

THE CHROMIC ACID OXIDATION OF OXALIC ACID

EVIDENCE OF CHROMIUM(IV) OXIDATION

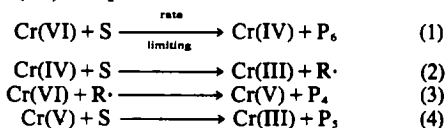
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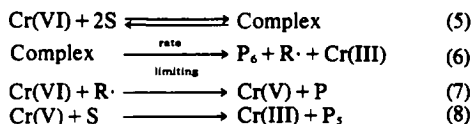
Abstract—In the chromic acid oxidation of oxalic acid in the range where the reaction is first order in the substrate, oxalic acid is very reactive toward chromium(IV) and rather unreactive toward chromium(V). A mechanism analogous to that of the chromic acid oxidation of alcohols and aldehydes is proposed for the first order kinetic term.

The mechanism of chromic acid oxidations of alcohols^{1,4} and aldehydes⁵ (Scheme 1)† consists of a rate limiting two-electron oxidation of a substrate molecule by Cr(VI) followed by a one-electron oxidation of a second molecule of the substrate by the Cr(IV) species formed in reaction 1. All available information indicates that Cr(IV) is a very strong oxidant which will react very rapidly with any available reducing agent. This conclusion is based both on kinetic studies^{1,5} and on the high value of the oxidation potential estimated for the Cr(IV)–Cr(III) couple.^{2,6}



SCHEME 1

If a relatively stable complex between Cr(VI) and the substrate can be formed, then another mechanism (Scheme 2) can take place⁷ in which the formation of the highly reactive Cr(IV) intermediate is avoided completely.‡



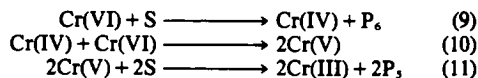
SCHEME 2

†P₆, P₃, and P₂ in this and following reaction schemes indicates oxidation products resulting from the initial interaction of the substrate with Cr(VI), Cr(V), and Cr(IV), resp.

‡Two different substrates instead of a single one may be included in the formation of the initial complex and in subsequent oxidation.⁸

§Wetton and Higginson⁶ estimate that the oxidation reduction potential for the couple Cr(IV)–Cr(III) is +1.8V leading to a standard free-energy change of not less than +20 Kcal/mol for reaction 10. The estimate of Csanyi¹⁰ is still considerably higher (+2.10V) leading to a value of 4×10^{-14} for the equilibrium constant of reaction 10.²

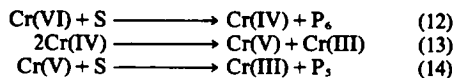
Two other types of reaction mechanisms have been proposed for chromic acid oxidation of substrates undergoing two-electron oxidations by Cr(VI). Scheme 3 gives the mechanism which until recently has been widely accepted for the oxidations of alcohols and two-electron reductants in general.⁹ The possibility that any oxidation could follow this mechanism has been questioned because the oxidation of Cr(IV) by Cr(VI) is thermodynamically unfavorable.§ In fact, there is growing evidence that the reverse of reaction 10, the disproportionation of Cr(V) into Cr(IV) and Cr(VI) plays an important part in chromic acid oxidation at low acidities.^{3,11} Nevertheless, a mechanism based on Scheme 3 was proposed again quite recently for the chromic acid oxidations of phenylphosphonous acid,¹² hydrazine,¹³ and uranium(IV).¹⁴



SCHEME 3

Rather strong arguments in support of the mechanism were presented in the last two cases and Espenson¹⁴ questioned the assumptions used to estimate the high positive value for the free energy of the oxidation of Cr(IV) by Cr(VI) (reaction 10).

Another interesting mechanism was recently proposed by Haight¹³ and applied to the chromic acid oxidation of oxalic acid (Scheme 4).



SCHEME 4

No objections to this mechanism can be raised on thermodynamic grounds: the disproportionation of Cr(IV) according to reaction 13 should be facile and essentially irreversible; an equilibrium constant of 7.6×10^{12} for the reaction can be estimated from

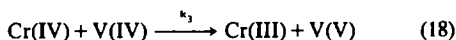
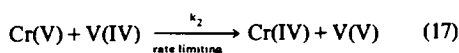
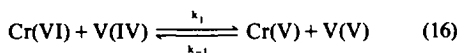
oxidation potentials.* However, a rather serious objection to this mechanism is that it requires an accumulation of the Cr(IV) intermediate in high enough concentrations to make its second order disproportionation possible. This could happen only if reaction 2, the reduction of Cr(IV) by the substrate were quite slow. Hence mechanism IV requires a substrate which is unreactive towards Cr(IV). The suggestion that this mechanism could be operative in the chromic acid oxidation of oxalic acid¹³ makes it desirable to test the reactivity of this substrate towards Cr(IV).

