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Oxidation of Hydrazine by Cr(VI) Oxide. Kinetic and Mechanistic Studies in the Presence of Complexing Agents

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The kinetics of the Cr(VI) oxidation of hydrazine sulphate have been investigated both in the presence and absence of aqueous sulphuric acid. At low concentrations of hydrazine sulphate ($< 0.02\,M$), the reaction exhibits a total second order dependence being first with respect to the gross [Cr(VI)] and also first with respect to [hydrazine sulphate]. But a plot of $1/k_1$ versus 1/[substrate] is linear with an intercept when $[N_2H_4 \cdot H_2SO_4]$ is $> 0.02\,M$ pointing to the formation of an equilibrium complex between the reactants prior to the main reaction. The effect of added H_2SO_4, sulphate, bisulphate and chloride ions has been analysed. A stoichiometry of [Cr(VI)]: $[N_2H_4]$ = 4:3 and the absence of ammonia in the reaction product (nitrogen being the only product) indicate that Cr(VI) behaves as a two-electron oxidant. Effect of added EDTA on this system is quite interesting and has been investigated thoroughly. A study of the UV spectrum of Cr(VI) solution in the presence of EDTA indicates the formation of mono and binuclear complexes of Cr(VI) with EDTA. Suitable mechanisms have been proposed to account for these observations.

Introduction

The kinetics of the oxidation of hydrazine sulphate ($N_2H_4 \cdot H_2SO_4$) by various metal ions and metal oxides have been investigated from time to time[1,2]. This reductant has generally been used to distinguish between one-electron and two-electron oxidants on the basis of the products obtained[3–6]. Thus two-electron oxidants like Tl(III), Pb(IV) and Hg(II) give with hydrazine, nitrogen as the product and one electron oxidants like Ag(I), Co(III) and Ce(IV) give nitrogen and ammonia as products. In view of the fact that Cr(VI) undergoes a three-electron change in its reduction to Cr(III) and the stages of this reaction are not well elucidated, we have now carried out a thorough investigation of the kinetics of oxidation of hydrazine sulphate by Cr(VI) oxide. A preliminary report of this work has been published by us recently[7]. While this work was in progress, similar pieces of research work have been published[8–12]. While some of the results of the present work particularly on the stoichiometry, kinetics and mechanism of the oxidation in the absence of any added ligand are in complete agreement with Haights' recent work[8], our results on the effect of added EDTA on this redox reaction are at variance with the results of Beck and Durham.

Experimental

All the compounds like hydrazine sulphate, CrO_3, Na_2SO_4, $NaHSO_4$, disodium salt of EDTA and NaCl were of extra pure variety (BDH–AR) and were used without further purification. The oxidation rate was followed as in our earlier investigations from these laboratories[13] by following the disappearance of Cr(VI) iodometrically. Kinetic experiments were carried out both in the presence and absence of sulphuric acid. The UV measurements were made with a Beckmann DU2 spectrophotometer.

Nitrogen was identified as the only product of oxidation (no ammonia being detected), and the reaction exhibits a stoichiometry of Cr(VI):N_2H_4 = 4:3.

Results

Dependence on [Cr(VI)]

The reaction exhibits a first order dependence on the gross Cr(VI) concentration as evidenced by a linear plot of log(b–x) *versus* time up to 75% conversion of Cr(VI) (Figure 1), and also by the constant value of k_1 over the concentration range of 0.002 to 0.005 *M* of Cr(VI) (Table I).

Dependence on [Hydrazine Sulphate]

The dependence of the reaction rate on hydrazine sulphate has been investigated both in the presence and absence of sulphuric acid. The pseudo unimolec-

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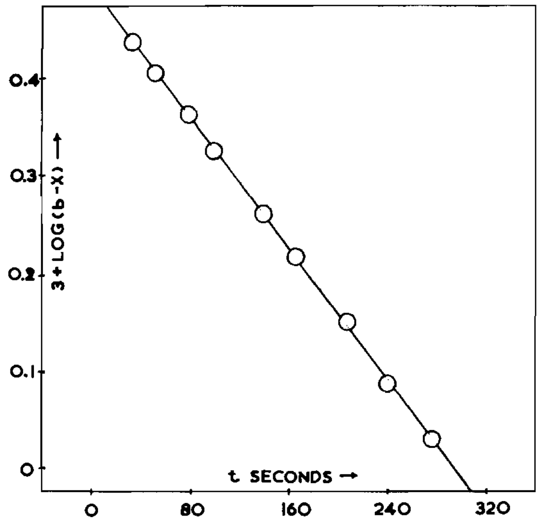


Figure 1. Kinetics of Cr(VI)–Hydrazine Sulphate system. First order dependence on the gross [Cr(VI)] at 25° C. [Hydrazine Sulphate] : 0.01466*M*, [Cr(VI)] : 0.003131*M*.

