



MECHANISTIC PROPOSAL OF INDUCED OXIDATION OF POTASSIUM TELLURITE

Syed Asif*¹, Syed Sultan¹, Syed Abed² and Mazahar Farooqui¹

¹Post Graduate and Research Centre, Maulana Azad College, Aurangabad.

²Govt. College of Arts and Science, Aurangabad.

*E-mail: mazahar_64@Rediffmail.com

ABSTRACT

The induced oxidation of potassium tellurite 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 Potassium tellurite. The effect of added salt on induction has been studied and found to be negligible.

Keywords: Potassium tellurite, titration, mechanistic proposal, oxidation.

INTRODUCTION

There are several reactions which can be carried out simultaneously. Some of them are spontaneous and others are nonspontaneous. When a system of two reactions proceeding in one phase in which one depend on the other i.e. spontaneous reaction causes or accelerates a non spontaneous process is called chemical induction. Literature survey reveals that very less work is done on the mechanistic proposal of induced reactions¹⁻³. Though there is lots of work on inorganic reaction mechanism carried out⁴.

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 $1 \times 10^{-3}\text{M}$ acceptor and of 2M 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.

RESULTS AND DISCUSSION

Metal ion induced oxidation of inorganic substrate by permanganate have shown much interest in analytical chemistry particularly due to the presence of trace metal ion as impurities in the reagent. 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.

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 than 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 than 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 showed immediately disproportionate to yield Mn (V) and Mn (VII).



Mn (V) is also unstable and it immediately undergoes further disproportion.



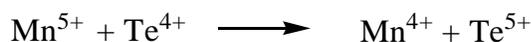
These two equilibria suggest that Mn (VI) still has a role to play as an intermediate. The other possibility with the inductor of multi equivalent nature is the formation of intermediate species such as Mn (IV) and Mn (III). It is also possible that Mn (III) present in solution in acidic condition undergoes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



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.

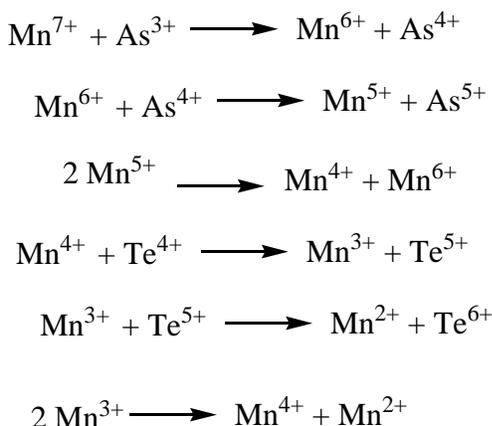
The induction factors calculated for system (Table-1) shows that it increases with increase in the concentration of acceptor and then becomes constant (Fig. 1). Considering all these factors and the chemistry of the systems, the mechanistic proposals for each reaction have been proposed. To avoid complexity, the mechanistic reactions have been given by considering skeleton forms of the participating reactants and products. In any induced reaction the induction factor is defined as the ratio of the number of equivalence of the reducing agent oxidized to the number of equivalents of the inductor oxidized. The inductor factor theoretically can be calculated by using equation

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. For potassium tellurite at 1×10^{-3} M inductor concentration the inductor factor found to be 1.7 which indicates participation of Mn^{5+} hence we can suggest following steps.



The last step has no experimental justification so far as our perusal of permanganate related reaction are concerned Also there is no formation of MnO₂ in the reaction under the experimental condition potassium tellurite selectively reduces the reactive transient species Mn⁵⁺ thereby providing a mean of detection of this elusive intermediate virtually the life time of Mn⁵⁺ is very short the effective intermediate therefore should be Mn³⁺ or Mn⁴⁺.

At the concentration of 3 x 10⁻³ M arsenite concentration induction factor changes to 0.47 which indicate involvement of Mn⁴⁺ the reaction steps can be proposed as-



Mn⁴⁺ and Mn³⁺ are more stable than Mn⁵⁺ and Mn⁶⁺ in acidic solution Mn⁶⁺ not yet been reported in any of the redox system involving permanganate as an intermediate in acidic media . since the solution after titration does not show any precipitation, it is quite logical to state that Mn³⁺ reacts with potassium tellurite in a fast step or it s disproportionate product Mn⁴⁺ instantaneously reacts with the substrate giving the final product Mn²⁺

When the concentration of arsenite is further increased to 5 x10⁻³ M and 8 x10⁻³ M, the induction factor becomes two close to 0.25 which indicate involvement of Mn³⁺.

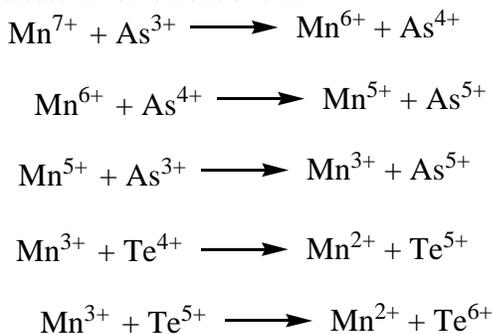


Table-1: Effect of Variation of Acceptor on inductor factor at different temperature
KMnO₄ 0.0025M

Acceptor	Induction Factor		
	27°C	50°C	70°C
NaAsO ₂			
0.001M	1.70	1.84	1.98
0.003M	0.47	0.52	0.56
0.005M	0.31	0.34	0.36
0.008M	0.21	0.23	0.24

REFERENCES

1. Ahmed Zaheer, Mazhar Ahmed Farooqui, Pathan M Arif, *Asian J Chem.*, **13**, 721(2001).
2. Ahmed Zaheer, Mazhar Ahmed Farooqui, *Asian J Chem.*, **13**(2),656(2001).

