



Cooxidation not to be Confused with Catalysis: A Chemical Education Article to Physical-organic Chemists

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ABSTRACT

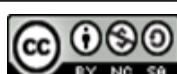
Two substrates (A) and (B) are oxidized separately by an oxidant (Oxi) with the rate constants k_1 and k_2 and they are oxidized taken together (A + B) under similar conditions with a rate constant k_3 , if the value of $k_3 = (k_1 + k_2)$, then it is said to be an example of two reactions “going parallel”. If the value of $k_3 >>> (k_1 + k_2)$, then the redox process is termed as “co-oxidation” (Hasan and Rocek 1972, *JACS*). In this process in the mixture the two substrates are oxidized synchronously by a direct three electron transfer route if the oxidant happens to be Cr(VI) and by a direct four electron transfer route if the oxidant happens to be Mn(VII) (Jagannadham *et al.*, 1986, *Oxidation Communications*). It was realized that the essential condition of the synchronous oxidation of two substrates A and B is that one substrate must have two functional groups and the other must have one functional group or vice-versa. The compound with two functional groups must be a good chelating agent with the metal ion oxidant. A substrate (A) is oxidized by an oxidant (Oxi) with a rate a constant k_4 and is oxidized in presence of a catalyst (Cat) with a rate constant k_5 , if $k_5 > k_4$ the redox process is termed as “catalyzed process”. It is to be noted that in the catalytic process the catalyst (Cat) is not oxidized and its concentration does not change during the reaction. It only increases the rate of oxidation with lower activation energies. If $k_5 = k_4$ it is to be understood that there is “no catalysis”. If $k_5 < k_4$ it is to be understood that the catalyst is called a negative catalyst or “inhibitor” and the reaction goes with higher activation energy. In this paper a lucid description is given for the two processes “co-oxidation” and “catalysis” with putative examples.

Keyword: Cooxidation, Catalysis, Chemical education.

INTRODUCTION

Hasan and Rocek were the first to report a direct synchronous three electron oxidation

process where in isopropyl alcohol and oxalic acids were oxidized¹. Later several publications appeared from his laboratory²⁻¹⁸. Sequel to Rocek's discovery¹ of one step three electron oxidations several



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researchers reported numerous studies in this area. Quoting them in this article is beyond the scope and limit of this article. However to one of the authors of this article the situation warrants to quote our own examples of oxidation of aliphatic esters in presence of oxalic acid again by a synchronous three electron transfer route¹⁹, and oxidation of *iso*-propanol and lactic acid by Cr(VI)²⁰ and a mixed substrate system of an aldehyde and an alcohol²¹. Another interesting study by Roèek on three electron oxidation is the intra-molecular cooxidation of a single substrate having three functional groups such as 2,7-dihydroxyheptanoic acid by chromic acid¹³. 2,7-dihydroxyheptanoic acid is a substitute of two substrates one with two functional groups and the other with one functional group. Though not effective as 2,7-dihydroxyheptanoic acid oxidation, a similar study was also reported from our laboratory where in oxidation of glycerol which has three hydroxyl groups by chromic acid did take place by a three electron transfer route²². Our study was further extended to permanganate ion oxidations where in *iso*-propanol was oxidized by permanganate ion in presence of several bi-functional compounds by synchronous four electron transfer route²³.

The end product of the oxidant in three electron oxidations by Cr(VI) is Cr(III). As Cr(III) is stable it does not undergo any further reduction. But the situation in the four electron transfer reaction by Mn(VII) is different. The end product of Mn(VII) is Mn(III) which is known to be reasonably a good oxidant ending with the formation of Mn(II) as the stable end product²⁴. In the previous work²³ from our laboratory care is taken so that the similar conditions were adopted where in the oxidation of either *iso*-propanol or the bi-functional compounds by Mn(III) was negligible.

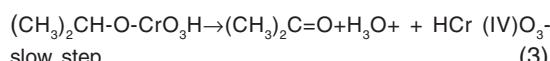
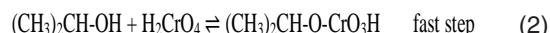
Catalysis is the process that increases the rate of a chemical reaction due to the participation of a third substance called a catalyst. The catalyst is not consumed in the course of the catalyzed reaction and can continue in several cycles until the completion of the reaction. Very often only micro-molar quantities of the catalyst are required in principle²⁵. In catalytic process the catalyst is not oxidized or reduced. Hence the process of co-oxidation should not be confused with catalysis.

