

## Fe(II) Induced Oxidation of Formic Acid

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The mechanistic proposals of induced oxidation of formic acid (acceptor) by Fe(II) (inductor) were investigated. A volumetric method was used to calculate the induction factor (I.F). The oxidation is carried out in acidic media by using  $\text{KMnO}_4$  as an actor. The effects of salts were studied by keeping the sulphuric acid concentration constant to understand their role in characterization of induced oxidation. A probable mechanism has been suggested on the basis of induction factor. It is observed that Mn(V) acts as reactive intermediate and induces the oxidation of formic acid through anhydride formation.

### INTRODUCTION

Various oxidants can be used for the oxidation of formic acid under different conditions.<sup>1</sup> Saha and others<sup>2</sup> used dioxo-tungsto cobaltate(III). Suri *et al.*<sup>3</sup> investigated oxidation of formic acid by benzyl trimethyl ammonium tribromide in acetic acid medium. Tompkins<sup>4</sup> have made detailed studies of the oxidation of the formate ions by potassium permanganate in dilute alkaline solution. Here an attempt was made to investigate Fe(II) induced oxidation of formic acid.

### EXPERIMENTAL

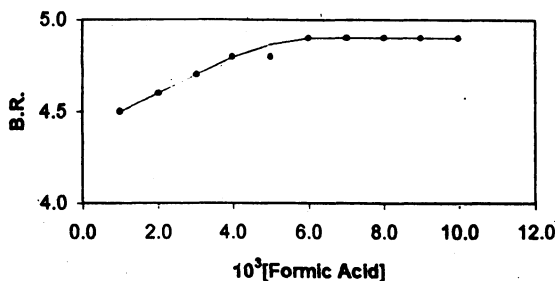
All the solutions and the reagents required during the course of study were prepared and standardized using suitable methods prescribed in literature. The chemicals were of AR grade and used as received without any further treatment. All solutions were prepared in doubly distilled water. Variation of inductor was carried out by keeping acid and acceptor concentrations constant (Table-1). Variation of acceptor was performed by keeping acid and inductor concentrations constant (Table-2). Similarly effect of salt has been studied.

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TABLE-1  
VARIATION OF INDUCTOR

Actor:  $\text{KMnO}_4$ , 0.0025 M  
Temp:  $27 \pm 0.5^\circ\text{C}$   
Acceptor: FA,  $5 \times 10^{-3}$  M  
Inductor: Fe(II)

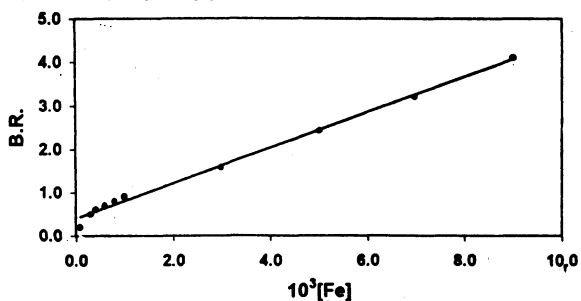


$10^3$ [Fe]	B.R. (mL)	mmols of Fe	mmols of F.A.	I.F.
0.2	0.4	4.48	14.72	3.29
0.4	0.6	8.96	20.24	2.26
0.6	0.7	13.44	21.16	1.57
0.8	0.8	17.92	22.08	1.23
1.0	0.9	22.40	23.00	1.03
3.0	1.6	67.20	17.48	0.26
5.0	2.4	112.00	19.32	0.17
7.0	3.2	156.80	18.40	0.12
9.0	4.1	201.60	23.00	0.11

Mean IF value 1.11

TABLE-1  
VARIATION OF ACCEPTOR

Acceptor: Formic acid  
Actor:  $\text{KMnO}_4$ , 0.0025 M  
Temp:  $27 \pm 0.5^\circ\text{C}$   
Inductor: Fe(II),  $5 \times 10^{-3}$  M

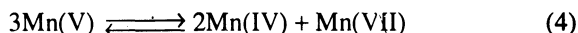
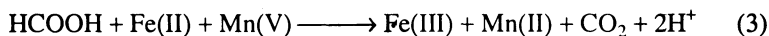
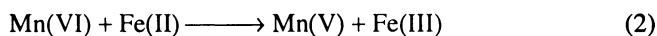
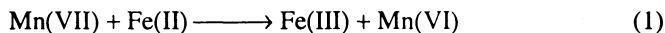


$10^3$ [F.A.]	B.R. (mL)	mmols of Fe	mmols of F.A.	I.F.
1.0	4.5	112.00	115.00	1.03
2.0	4.6	112.00	119.60	1.07
3.0	4.7	112.00	124.20	1.11
4.0	4.8	112.00	128.80	1.15
5.0	4.8	112.00	128.80	1.15
6.0	4.9	112.00	133.40	1.19
7.0	4.9	112.00	133.40	1.19
8.0	4.9	112.00	133.40	1.19
9.0	4.9	112.00	133.40	1.19
10.0	4.9	112.00	133.40	1.19

