids, the cyclic intermediates formed can be either hexa- [56] or penta- coordinate [74]; in the first case the carboxylic –OH is involved, while in the second not.

Usually, as discussed, the redox decomposition of the intermediates is the slowest step of the mechanism.

Three-electron oxidations require similar complexes, but involving two substrate molecules [18].



(1) (2)

(1) the intermediate in aqueous media (hexacoordinate)

(2) the intermediate in non-aqueous media (DMSO) (pentacoordinate); the oxidant is pyridin bromochromate

Depending on the lifetime of Cr(V) intermediate in a given system, in certain cases substrate oxidation can proceed through two measurable steps, corresponding to Cr(VI) and Cr(V) reduction respectively. Haight and co-workers found such a situation for lactic acid oxidation [18] under excess of substrate conditions, in acidic medium ($HClO_4$). Cr(V) reduction follows analogous path ways as Cr(VI).

From the assumed mechanism:

$$\mathrm{Cr(VI)} \xrightarrow[k_6]{+\,H_2L} \mathrm{Cr(IV)} \xrightarrow[\text{fast}]{+\,H_2L\ +\,Cr(VI)} \mathrm{Cr(V)} \xrightarrow[k_5]{+\,H_2L} \mathrm{Cr(III)} + \mathrm{HPy} \qquad (18)$$

$$+\,Cr(III)$$
$$+\,HPy$$

composed rate laws are obtained:

$$-\frac{d[Cr(VI)]}{dt} = 2k_6[Cr(VI)] \qquad (19)$$

$$-\frac{d[Cr(V)]}{dt} = k_5[Cr(V)] - k_6[Cr(VI)] \qquad (20)$$

where: $$[Cr(V)] = \frac{k_6[Cr(VI)]_0}{2k_6 - k_5}(e^{-k_5 t} - e^{-2k_6 t}) \qquad (21)$$

Intermediate complexes involving Cr(V) of the similar type with those of Cr(VI) are formed in the process.

In all cases, hydroxy-compounds oxidations with Cr(VI) are subjected to catalysis. Metal ions can play the role of the catalyst in many cases, but the general situation is of acid-base catalysis.

In acidic media, where most of the studies were carried out, both intermediate formation and its decomposition could be hydrogen ion assisted. The rate laws show, therefore, observed rate constants consisting of a sum of zeroth, first and/or second order acid dependent terms:

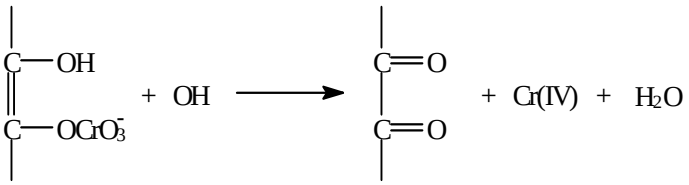
$$k_{obs} = k^0 + k^I[H^+] + k^{II}[H^+]^2 \quad (22)$$

For each given reaction system, one or another (alternatively more of them) of these terms prevails, depending on the pH value in the reaction mixture and on the nature of the substrate. Under strong acidic conditions, lactic [18, 38] and malic [38] acids exhibit two parallel paths, one first-order and the other one second-order in $[H^+]$. On the contrary, for lactic acid oxidation under weaker acidic conditions, Haight and all [18] found the zeroth-order and second-order in $[H^+]$ paths to be effective.

Ascorbic acid oxidation [36, 60] shows an acid dependence ranging between zeroth and first-order, under mild acidic conditions.

$$k_{obs}^{redox} = \frac{\alpha[ROH]}{1+\beta[ROH]} \quad (14')$$

Under this setting, the cyclic intermediate formation, which would require an extra hydrogen ion, does not take place, accordingly with the fact that second-order dependence in $[H^+]$ is not observed. Alternatively, the non-cyclic chromic ester will undergo a base-assisted two-equivalent electron transfer in the rate determining step:



(23)

Few situations were found in which the hydroxy compounds could be oxidised by Cr(VI) by outer-sphere mechanisms. Such ones were assumed for some α-hydroxy-acids (glycolic, lactic and mandelic acids) oxidations with pyridin chlorochromate in acetic acid medium [75] and in absence of catalysts. However, in Ru(III) catalysis, the reaction proceeds *via* an intermediate, showing an inner-sphere process. In the Cr(VI)-Ru-substrate complex, Cr(VI) is linked to Ru(III) by means of the chlorine atom, while between the catalyst and substrate a Ru-O bond is formed.