TABLE I. Cr(VI) Oxidation of Hydrazine. Dependence on [Cr(VI)]. [Hydrazine Sulphate] : 0.006138*M*, [H_2SO_4] : 0.01*M*. Temperature 25° C.

[Cr(VI)] *M*	$k_2 \times 10^1$ l $mol^{-1} sec^{-1}$
0.002093	8.88
0.003035	8.54
0.004186	8.86
0.005232	8.94

TABLE II. Hydrazine – Cr(VI) Reaction. Dependence on [$N_2H_4 \cdot H_2SO_4$]. [Cr(VI)] : 0.003*M*, Temperature 25° C.

[$N_2H_4 \cdot H_2SO_4$] *M*	[H_2SO_4] *M*	$k_1 \times 10^3$ sec^{-1}	$k_2 \times 10^1$ l $mol^{-1}sec^{-1}$
0.003620	...	...	2.48
0.007330	...	1.90	2.59
0.010995	...	2.85	2.59
0.014660	...	3.86	2.63
0.003591	0.01	...	8.69
0.004093	0.01	...	8.57
0.005388	0.01	...	8.75
0.006138	0.01	...	8.54
0.02199	...	5.66	...
0.03334	...	7.69	...
0.04548	...	9.91	...

ular constants obtained in the presence of excess reductant are directly proportional to [hydrazine sulphate] indicating that the order with respect to substrate is one (Table II). The reaction is thus of total second order. This is further proved by a plot of $\log k_1$ *versus* log[hydrazine sulphate] which is linear in the concentration range of 0.007 to 0.015*M* with a slope of unity (Figure 2A). However, at high [$N_2H_4 \cdot H_2SO_4$] (> 0.02*M*), the order is lower than one (= 0.77; Figure 2B, Table II). A plot of $1/k_1$ *versus* 1/[hydrazine sulphate], under these conditions, is linear with an intercept pointing to the formation of an equilibrium complex between Cr(VI) and the substrate prior to the main reaction (Figure 3). From the slope and intercept of this line (intercept = 32.81, slope = 3.171, Correlation coefficient = 0.999), the equilibrium constant for the formation of the complex between N_2H_4 and Cr(VI) oxide has been evaluated and is equal to 10.35 l mol^{-1} at 25° C. It is interesting to compare that Haight *et al.*, have obtained a value of K = 3.9 l mol^{-1} at 25° C for a similar complex.

Dependence on Acidity

The reaction is considerably influenced by variation in the acidity of the medium even over a small range (0.01*M*–0.5*M*) of sulphuric acid – a region where it exhibits an order very nearly unity (Figure 4). Beyond this concentration (i.e., 0.5*M* of H_2SO_4), however, the reaction is retarded with increasing concentration of H_2SO_4. Very large concentrations of H_2SO_4 (5.0*M* to 6.0*M*) again lead to an increase in reaction rate (Table III).

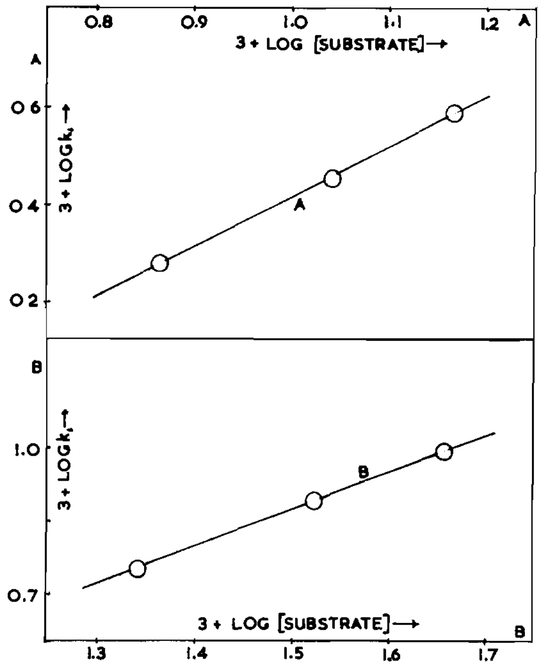


Figure 2. Cr(VI)–Hydrazine Sulphate system. Plot of $\log k_1$ *versus* log[Hydrazine Sulphate] at 25° C.
A : [substrate] < 0.02*M*; slope = 1.0;
B : [substrate] > 0.02*M*; slope = 0.77.

