www.sphinxsai.com

A study of mechanistic proposals of Induced oxidation using permanganate under acidic condition

Syed Asif*[1], Syed Sultan[1], Syed Abed[2], Mazahar Farooqui[1]

[1]Post Graduate and research centre Maulana Azad College, Aurangabad,MS,India

[2]Govt. College of Arts and Science, Aurangabad,MS,India

Corres.author: mazahar_64@Rediffmail.com

Abstract: The induced oxidation of carboxylic acid is carried out in presence of As (III) using $KMnO_4$. The induction factor, that is the ratio of oxidation equivalent consumed by the equivalent of acceptor and the inductor, is determined under varied experimental conditions. The inductor factor indicates the involvement of Mn^{5+}, Mn^{4+} and Mn^{3+} as reactive intermediate. The probable mechanism based on induction factor is suggested. It was concluded that As (III) titration with $KMnO_4$ gets influenced by the presence of trace amount of carboxylate ions. The effect of added salt on induction has been studied and found to be negligible.
Key words: mechanistic proposals ,Induced oxidation ,permanganate ,acidic condition.

Introduction:
There are several reactions which can be carried out simultaneously. Some of them are spontaneous and others are nonspontaneous. When a system consist of two reactions one is spontaneous and other is nonspontaneous, the spontaneous reaction causes or accelerates a non spontaneous process. This is called chemical induction. Literature survey reveals that very less work is done on the mechanistic proposal of induced reactions [1-3]. Though there is lots of work on organic reaction mechanism carried out.

Experimental:
All chemicals used were of AR grade and used without further purification. Double distilled water was used for the preparation of solutions.
A solution of $KMnO_4$ was prepared and standardized by oxalic acid. In a series of conical flask inductor with different concentration was taken. To each flask 5ml of $1x10^{-3}$mole dm^{-3} acceptor and of 2mole dm^{-3} H_2SO_4 was added. The solutions were titrated against standard $KMnO_4$. Similarly by keeping inductor and

acid concentration constant, variation of acceptor was determined.

Result and discussion:
The estimation of As (III) by permanganate can be carried out accurately in H_2SO_4 medium where as the same titration fails to give correct concentration of As (III) in the presence of HCl. The reason assigned to this discrepancy is the induced oxidation of chloride ion by permanganate despite the medium being acidic. When the reaction is carried out in HCl, As (III) induced oxidation of chloride ion by permanganate takes place, where as H_2SO_4 gives only sulphate ions which are inert towards oxidation. The important question that still remains to be answered is about the role of such metal ions which are not behaving as a catalyst but induces reactions tremendously. There had been a logical view that the interaction of actor and inductor is possibly creating some kind of driving force in situ which is responsible for such an induced phenomenon. We can assume that, in the induced

reaction, some intermediate with high potential oxidizing agents are formed which are more powerful oxidant than the actor, these species are responsible for the induced oxidation of the substrate. For the present study we have carried out induced oxidation of Potassium Phthalate, Sodium potassium tartarate, Potassium hippurate, Malonic acid, Potassium torochlorate at three different tempratre. The results are shown in table-1, in which induction factors obtained from titrations were given.

Table –1. induction factor at different temperature for oxidation of carboxylate salts

Actor	$[Na\,AsO_2]$ mol/dm^3	$[Na\,AsO_2]$ mol/dm^3	Temperature		
			27 $^\circ$ C	50 $^\circ$ C	70 $^\circ$ C
Potassium Phthalate = 0.01 mole/dm^3	0.002	0.0025	1.36	1.55	2.09
	0.005	0.0025	0.94	1.05	1.16
	0.007	0.0025	0.67	0.75	0.88
	0.010	0.0025	0.47	0.52	0.60
So dium potassium tartarate = 0.01 mole/dm^3	0.002	0.0025	1.31	1.97	2.96
	0.005	0.0025	0.82	1.09	1.37
	0.007	0.0025	0.59	0.72	0.92
	0.010	0.0025	0.61	0.63	0.68
Potassium hippurate= 0.01 mole/dm^3	0.002	0.0025	1.79	2.19	2.39
	0.005	0.0025	0.46	0.66	0.86
	0.007	0.0025	0.27	0.43	0.55
	0.010	0.0025	0.22	0.31	0.39
			0.17	0.23	0.29
Malonic acid= 0.01 mole/dm^3	0.002	0.0025	0.69	1.27	1.73
	0.005	0.0025	0.23	0.46	0.61
	0.007	0.0025	0.13	0.25	0.41
	0.010	0.0025	0.08	0.21	0.28
			0.06	0.13	0.17
Potassium taurochlorate= 0.01 mole/dm^3	0.002	0.0025	2.28	2.85	3.43
	0.005	0.0025	1.71	2.28	2.85
	0.007	0.0025	1.02	1.71	2.05
	0.010	0.0025	0.47	0.52	0.56

The induction factor of acid shows that when As(III) concentration is low, IF is more. It decrease with increase in concentration of As(III). The possibility of involvement of Mn(VI) can not be ruled out. There is every possibility that 1-equivalent change, which is more facile that 2-equivalent change on energetic preposition[4].