OXIDATION OF THIOLS AND THIO-ACIDS

The oxidation of thio-compounds yields disulphides, according to the fact that not the carbon atom bearing the –SH group, but the sulphur atom of the thiol function is oxidised.

The processes follow an inner-sphere mechanism as well, consisting of sequences of steps involving first an equilibrium path in which an 1:1 chromate: substrate intermediate complex of thioesteric type is formed (eq. 24) [16, 21-25, 29-34, 43, 76]:

$$HCrO_4^- + RSH \rightleftharpoons RSCrO_3^- + H_2O \qquad k_1, k_{-1}, K_1 \qquad (24)$$

This intermediate reacts by either a bimolecular two-electron transfer redox reaction involving a second substrate molecule and leading to Cr(IV) and disulphide formation (eq. 25):

$$RSCrO_3^- + RSH \longrightarrow Cr(IV) + RSSR \qquad k_2 \qquad (25)$$

or an internal unimolecular one-electron transfer giving Cr(V) and thiyl free radicals (eq. 26) which dimerize to disulphide (eq. 27):

$$RSCrO_3^- \longrightarrow Cr(V) + \dot{R}S \qquad k_3 \qquad (26)$$

$$2\dot{R}S \longrightarrow RSSR \qquad (27)$$

The Cr(IV) and Cr(V) species undergo further fast redox processes yielding Cr(III) products, as in the following sequences:

IV. $$Cr(IV) + RSH \longrightarrow Cr(III) + \dot{R}S \qquad (28)$$

$$2\dot{R}S \longrightarrow RSSR \qquad (27)$$

V. $$Cr(IV) + Cr(VI) \longrightarrow 2Cr(V) \qquad (29)$$

$$Cr(V) + 2RSH \longrightarrow Cr(III) + RSSR \qquad (30)$$

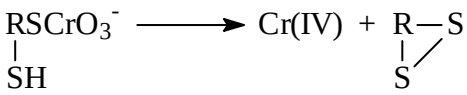
Cr(V) reaction with RSH (eq. 30) is not an elementary process. The behaviour of Cr(V) resembles that of Cr(VI), forming – by similar paths – thio-esters which subsequently also decompose to give Cr(IV) or Cr(III). The overall stoichiometry for all these cases was found 3 : 1 RSH : Cr(VI).

The reaction conditions play an important role on the mechanism. Thus, under the settings of excess concentration of substrate – as the case for most of the studies – the path (30) seems to be less effective, being ultimately dismissed.

Both alternatives described by equations 25 and 26 are of comparable importance on the general picture of thio-compound oxidations. The substrate structure is determining when choosing one or another reaction pathways. Thio-compounds like cysteine [15, 32] and some of its derivatives [15], mercaptoetanol [15], thioglicolate [15], thioglicolic acid [30], thiomalic acid [29], methionine [77] or glutathione [15, 25] where found to follow the route involving the bi-molecular redox process leading to Cr(IV), under both aqueous acidic or neutral-basic conditions. On the other hand, the reactions of other thiol substrates like benzenethiol and α-toluenethiol in acetic acid solutions [39] or unithiol in neutral medium [15] more likely undergo the unimolecular process to form Cr(V). For penicillamine in neutral-slight basic medium [25], both (25) and (26) paths seem to be effective to some extent.

A particular behaviour is found for those dithio-compounds able to form intramolecular S-S bond.

In these cases, another kind of unimolecular internal electron-transfer takes place, involving two electrons and leading to Cr(IV) and the intramolecular disulphide:



k_4 (31)

Such an example is the oxidation of dithiotreitol in neutral aqueous medium [15]. The overall stoichiometry changes to 1,5 : 1 R-$(SH)_2$: Cr(VI) for these situations.

Although all the papers dealing with the reactions of the type discussed present the bimolecular path as yielding disulphide and Cr(IV), there is an alternative path way, kinetically indistinguishable, in which Cr(V) and a disulphide radical is formed in an one-equivalent process:

$$RSCrO_3^- + RSH \longrightarrow Cr(V) + RS\therefore SR^- \qquad k_5 \qquad (32)$$

Disulphide radical, having a sulphur-sulphur three electron bond, with the third electron in an antibonding orbital, has been identified [78] and characterised for several cases. It was found to be far more stable than the thiyl radical. However, this higher stability allows other interpretations for its appearance.