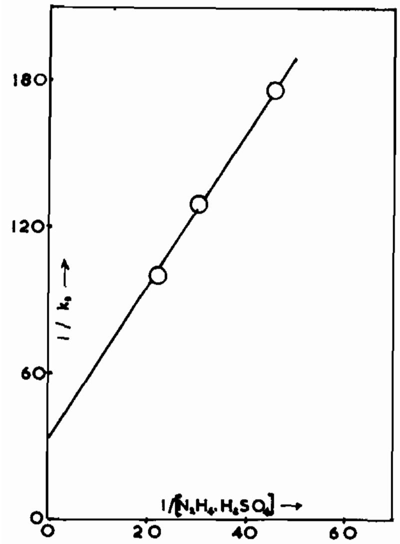


Figure 3. Formation of an equilibrium complex between Cr (VI) and Hydrazine Sulphate at 25° C. Plot of $1/k_1$ *versus* 1/[hydrazine sulphate] at [substrate] $> 0.02M$; intercept = 32.81; correlation coefficient 0.999.

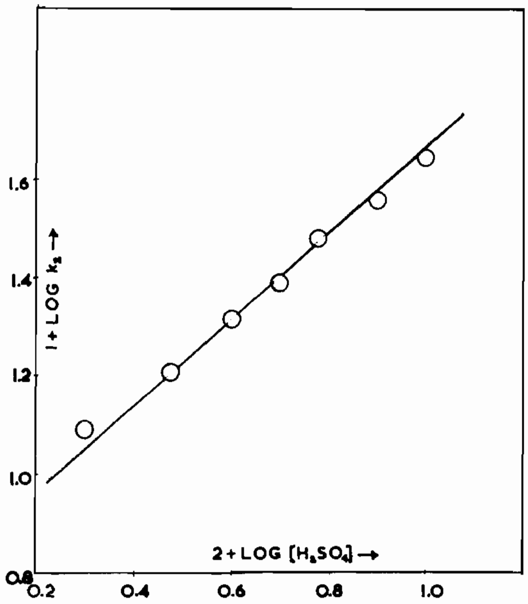


Figure 4. Cr(VI)–Hydrazine Sulphate system. Dependence on acidity at 25° C. [Hydrazine Sulphate] : $0.003676M$, [Cr (VI)] : $0.0031M$; slope = 0.9.

TABLE III. Effect of Acidity on the Rate of Cr(VI) Oxidation of Hydrazine. [Cr(VI)] : $0.0031M$, $[N_2H_4 \cdot H_2SO_4]$: $0.003676M$, Temp. 25° C.

$[H_2SO_4]$ *M*	$k_2 \times 10^1$ l $mol^{-1} sec^{-1}$	$[H_2SO_4]$ *M*	$k_2 \times 10^1$ l $mol^{-1} sec^{-1}$
...	2.48	0.10	44.6
0.01	8.69	0.50	98.8
0.02	12.4	1.00	89.9
0.03	16.3	2.00	70.6
0.04	20.9	3.00	61.1
0.05	24.8	4.00	57.3
0.06	30.7	5.00	72.0
0.08	36.5	6.00	201

TABLE IV. Influence of Added Salts on the Cr(VI)–N_2H_4 System. $[N_2H_4 \cdot H_2SO_4]$: $0.0037M$, $[H_2SO_4]$: $0.01M$, [Cr (VI)] : $0.003M$, Temperature 25° C.

[salt] *M*	$k_2 \times 10^1$ l $mol^{-1} sec^{-1}$		
	SO_4^{2-}	HSO_4^-	Cl^-
...	8.69	8.69	8.69
0.1	3.95	...	6.29
0.2	...	26.5	...
0.3	2.00	...	5.08
0.5	1.54	31.4	5.20
1.0	1.12	28.7	5.20
1.5	0.890	...	...
2.0	0.890	28.5	...