 Thus we can write

Mn(VIII) + As(III)------- As(IV) + Mn(VI)--------1

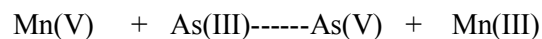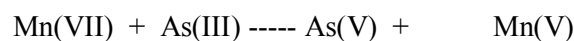As(IV)   + Mn(VI)------As(VI) + Mn(VI)-------2

As(IV) as an intermediate is not a unique proportions. Moreover, if Mn(VI) and As(III) are caed in a solvent, there is no quantitative estimation to decide the percentage of this reaction. The reaction condition indicates that Mn(V) is responsible for induced phenomenon. Since certain experimentalresults indicate participation of Mn(IV), it is not the situation more likely in view of Mn(V) reduction to Mn(VI) which finally under experimental condition disproportionate to Mn(IV) and Mn(II). Had it been the situation, the reaction system would have indicated black or colloidal black or slightly yellow   colour, none of these changes were observed eliminating the probability of Mn(IV) formation by step

2Mn(III) ------- Mn(IV) + Mn(II)

In all probability it appears reasonable to assume that Mn(III) further interacts with intermediate form of the substrate. Also Mn(IV) may interact with substrate instead of precipitating in a colloidal form. Consider Malonic acid, considering Mn(III) as an intermediate species

Mn(VII) + As(III) ----- As(V) +   Mn(V)

Mn(V)   + As(III)------As(V) +   Mn(III)

Mn(III)   + $CH_2(COOH)_2$-----Mn(II) + oxidation product

Comparing the IF of different sodium or potassium salt of carboxylate acid, we observed following trend PTC> PH>KHP>MA.

These indicate that various intermediate species are involved in their oxidation. The effect of salt on induction factor is given in table-2 which indicate that each cation has its own impact on oxidation process.

Table- 2 Effect of Salt on induction factor

| Salts	Potassium Phthalate	Sodium Potassium	Potassium hippurate	Malonic acid	Potassium taurochlorate
KNO_3	0.82	0.98	-	-	0.85
$NaNO_3$	0.66	0.26	0.33	0.33	0.45
$LiNO_3$	0.83	0.60	0.51	0.51	1.33
Na_2SO_4	0.41	-	-	-	-
$ZnSO_4$	0.21	0.40	-	-	0.24
Na_3PO_4	-	0.85	0.31	0.31	0.45
K_2SO_4	-	-	0.79	0.79	-
$ZnCl_2$	-	-	0.06	0.06	-

In the reference systems permanganate is an actor which under experimental condition is not capable to oxidize the substrate during the titration, however, when an inductor is interacting with the actor there are number of possibilities. If one takes into consideration the activation parameter of reaction system, the reduction of actor in one equivalent step appears to be a more facile process rather then transfer of more than one electron in a single step. Thus Mn (VI), Mn (V), Mn (IV) and Mn (III) are potential intermediates.

It has been established fact that Mn (IV) and Mn (III) are more stable then Mn (V) and Mn (VI) in acidic solution. Moreover, the possibility of the formation of the Mn (VI) in acid medium is remote. Mn (VI) has only been observed to be the reacting species in alkaline medium. It is assumed that Mn (VI) is the species initially formed with 1-equivalent inductor in acidic solution. It should immediately disproportionate to yield Mn (V) and Mn (VII).

2 Mn (VI) ⇆ Mn (V) + Mn (VII) ---------- (1)
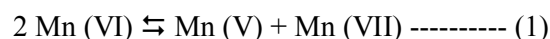
Mn (V) is also unstable and it immediately undergoes further disproportion.

2 Mn (V) ⇆ Mn (IV) + Mn (VI) ---------- (2)
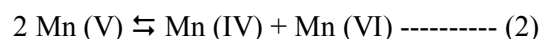
These two equilibria suggest that Mn (VI) still has a role to play as an intermediate. The other possibility with the inductor of multi equivalent nature is the formation of intermediate species such as Mn (IV) and Mn (III). It is also possible that Mn (III) present in solution in acidic condition undergoes disproportionation.

$$2 \text{ Mn (III)} \leftrightarrows \text{Mn (IV)} + \text{Mn (II)} \text{ ---------- (3)}$$
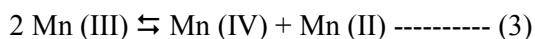
In fact, the reactive species Mn (III) which apart from attacking the acceptor, partly undergoes disproportionation because of its low stability. The distinction between the reactivity and participation of Mn (III) and Mn (IV) can be understood only through the measurement of induction factor.

Induced reactions are very similar to catalysis the difference is that catalyst recovered after the completion to reaction whereas inductor gets consumed into the reaction. The free energy liberated in the spontaneous reaction compensate for the expenditure of energy required for the formation of product.

References:
1. Ahmed Zaheer, Mazhar Ahmed Farooqui, Pathan M Arif, *Asian J Chem.*13, (2001) 721-724.
2. Ahmed Zaheer, Mazhar Ahmed Farooqui, *Asian J Chem.*13(2), (2001) 656-660.
3. Syed Asif, Syed Sultan, Syed Abed and Mazahar Farooqui, *RASAYAN J Chem* 3(2), 2010, 232-235
4. Menka Bhasin, Sapna Dubey, Indu Sharma, P D Sharma, *Ind.J.Chem.* 39A, 2000, 1036-1040.

*****