DISCUSSION

Before understanding the difference between cooxidation and catalysis it is noteworthy to discuss the oxidations of related compounds by Cr(VI) and Mn(VII) in detail.

Oxidation of *iso*-propanol by Cr(VI)

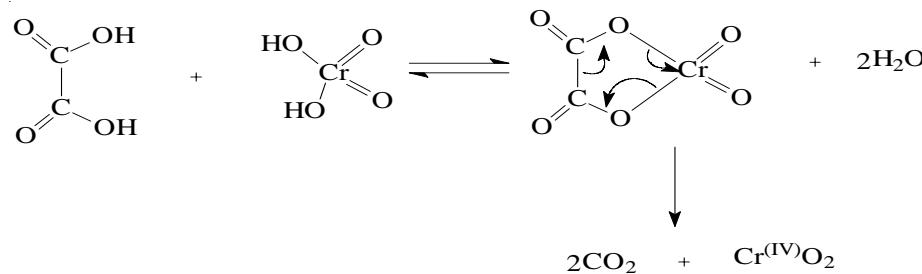
Rocek and Krupicka^{26a} and Wiberg and Schaefer^{26b} reported the oxidation of *iso*-propanol by chromic acid. The reaction was shown to undergo via a chromate ester which is formed in a reversible step and then decomposes in a rate determining step to give acetone as shown in the following mechanism (Scheme 1).



Scheme 1

Oxidation of oxalic acid by Cr(VI)

Oxidation of oxalic acid was studied by Bakore and Jain²⁷ and later by Hasan and Rocek²⁸. The reaction involves a cyclic transition state between chromic acid and oxalic acid which later decomposes in a rate determining step to give CO₂ as the end product. The mechanism is shown in Scheme 2.



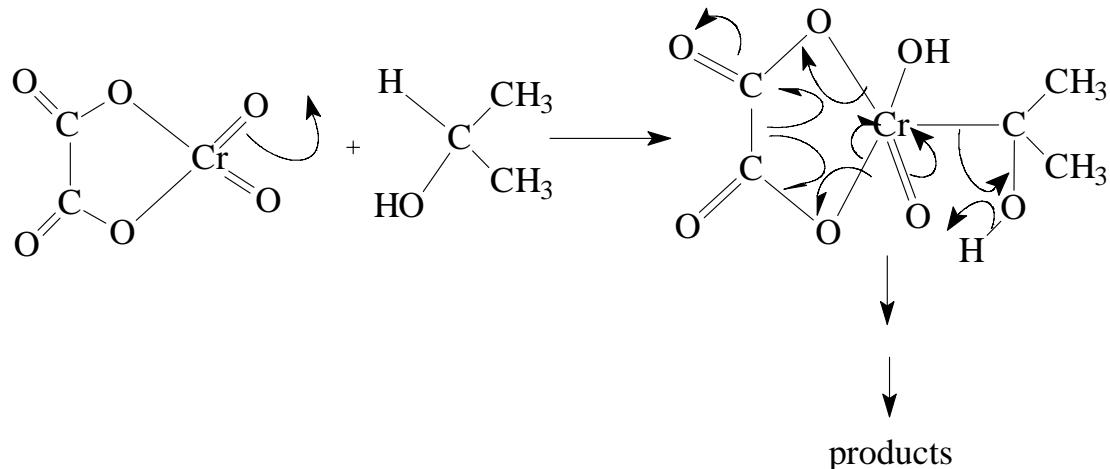
Scheme 2

Oxidation of a mixture of iso-propanol and oxalic acid by Cr(VI)