Effect of Added Sulphate, Bisulphate and Chloride Ions

Increasing concentrations of sodium sulphate decrease the rate of oxidation while the trend is the opposite with added bisulphate (Table IV). This can be attributed to the following equilibrium:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad (1)$$

The effect of the above equilibrium will be such that with increasing concentrations of bisulphate ion, the acidity increases with a subsequent increase in rate. However, as the sulphate ions have a retarding effect on the reaction (presumably due to the formation of the less reactive sulphate complexes of Cr(VI)), the increase in rate is much less pronounced.

Addition of NaCl produces a definite drop in rate in the oxidation of hydrazine sulphate. This is presumably an outcome of the formation of the less reactive chlorochromate ($ClCrO_3^-$) species.

Effect of Added Disodium Salt of Ethylenediaminetetraacetic Acid (EDTA)

The effect of added EDTA (disodium salt) on the rate of oxidation of hydrazine sulphate is quite interesting. The experimental observations are recorded in Table V. The data reveal that even a small quantity of this complexing agent (as low as $0.5 \times 10^{-3} M$ as against an initial Cr(VI) concentration of $3 \times 10^{-3} M$)

TABLE V. Effect of Added EDTA (Disodium Salt) on Cr(VI) Oxidations. [Cr(VI)] : 0.003*M*, Solvent : 100% H_2O.

[EDTA] × 10^3 *M*	$k_2 \times 10^1$ l $mol^{-1}sec^{-1}$	$k_2 \times 10^4$ l $mol^{-1}sec^{-1}$	
	Hydrazine[a]	Mandelic acid[b]	Lactic acid[b]
...	2.48	41.1	6.06
0.5	4.74	49.3	9.31
1.0	6.37	...	...
1.2	11.2	...	...
1.3	13.9	...	...
1.4	16.6	...	...
1.5	...	62.0	10.3
1.8	12.2	...	...
2.0	11.1	55.6	9.10
2.4	12.4	...	...
2.5	...	57.8	9.54
2.8	13.8	...	...
3.0	...	60.4	10.0
3.2	12.0	...	...
3.6	10.2	...	...
4.0	8.05	56.0	8.56
6.0	7.59	47.5	8.16
8.0	5.86	...	...
10.0	5.03	35.0	7.61
20.0	3.60	...	...

[a] At 25° C; [$N_2H_4 \cdot H_2SO_4$] : 0.003630*M*. [b] At 55° C; [Substrate] : 0.015*M*.

gives a two-fold rate benefit. The reaction rate reaches a maximum when the ratio of [EDTA] : [Cr(VI)] = 1 : 2. Once this ratio of concentrations has been reached, the rate drops and once again reaches a second maximum at a 1 : 1 ratio of EDTA to Cr(VI). Beyond this ratio, no such maximum limits are any longer observed. These results are at variance with some of the studies of Durham and Beck on the role of EDTA in the reduction of Cr(VI) by hydrazine[9]. While these workers also observed that, in the presence of the ligand EDTA, the rates of oxidation of hydrazine, hydroxylamine and nitrous acid by Cr(VI) are increased, these increases were monotonous with no detectable maximum in the rate enhancement.

The kinetic evidence detailed above for the formation of two complexes between Cr(VI) and EDTA is further substantiated by UV spectral studies. A plot of the UV absorption maxima at 350 nm against the concentration of EDTA (Figure 5) confirms the formation of such Cr(VI)–EDTA complexes (binuclear and mononuclear) at [EDTA] to [Cr(VI)] ratios of 1 : 2 and 1 : 1. It must also be noted that under similar conditions of concentration and pH, the rate of oxidation of EDTA by Cr(VI) is negligbly small compared to the reaction with hydrazine. Also the inorganic end product is not the normal aquo-chromium(III) but the purple EDTA–Cr(III) species.

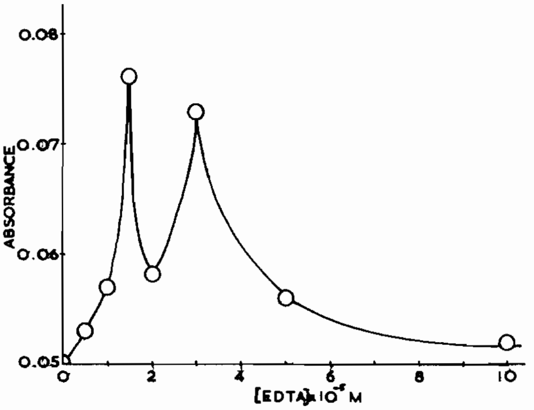


Figure 5. Cr(VI)–EDTA disodium salt. Plot of UV absorbance maximum at 350 nm against [EDTA disodium salt]. [Cr(VI)] : 3.0 × 10^{-5}*M*.