Mean IF value 1.15

## RESULTS AND DISCUSSION

All permanganate oxidations are usually complicated because of the many different oxidation states of Mn (+7, +6, +5, +4, +3 and +2). Each species has its own induction factor.<sup>5</sup> Identification of intermediate species is possible if theoretical value of I.F. is compared with experimental value.<sup>5</sup> We have observed that if the oxidation of Fe(II) is carried out in the presence of formic acid, permanganate is consumed in excess of the amount required by Fe(II), when no formic acid is present. Thus the over-consumption of permanganate, what we encounter here, is due to an induced oxidation of formic acid involving an intermediate ion. In case of permanganate in the presence of Fe(II) as an inductor, Mn(VI) is expected to be an intermediate. Since Mn(VI) has not yet been reported in any of redox system involving permanganate as an intermediate in acidic solutions, the possibility of formation of Mn(VI) is ruled out. However, it is possible that interaction of Mn(VI) with Fe(II) may give Mn(V), because one-electron transfer process in redox systems is most facile as compared to two-electron or multi-electron transfer step.

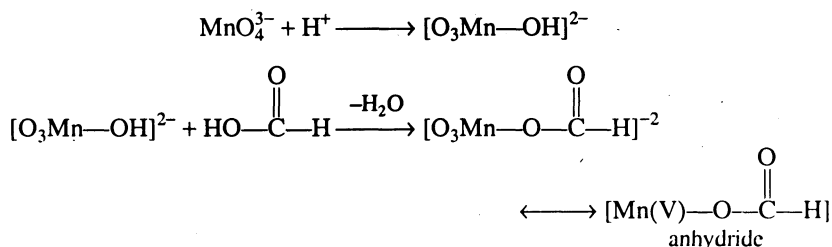


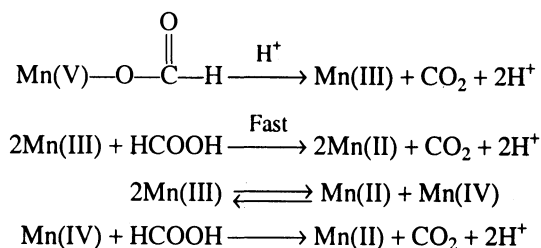
Under the experimental conditions formic acid selectively reduces the transient Mn(V) thereby providing a means of detection of this elusive intermediate.

Virtually the lifetime of Mn(V) is very short; the affective intermediate, therefore, should be either Mn(II) or Mn(IV). However, the disproportionate of Mn(III) might also be responsible for the formation of Mn(IV). It appears that whatever little amount of Mn(IV) is formed, immediately reacts without precipitating as MnO<sub>2</sub>.

Apparently oxidation by Mn(V) may occur by electron transfer *via* the oxo-bridge of the anhydride intermediate. The reason why this Mn(V) species is selectively reduced by formic acid in the presence of MnO<sub>4</sub><sup>-</sup> seems to be its ability to form an anhydride in which oxo-bridge may readily occur.

For anhydride formation to take place, at least one —OH group must be available in both formic acid and Mn(V) species. This is possible because MnO<sub>4</sub><sup>3-</sup> is a stronger base than MnO<sub>4</sub><sup>-</sup> species. A tentative proposal for modelling the reaction events can be suggested as:





where anhydride formation has been considered to be an intermediate for the final consumption of the reactants.

The intermediate anhydride is the best possible way to indicate the passage of electron from the substrate to the oxygen bonded Mn(V).<sup>6-8</sup> As the life of Mn(V) is short lived, the oxygen bridge provides a facile pathway for the transport of electrons from the substrate to the oxygen. Thus this bridge in the presence of acid due to protonation ruptures to Mn(III) species. Since the solution after titration does not indicate any presence of Mn(III) or precipitated MnO<sub>2</sub>, it is quite logical to state that Mn(III) reacts with formic acid in a fast step or its disproportionated product Mn(IV) instantaneously reacts with the substrate giving the final end product Mn(II).

In case of effect of salt, the presence of anions or cations has no effect or very negligible effect on induced oxidation of formic acid.

## REFERENCES

1. D.G. Lee, in: W.S. Trahanovsky (Ed.), *Oxidation in Organic Chemistry*, Part D, Academic Press, New York (1982).
2. K.K. Saha, M.C. Ghosh and P. Banerjee, *J. Chem. Soc. Dalton Trans.*, 1301 (1986).
3. Deepa Suri, Seema Kothari and K.K. Banerjee, *Indian J. Chem.*, **37B**, 448 (1998).
4. F.C. Tompkins, *Trans. Faraday*, **38**, 131 (1942).
5. Kessler F. Pogg, *Ann.*, **119**, 218 (1863).
6. L.I. Simandi, M. Jaky and Z.A. Sehely, *J. Am. Chem. Soc.* **106**, 6866 (1984).
7. L.I. Simandi, M. Jaky, C.R. Sarage and Z.A. Sehely, *J. Am. Chem. Soc.*, **107**, 4220 (1985).
8. P. Budo Zahenyi and L.I. Simandi, *Inorg. Chim. Acta*, 149 (1991).

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