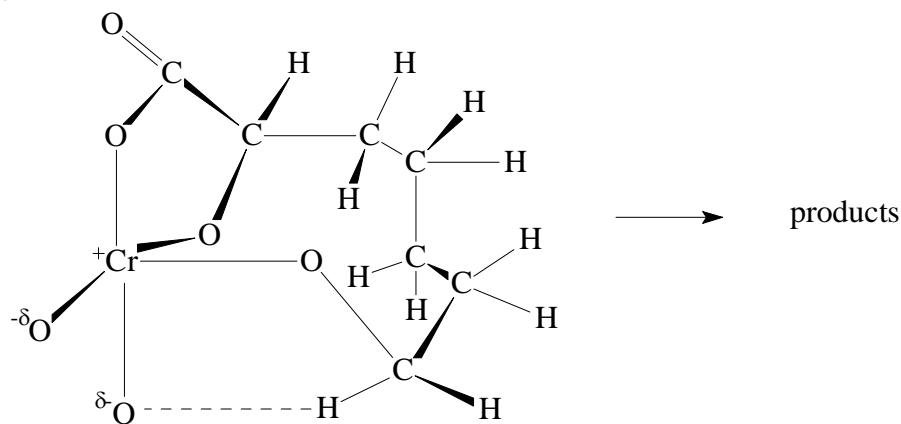
Hasan and Rocek for the first time reported a direct synchronous three electron oxidation process where in isopropyl alcohol and oxalic acids were both oxidized¹. They strongly advocated the reaction to be a direct three electron transfer route based on the increase in the rate of oxidation by several orders of magnitude compared to the rates of oxidation of the two substrates taken alone. Further their studies were supported by the presence of free radicals and stoichiometry of the reaction. In the mixture oxalic acid was oxidized by one electron transfer and *iso*-propanol by two electron transfer process. The end products are acetone and CO₂. The brief mechanism where in a ter-molecular complex formed was supposed to give products in a slow step as shown in scheme 3.

Oxidations of a substrate with three functional groups

Another interesting study by Rocek on three electron oxidation is the intra-molecular cooxidation of a single substrate having three functional groups such as 2,7-dihydroxyheptanoic acid by chromic acid¹³. This was successfully discovered from the study of a series of dihydroxy carboxylic acids (HO(CH₂)_nCHOHCO₂H). With n = 5 that is 2,7-dihydroxyheptanoic acid reacted completely in a different way compared to the other members of the series. 2,7-dihydroxyheptanoic acid is a substitute of two substrates one with two functional groups and the other with one functional group. The end products were corresponding aldehyde and alcohol. The transition state that formed is shown in scheme 4.

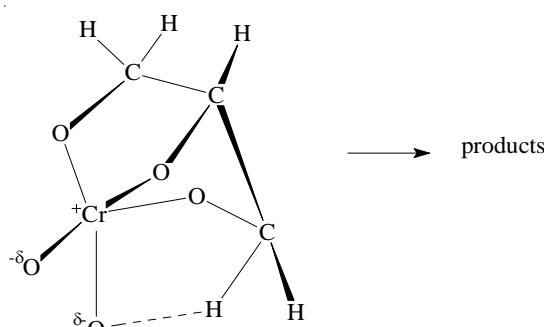


Scheme 3



Scheme 4

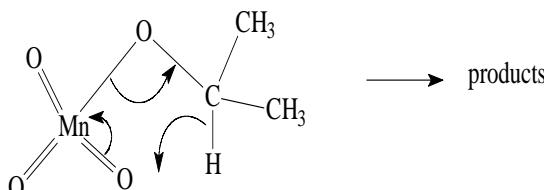
Though the reaction sequence is not as efficient as the 2,7-dihydroxyheptanoic acid oxidation by Cr(VI), a similar study was also reported from our laboratory where in oxidation of glycerol which has three hydroxyl groups by chromic acid did take place by a three electron transfer route²². The end product of the reaction was glyoxal. The transition state is shown in scheme 5.



Scheme 5

Oxidation of iso-propanol by Mn(VII)

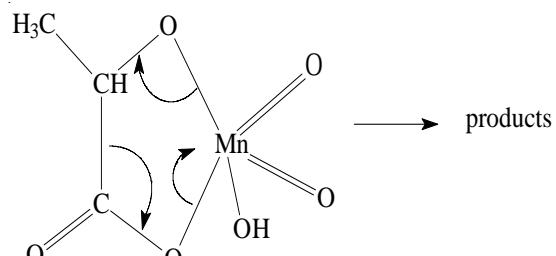
Kinetic study of oxidation of *iso*-propanol is more than a century old²⁹. The reaction sequence involves the formation of permanganate ester which later gives the acetone as the product in a slow step. The reaction is shown in scheme 6.