In order to find whether this were a general phenomenon in all Cr(VI) oxidations, experiments were carried out using lactic and mandelic acids instead of hydrazine sulphate. It is interesting to note that for these substrates, the same type of behaviour prevails in aqueous medium (*i.e.*, two upper limits, at 1 : 2 and 1 : 1 ratios of EDTA to Cr(VI); Table V). But in acetic acid–water mixtures, with mandelic acid as the substrate, the reaction rate increases monotonously with increasing [EDTA] without reaching a maximum limit (Table VI). Similar monotonous rate accelerations have been observed with added complexing agents like α,α'-Dipyridyl and *o*-phenanthroline in the Cr(VI) oxidations of lactic acid and malic acid in HOAc–H_2O media[14].

Temperature Dependence and Reaction Rate

The temperature dependence of the rate of the reaction has been studied in the temperature range 25°–35° C. The rate data and the activation parameters derived therefrom (from plots of logk_2 *versus* 1/T) are collected in Table VII.

TABLE VI. Oxidation of Mandelic Acid by Cr(VI) in Aqueous Acetic Acid.
Effect of Added EDTA (Disodium Salt).
[Mandelic acid]: 0.01834*M*, [Cr(VI)]: 0.003*M*, [NaOAc]: 0.2*M*, Temperature: 55° C, Solvent: 40% HOAc (v/v).

[EDTA] × 10^3 *M*	$k_2 \times 10^3$ l $mol^{-1}sec^{-1}$	[EDTA] × 10^3 *M*	$k_2 \times 10^3$ l $mol^{-1}sec^{-1}$
...	4.03	4.00	6.91
0.5	4.52	5.00	7.23
1.0	5.02	10.0	8.16
1.5	5.50	15.0	9.29
2.0	5.82	20.0	10.2
2.5	6.13	50.0	14.2
3.0	6.42	70.0	21.1

TABLE VII. Temperature Dependence and Activation Data for the Oxidation of Cr(VI) with Hydrazine. $[N_2H_4 \cdot H_2SO_4]$: 0.0037*M*, [Cr(VI)]: 0.003*M*.

$[H_2SO_4]$ *M*	$k_2 \times 10^1$ l mol^{-1}sec^{-1} 25° C	30° C	35° C	ΔE_a[a]	$\Delta H^{\ddagger a}$	logPZ at 25° C	$\Delta S^{\ddagger b}$
...	2.48	3.31	4.36	9.50	8.91	6.36	–29.5
0.01	8.69	11.9	15.1	9.20	8.61	6.68	–28.0

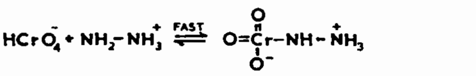
[a] Kcal/mol. [b] cal/deg/mol.

Discussion

The rate-law for the oxidation of hydrazine sulphate by Cr(VI) is of the form

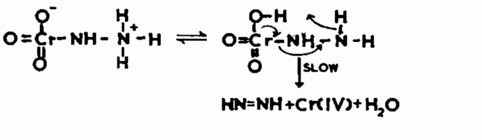
$$-\frac{d[Cr(VI)]}{dt} = k_2\,[N_2H_4 \cdot H_2SO_4][Cr(VI)][H^+] \tag{2}$$

in the presence of sulphuric acid and the last term is absent for the reactions carried out in the absence of added acid. However, there is a deviation from first order dependence on [Hydrazine sulphate] at higher concentrations where the formation of an equilibrium complex can be inferred from the double reciprocal plot of Figure 3. Even at low concentrations an equilibrium complex might be involved, but its equilibrium constant would be low. According to Hintz and Johnson[15], this would lead to second order kinetics. Recently Jijee and Santappa[2] have observed a similar behaviour in the oxidation of hydrazine sulphate by Cobalt(III). The product in the present instance is exclusively nitrogen (no ammonia being detected) indicating that Cr(VI) behaves essentially as a two-electron oxidant. A mechanism can be postulated to explain the above rate law along lines similar to alcohol oxidation. It may be assumed that there is a rapid equilibrium between the Cr(VI) species and the reductant hydrazine, with the elimination of water to form a condensation product in which the chromium remains in the hexavalent state.