In neutral or weak acidic solutions, where the thiol substrate could also exist, and therefore react, as deprotonated negative charged species RS^-, the equilibrium reaction between RS^- and thiyl free radicals $R^{\bullet}S$ takes place [17].

$$\overset{\bullet}{R}S + RS^- \rightleftharpoons RSS\overset{\bullet}{R}^- \qquad (33)$$

The thiyl radicals result from one-electron reductions of Cr(V) or Cr(IV) in reactions with other substrate molecules of RS^- form.

All these mechanisms were suggested in accordance with the rate laws.

The equations for both formation and disappearance of the complex can be written. Under excess of thio-compound, pseudo-first-order observed rate constants are dependent only on thiol substrate concentration, as deduced from rate expressions:

$$r_{obs}^{f} = k_1[RSH][Cr(VI)]_t \qquad (34)$$

$$k_{obs}^{f} = k_1[RSH] \qquad (35)$$

$$r_{obs}^{redox} = (k_2[RSH] + k_3)[RSCrO_3^-] = \frac{a[RSH]^2 + b[RSH]}{1 + c[RSH]}[Cr(VI)]_t \qquad (36)$$

$$k_{obs}^{redox} = \frac{a[RSH]^2 + b[RSH]}{1 + c[RSH]} \quad (37)$$

where a, b, c coefficients are certain combinations of the rate constants.

When acidic media are employed, both formation and decay of the thioester can show parallel hydrogen ion assisted path ways. Therefore:

$$k_i = k_i^0 + k_i^I[H^+]; \qquad i \in \{1,2,3\} \quad (38)$$

In most of the cases, the redox decomposition of the intermediate is rate determining.

General rate laws of the form:

$$-\frac{d[Cr(VI)]}{dt} = \frac{(a^0 + a^I[H^+])[RSH]^2 + (b^0 + b^I[H^+])[RSH]}{1 + c[RSH]}[Cr(VI)]_t \quad (39)$$

can be written in acidic media, while the terms first-order in $[H^+]$ can be neglected in neutral-basic media, giving:

$$-\frac{d[Cr(VI)]}{dt} = \frac{a^0[RSH]^2 + b^0[RSH]}{1 + c[RSH]}[Cr(VI)]_t \quad (40)$$

which is a particular case of the more general equation for acidic media.

Depending on the reaction mechanism – as discussed – the term of second or of first order in substrate – corresponding to the bimolecular or monomolecular step respectively – can prevail, leading to two limiting cases, when the secondary process is ruled out.

The ratio formation/decay of the intermediate is a function of the nature of thio-compound. Sometimes, formation is so rapid that stopped-flow technique is necessary to record it. In such situations, the complex formation can be assimilated with either a steady-state – as for cysteine, ethanethiol, thioglicolate, etc. [15] – or pre-equilibrium – like in the glutathione or unithiol oxidations by Cr(VI) [15].

In other cases, where both steps are of comparable speed (the ratio does not exceed the value of 10), a two-stage consecutive process is the theoretical model for approaching the reaction:

$$Cr(VI) \xrightarrow[k_f]{+\,RSH} complex\ Cr(VI):tiol \xrightarrow[k_{redox}]{+\,RSH} Products \quad (41)$$

Some situations were found where the intermediate formation is rate-determining, as being the slower step of the global mechanism.

$$-\frac{d[Cr(VI)]}{dt} = k_1[RSH][Cr(VI)] \quad (42)$$

Penicillamine, thiolactate, thiomalate, dithiothreitol and 2,3 dimercaptosuccinate oxidation in neutral media are such example [15].

DISCUSSIONS AND CONCLUSIONS

The reaction mechanisms for thio-compound oxidations with Cr(VI) show both similarities and differences when compared to those of the analogous hydroxy-compounds.

The fundamental difference between the oxidation reactions of the two classes of substances is – as already noted – that, while for hydroxy-compounds the carbon atom bearing the –OH functional group suffers the oxidation, the thio-compound oxidation takes place at the sulphur atom in the –SH functional group. As a consequence, the reaction products are also of different type.

On the other hand, unlike hydroxy-compounds, which are generally known as bi-equivalent reducing agents, the sulphur atom of thio-compounds provides one electron only. Thus, further consequences on the stoichiometry and reaction mechanism occur. It is known for a fact that the stoichiometric ratios for mono hydroxy-compounds oxidation are generally 1,5 : 1 R–OH : Cr(VI), while ratios of 3 : 1 R–SH : Cr(VI) are valid for oxidations of mono thio-compounds.