In a recently completed study of the mechanism of the chromic acid oxidation of oxalic acid⁷ we have shown that the oxidation proceeds by two mechanisms characterized by a first order and second order term in oxalic acid. (Eq 15).⁷

$$v = [\text{Cr}_T][\text{OxH}_2] \left(k_1 h_0 + \frac{kK_1 K_{II} K_a^{\text{OxH}_2} [\text{OxH}_2]}{1 + h_0/K_a^{\text{H}_2\text{CrO}_4} + K_1 [\text{OxH}_2] h_0 + K_1 K'_{II} K_a^{\text{OxH}_2} [\text{OxH}_2]^2 / h_0} \right) \quad (15)$$

We were able to demonstrate that the reaction leading to the second kinetic term in Eq 15 follows Scheme 2 and therefore does not involve the formation of a Cr(IV) intermediate. However, Cr(IV) must be formed in the process which is responsible for the kinetic term which is first order in oxalic acid and the fate of this intermediate must be understood before a full description of the mechanism of the chromic acid oxidation of oxalic acid can be given.

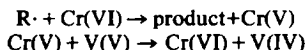
The approach used in this study was developed previously^{2a} and consists in the examination of the effect of an organic compound on reaction rates and yields in the chromic acid oxidation of V(IV). The Cr(VI) oxidation of V(IV) proceeds by the mechanism given in Scheme 5.



SCHEME 5

*Based on the oxidation reduction potentials of +1.34 for the Cr(V)–Cr(IV) couple and at +2.10V for Cr(IV)–Cr(III).^{2,10}

†Or:



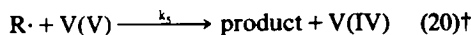
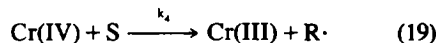
These two reactions are equivalent to Eq 20. The second step is the reverse of the fast equilibrium reaction 16; it is known that the equilibrium strongly favors Cr(VI) + V(IV) over Cr(V) + V(V).¹⁵

Table 1. Effect of oxalic acid on the yield of V(V) in Cr(VI) oxidation of V(IV) at 25°. V(IV) = 0.0157M, Cr(VI) = 0.0020M, perchloric acid = 1.25M, V(V) = 0.0011M

Oxalic acid, M	Vanadium(V) yield, %
0	100
0.00156	86.6
0.00312	71.6
0.00781	61.6
0.0156	56.6
0.0242	50.8
0.0312	46.6

The introduction of a substrate into the V(IV)–Cr(VI) system can result in a decrease of the yield of V(V). If direct oxidation of the substrate by

either Cr(VI) or V(V) under the reaction conditions employed can be excluded, then a drop in the yield of V(V) indicates that an induced oxidation of the substrate by one of the reaction intermediates, Cr(IV) or Cr(V), took place. The overall reaction rate, measured by the disappearance of Cr(VI), should be increased if the induced oxidation involves Cr(V). An example of this behavior can be observed in the oxidation of hydrogen iodide in the Cr(VI)–V(IV) system.¹⁵ On the other hand, no change in rate is expected if the substrate reacts with Cr(IV). In such a case, two additional reactions (19 and 20) have to be added to Scheme 5.



A quantitative relationship² (Eq 21) between the yield of V(V) and the concentration of the substrate and V(IV) can be used to determine the relative rate of Cr(IV) oxidation for the added substrate.

$$\frac{V_{\max} - V}{V - 0.33V_{\max}} = \frac{k_4[S]}{k_3[V(IV)]_{av.}} \quad (21)$$

In Eq 21, V represents the yield of V(V) in the presence of an organic substrate of a given initial concentration [S]; V_{max} is the yield in the absence of the organic compound; [V(IV)]_{av} is the average concentration of V(IV) during the run.