3. G. S. Gokavi, *Ind.J.Chem.* 40A, 307(2001)
4. K. S.Gupta, P Bhargava and S V Manoj, *Ind.J.Chem.* ,38A, 692(1999).
5. Menka Bhasin, Sapna Dubey, Indu Sharma, P D Sharma, *Ind.J.Chem.* ,39A, 1036(2000).

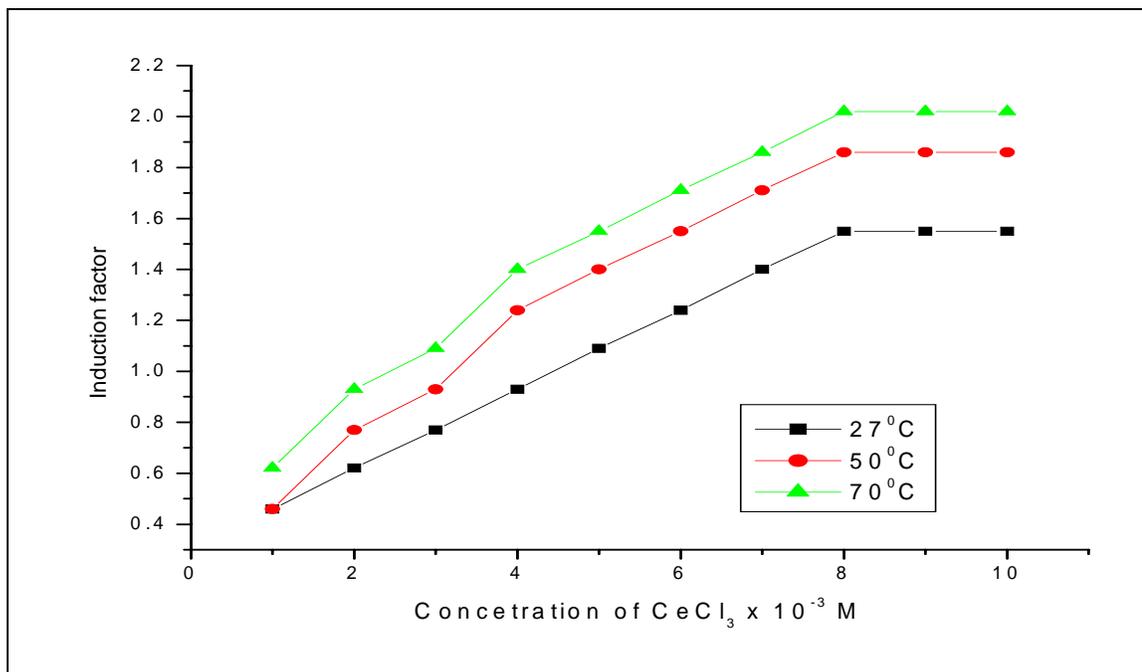


Fig.-1: Effect of temperature on the induction factor.

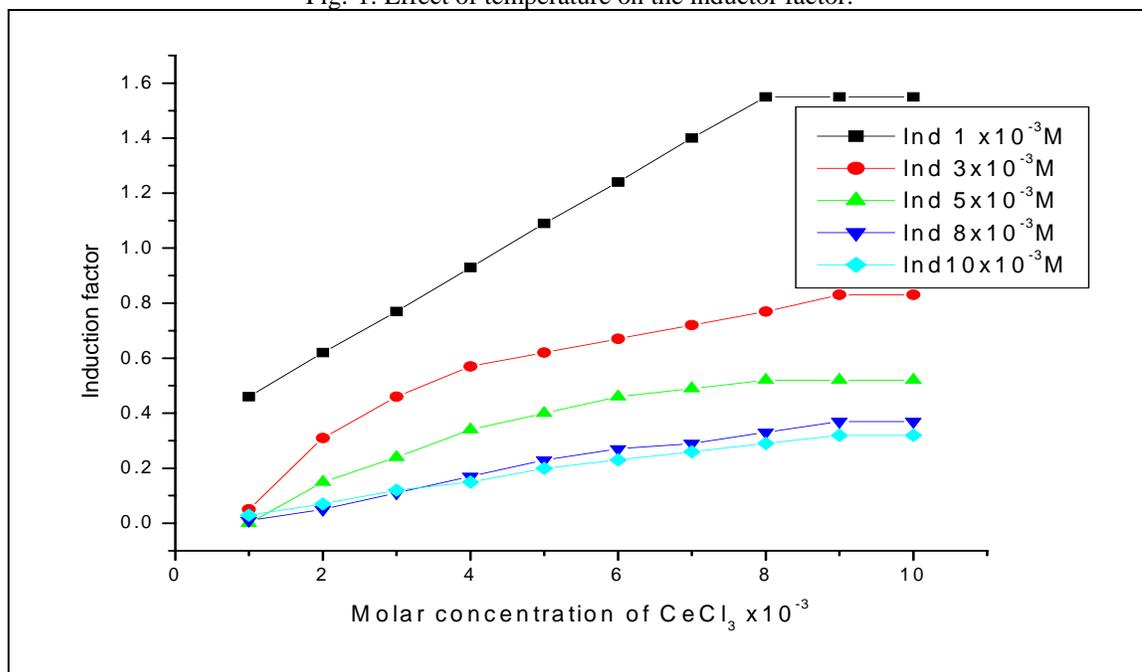


Fig.-2: Effect of variation of inductor concentration on induction factor.

(Received: 21 May 2010)

Accepted: 1 June 2010

RJC-562)