Referring to the reaction mechanisms, both classes of compounds undergo inner-sphere processes, *via* analogous intermediate complexes of esteric and thioesteric type respectively (eqs. 2, 24). No or very small difference in the absorption maxima position can be observed for the esteric type intermediates, while the thioesteric intermediates present in most of the cases maxima significantly shifted to the red region. Figure 1 shows the spectrum of Cr(VI)-glutathione mixture [79] in its time evolution, as compared to the spectrum of chromate ion in perchloric acid medium. The intermediate spectrum exhibits a maximum at 428 nm, shifted to the red compared with the $HCrO_4^-$ maximum at 350 nm, as recorded by us using a Jasco 530 spectrophotometer.

The intermediate is formed in an equilibrium step of substitution type; in a limited number of cases its formation is the rate-determining step. Still, for both hydroxy- and thio- compounds, its subsequent redox decomposition is more likely to be rate-determining. This can be done in several ways and here is where new differences appear.

The Cr(VI) preference for bi-electronic reductions combines with the bi-equivalent character of the hydroxy-compounds or the rather mono-equivalent one of thio-compounds. The matching tendency in the case of hydroxy-compounds results in a clear favouring of the bi-electronic route for these substrates. The two-electron donor being already bonded to Cr(VI), the process is a monomolecular internal one, leading to Cr(IV).

In thio-compound oxidations, the bi-electronic route is still important, but requires a second substrate molecule (or at least a second substrate reaction centre – sulphur atom of a –SH group – therefore being a bimolecular

one. For not too bulky thiol substrates, Cr(VI) species and/or solvent molecules, this path way is very likely, taking into account that thiols have good co-ordination properties and therefore easily bound to Cr(VI) centre.

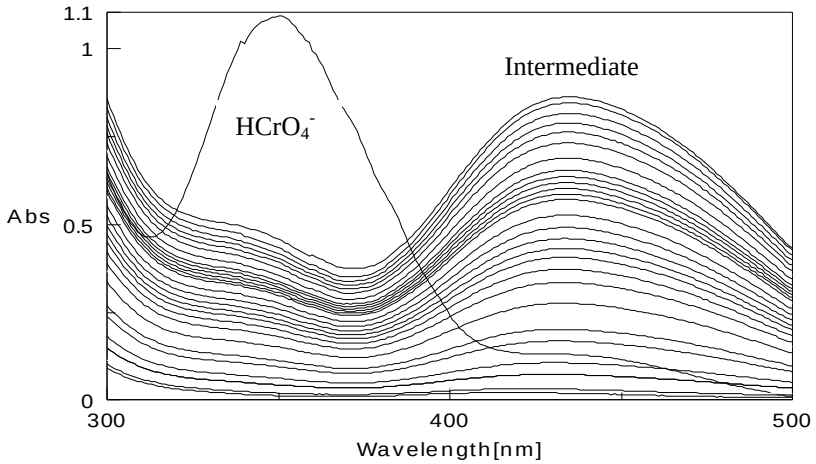


Figure 1. Glutathione : Cr(VI) intermediate complex time-delay spectra in aqueous acidic medium ([GSH]=3.33 x 10^{-3}, [$HCrO_4^-$]=6.67 x 10^{-4}, [$HClO_4$]=3.67 x 10^{-2})

Both thiol substrate mono-electronic character (tendency to form free radicals) and steric impediments contribute to offer an alternate one-electron route for Cr(VI) reduction – this being the unimolecular step in the case under discussion – and leading to Cr(V) formation. The route is of significant importance, being the only available one in some cases or competing with the bi-electronic one in others.

On the contrary, in the case of hydroxy-compounds the mono-electronic reduction of Cr(VI) only occasionally is a viable alternative. A particular manner of combining a two-electron and one-electron redox pathways is through a concerted one-step action, the overall process being assimilated with a three-electron transfer. These situations are also quite rare. For the thio-compound oxidations, three-equivalent processes have not been reported.

The fate of Cr(IV) or Cr(V) species resulted in the above processes is quite similar for both classes. Cr(V) tends to behave bi-electronically, like Cr(VI), yielding Cr(III). Cr(IV) has a number of choices, approximately the same ones regardless the substrate type (alcohol or thiol).

Another common feature of the systems under discussion is the involvement of free radical intermediates.

The rate laws elaborated on the basis of reaction mechanisms are consistent with the above-presented comments. Acidity of the medium strongly influences both classes of oxidations. Still, second-order dependencies, which are likely for hydroxy-compounds due to their need of a second hydrogen ion in the process of the cyclic intermediate formation, were rarely reported for thiocompound oxidation.

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