(3)

$$HCrO_4^- + NH_2{-}\overset{+}{N}H_3 \overset{FAST}{\rightleftharpoons} O{=}\underset{O^-}{\overset{O}{\overset{\parallel}{Cr}}}{-}NH{-}\overset{+}{N}H_3 \tag{3}$$

The next step is probably a slow internal reduction–oxidation step to produce Cr(IV).



(4)

The intermediately formed Cr(IV) may be converted to Cr(III) by the following reaction scheme for a two-electron transfer (since nitrogen is the product and free-raidcals do not seem to be involved)

$$Cr(VI) + Cr(IV) \rightleftharpoons 2\,Cr(V) \tag{5}$$

$$Cr(V) + N_2H_2 \rightarrow Cr(III) + N_2 \tag{6}$$

The following complete scheme will be in accord with the experimentally realised stoichiometry of Cr(VI) : N_2H_4 = 4 : 3.

$$2\,Cr(VI) + 2\,N_2H_4 \xrightarrow{\text{2 stages}} 2\,Cr(IV) + 2\,N_2H_2 +.4\,H^+ \tag{7}$$

$$2\,Cr(IV) + 2\,Cr(VI) \rightleftharpoons 4\,Cr(V) \tag{8}$$

$$Cr(V) + N_2H_4 \rightarrow Cr(III) + N_2H_2 + 2\,H^+ \tag{9}$$

$$3\,Cr(V) + 3\,N_2H_2 \rightarrow 3\,Cr(III) + 3\,N_2 + 6\,H^+ \tag{10}$$

$$4\,Cr(VI) + 3\,N_2H_4 \rightarrow 4\,Cr(III) + 3\,N_2 + 12\,H^+ \tag{11}$$

The final product is the hexa-aquochromium(III). The above formulation is quite similar to Haights' proposal.

When the kinetics of the redox reaction in the presence of EDTA are examined, it is found that there is a definite rate acceleration with added EDTA. This means that EDTA must be involved in the rate-determining step or in a reaction prior to this. Beck and Bardi[9, 16] indicated the possibility of the formation of a binuclear complex between Cr(VI) and EDTA in the oxidation of hydrazine by Cr(VI) although no spectral proof was adduced. Assuming that the rate-determining step is the reduction of Cr(VI) to Cr(IV), it is inferred that the added EDTA might take part in a reaction with Cr(VI). This can only be explained by assuming the formation of a ternary complex involving Cr(VI), hydrazine and EDTA. Such complexes involving EDTA and metal ions are known to be formed. In the reactions of rare earth ions with 2,3-dihydroxynaphthalene and EDTA, spectral evidences reveal that 1 : 1 : 1 complexes of the type, Ln–DN–EDTA (Ln = Lanthanide ion, DN = 2,3-dihydroxynaphthalene) are formed with the stability increasing from Ln = La to Ln = Lu, with an inflection point at the Gadolinium complex[17].

It is seen that with increasing EDTA concentration, the rate reaches a maximum at a Cr(VI) : EDTA ratio 2:1. After this point, the rate curve exhibits a downward trend with increasing concentration of EDTA, but a second maximum is discernible at a Cr(VI) : EDTA ratio of 1:1. This suggests that two reasonably stable complexes are formed containing Cr(VI) and EDTA in the ratios 2:1 and 1:1 respectively and of course, hydrazine too. Just what form the ternary complexes take is at present purely a matter of conjecture. Further Cr(VI) does form a condensation product with acetic acid.

$$HCrO_4^- + CH_3COOH \rightleftharpoons CH_3COOCrO_3^- + H_2O \qquad (12)$$

It is possible for an EDTA molecule, behaving as a monobasic or as a dibasic acid, to condense with a free hydroxyl group in the Cr(VI) moiety to form a complex. A study of the UV spectrum of Cr(VI) solutions in the presence of EDTA also seems to indicate the formation of two such complexes (Figure 5). Thus, there does seem to be an evidence for the formation of a Cr(VI)–EDTA complex which can condense with a molecule of hydrazine to form a ternary complex. The EDTA could still remain coordinated to the Cr(IV) after the internal redox reaction, and so lead to the final product EDTA–Cr(III) complex, purple in colour. The role of EDTA in the ternary complexes might be to decrease the electron density on the Cr(VI) atom and hence to accelerate the redox process.