Scheme 6

Oxidation of lactic acid by Mn(VII)

Lactic acid is determined by the reaction of Mn(VII) in acid medium³⁰. The products of oxidation were acetaldehyde and CO_2 . The reaction sequence is shown in scheme 7.



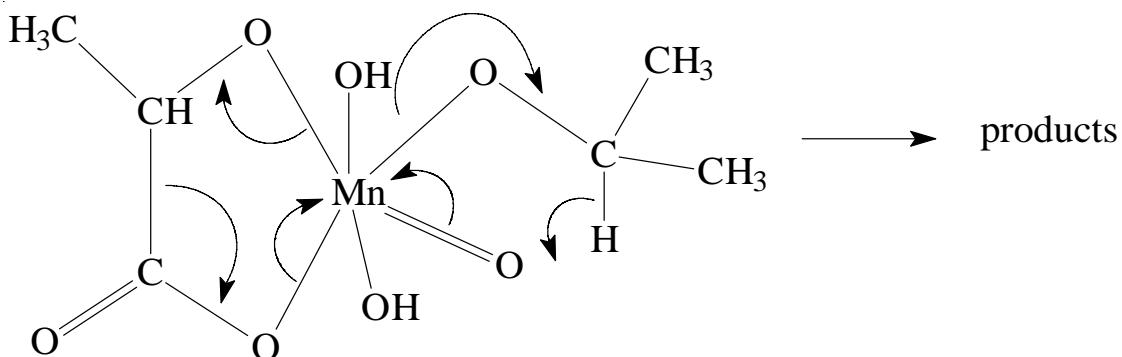
Scheme 7

Cooxidation by Mn(VII)

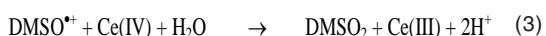
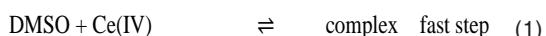
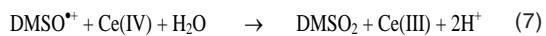
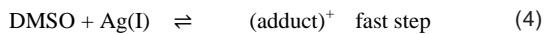
Our study was further extended to permanganate ion oxidations where in *iso*-propanol was oxidized by permanganate ion in presence of several bi-functional compounds by synchronous four electron transfer route²³. The transition state taking lactic acid and *iso*-propanol as example is shown in scheme 8.

Catalyzed and un-catalyzed reactions

There were several thousands of catalyzed reactions reported in literature. Quoting them in the present article is beyond the scope of this article. But as an example to understand the concept of catalysis we present here a study involving Ag(I) catalyzed and un-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Ce(IV) in nitric acid medium published from our laboratory³¹. The product of oxidation was found to be dimethyl sulfone (DMSO_2). The mechanism proposed for both the processes were shown in scheme 9.



Scheme 8

Un-catalyzed path**Catalyzed path****Scheme 9**

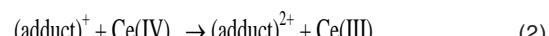
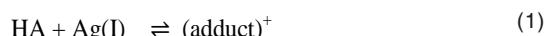
In these reactions there is no change in concentration of Ag(I) at the end of the reaction which was confirmed by chromate titration.

CONCLUSION

From the above examples it was very clear that the process of cooxidation is different from catalysis. The essential condition for cooxidation to occur is one of the two substrates having two

Only catalyzed reactions

There were some instances in literature those are only catalyzed reactions. In the absence of the catalyst even under boiling conditions there was no reaction. One of such reactions was kinetics of Ag(I) catalyzed oxidative decarboxylation of some organic acids by Ce(IV) in H₂SO₄ medium³². The reaction sequence taking acetic acid (HA) as an example is shown in scheme 10.

**Scheme 10**

The rest of the steps are similar to the steps 6 and 7 of the scheme 7.

functional groups must be a good chelating agent with the metal ion oxidant. And in the catalytic reaction a catalyst in micro molar (mM) quantities must be able to catalyze the reaction with lower activation energies compared to the un-catalyzed reaction.

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