RESULT AND DISCUSSION

In order for the approach outlined above to be applicable, the rate of the Cr(VI) and V(V) oxidations of the substrate must be low, compared with

the rate of the Cr(VI) oxidation of V(IV). Because of the second order term in the Cr(VI) oxidation of oxalic acid,⁸ this condition is not fulfilled at higher oxalic acid concentrations and the whole study therefore had to be carried out at concentrations of oxalic acid below 0.03M. Under these conditions the Cr(VI) oxidation of oxalic acid is about 1,000 times slower than the oxidation of V(IV).^{24,15} Also, no significant interference from the V(V) oxidation can be expected.¹⁶

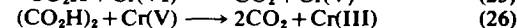
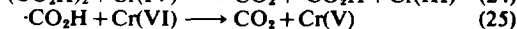
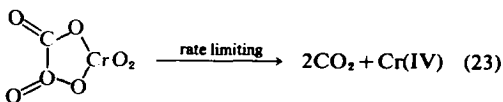
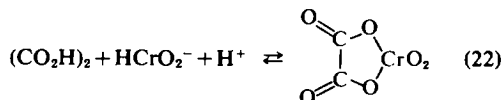
Table 1 shows the effect of oxalic acid on the yield of V(V).

The data show a decrease in the yield of V(V) when increasing amount of oxalic acid is added to the system. As the Cr(VI) oxidation of oxalic acid under these conditions is too slow, the decrease in the yield of V(V) is clearly the evidence of induced oxidation taking place. Nevertheless, the addition of oxalic acid had no effect on the overall rate of the reaction as measured by the consumption of Cr(VI). (Table 2).

Table 2. Effect of oxalic acid on the rate of Cr(VI)-V(IV) reaction. V(IV) = 0.00395M, V(V) = 0.00138M, Cr(VI) = 0.00047M, perchloric acid = 1.25M

Oxalic acid, M	k, M ⁻¹ sec ⁻¹
0	0.52
0.00078	0.55
0.00156	0.55
0.00312	0.56

The results given in Tables 1 and 2 indicate that Cr(IV) and not Cr(V) must be responsible for the observed induced oxidation. Oxalic acid thus shows a similar pattern of behavior to that of the previously investigated alcohols and aldehydes¹⁻³ and reacts by a mechanism of the type represented in Scheme 1. A more detailed mechanism is given below (Scheme 6).*



SCHEME 6

*Evidence for the formation of the oxalyl chromate (reaction 22) has been given earlier.⁸

Neither oxidation of Cr(IV) by Cr(VI) as required by Scheme 3 nor its disproportionation according to Scheme 4 are compatible with our results.

Using Eq 21 we determined (Fig 1) that oxalic acid actually reacts with Cr(IV) very rapidly. It is oxidized 1.83 times faster than V(IV) or about 44 times faster than isopropyl alcohol. Table 3 shows a comparison of relative oxidation rates of oxalic acid as compared with isopropyl alcohol towards Cr(VI),⁸ Cr(V),¹⁷ and Cr(IV), all extrapolated to one molar hydrogen ion concentration. The value for Cr(VI) reflects only the first order term for the Cr(VI) oxidation of oxalic acid.

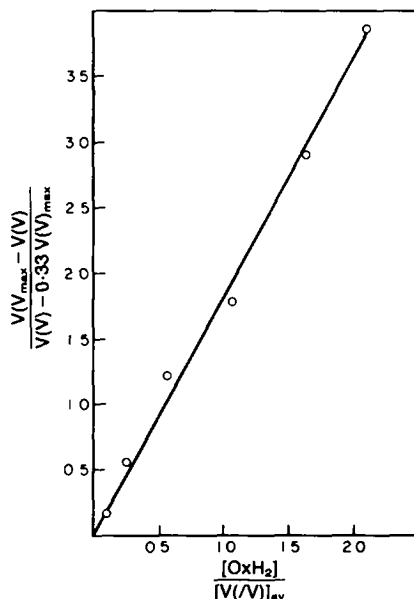


Fig 1. Determination of the relative rates of Cr(IV) oxidation of oxalic acid and V(IV) at 25°. Perchloric acid = 1.25 M, V(IV) = 0.0157 M, V(V) = 0.0011 M.

Table 3. Relative rates of oxidation of oxalic acid and isopropyl alcohol at 25°

Oxidant	k _{OxH₂} /k _{i-PrOH}
Cr(VI)	0.07
Cr(V)	3.7
Cr(IV)	44

EXPERIMENTAL

Materials. Oxalic acid (Mallinckrodt AR), sodium dichromate (J. T. Baker Reagent), vanadyl sulfate (Fisher), vanadium pentoxide (Fisher) and barium perchlorate (G. F. Smith Co.) were used without further purification.

Stock solns of V(IV) perchlorate and V(V) perchlorate were prepared according to the procedure described earlier.²⁴ Perchloric acid solns were prepared for 60% perchloric acid (B & A Reagent).

Kinetic measurements and yield of V(V). The rates of

Cr(VI) oxidation of V(IV), Cr(IV) oxidation of oxalic acid and the yield of V(V) were determined by the methods described by Rahman and Roček.²

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