On the basis of the foregoing analysis the following mechanism could be proposed for the oxidation of hydrazine by Cr(VI) in the presence of EDTA.

$$2\,\mathrm{Cr(VI)} + \mathrm{EDTA} \rightleftharpoons \underset{\text{binuclear complex}}{[2\,\mathrm{Cr(VI)}\cdot\mathrm{EDTA}]} \qquad (13)$$

$$[2\,\mathrm{Cr(VI)}\cdot\mathrm{EDTA}] + \mathrm{EDTA} \rightleftharpoons \underset{\text{mononuclear complex}}{2\,[\mathrm{Cr(VI)}\cdot\mathrm{EDTA}]} \qquad (14)$$

$$[\mathrm{Cr(VI)}\cdot\mathrm{EDTA}] + \mathrm{Hydrazine} \rightleftharpoons \underset{\text{ternary complex}}{[\mathrm{Cr(VI)}\cdot\mathrm{Hydrazine}\cdot\mathrm{EDTA}]}$$

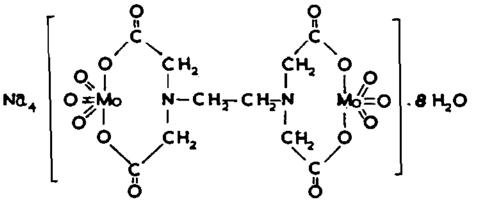
$$\downarrow \text{slow} \qquad (15)$$

$$[\mathrm{Cr(IV)}\cdot\mathrm{EDTA}] + N_2H_2$$

$$[\mathrm{Cr(III)}\cdot\mathrm{EDTA}] + N_2 \xleftarrow[\text{several steps}]{\text{fast}}$$

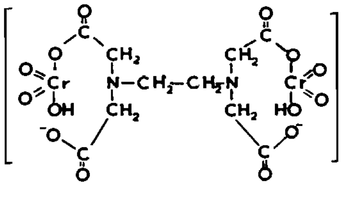
The final products Cr(III)–EDTA and N_2 are presumably formed via several steps similar to 8–11.

There also seems to be a justification for the above assumption on the formation of Cr(VI)–EDTA complexes; for, in the case of Mo(VI) of similar structure, complex formation with EDTA was observed by Pecsok and Sawyer[18]. These authors succeeded in preparing in solid form a complex characterised with the following structure:

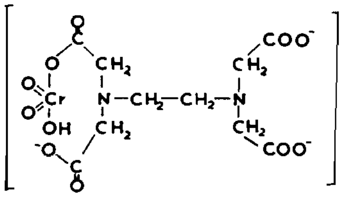


Mo(VI)–EDTA Complex

On an analogy, the Cr(VI)–EDTA complexes proposed could be formulated as follows:



Cr(VI)–EDTA binuclear complex



Cr(VI)–EDTA mononuclear complex

Also similar multicomponent complexes between Mo(VI) and hydroxylamine are known[19]. It has been established that while there is no reaction between NH_2OH and Mo(VI) in acidic media, the addition of complexing agents like sulphochlorophenol-S and sulphonitrophenol-K to this system leads to the formation of a three component complex in which Molybdenum is in the hexavalent state[17]. Elaborate potentiometric, titrimetric and spectrometric studies have been conducted on these systems. The molar ratio Mo:Ligand: NH_2OH in the three component complex has been found to be 1:1:1 for monofunctional and 2:1:2 for the bifunctional ligands. It is pertinent to point out here that thc UV spectral studies on these systems have shown two peaks at Mo(VI):Ligand ratios of 1:1 and 2:1 in the absorbance curve, corresponding to the mononuclear and binuclear complexes of Mo(VI) with the ligands. This, we feel, lends support to our mechanisms regarding a similar redox system and the Cr(VI)–EDTA complexes.

It is also interesting to observe that this type of double inflection on the rate curve is observed with increasing [EDTA] in the Cr(VI) oxidation of mandelic acid and lactic acid in aqueous medium (Table V). But when these reactions are carried out in 40%HOAc–60%H_2O mixture as the solvent, this behaviour is no longer evident; increasing concentrations of EDTA no doubt increases the reaction rate but only monotonously (Table VI). It would appear likely that, when these reactions are carried out in aqueous acetic acid, an outer sphere ternary complex is formed and that the Cr(VI) is reduced directly to Cr(III) without the substitution of EDTA into the inner sphere of chromium. Although a direct EDTA–Cr bond would not be formed, the EDTA could affect the electronic configuration and so accelerate the redox reaction.

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