

Mechanistic Study of Induced Oxidation of Formic Acid in presence of Sodium Arsenate

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The mechanistic proposal for induced oxidation by using As(III) as inductor and formic acid as acceptor were investigated. A probable mechanism has been suggested on the basis of induction factor (I.F.). It is observed that Mn^{5+} 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. Saha and others used¹ dioxo-tungsto cobaltate(III). Deepa *et al.*² investigated oxidation of formic acid by Benzyl trimethyl ammonium tribromide in acetic acid medium. Tompkins³ have made detailed studies of the oxidation of the formate ions by potassium permanganate in dilute alkaline solution. Here an attempt has been made to investigate 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.⁴ 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 keeping acid and acceptor concentration constant. Variation of acceptor was performed by keeping acid and inductor concentration constant. Similarly effect of salt has been studied. (Tables 1 and 2).

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TABLE-1
VARIATION OF ACCEPTOR

Acceptor: Formic acid Temp: $27 \pm 0.5^\circ\text{C}$
 Actor: KMnO_4 , 0.002 M Inductor: $\text{S.A.} \times 10^{-3} \text{ M}$

10^3 [F.A.]	B.R. (mL)	mmol of As(III)	mmol of F.A.	I.F.
1.0	7.5	187.25	230.00	1.23
2.0	7.6	187.25	234.60	1.25
3.0	7.8	187.25	243.80	1.30
4.0	8.0	187.25	253.00	1.35
5.0	8.1	187.25	257.60	1.38
6.0	8.3	187.25	266.80	1.42
7.0	8.6	187.25	280.60	1.50
8.0	8.6	187.25	280.60	1.50
9.0	8.8	187.25	289.80	1.55
10.0	8.8	187.25	289.80	1.55
11.0	8.8	187.25	289.80	1.55
12.0	8.8	187.25	289.80	1.55
13.0	8.8	187.25	289.80	1.55
14.0	8.8	187.25	289.80	1.55

Mean I.F. value: 1.44.

S.A.: Sodium arsenate; F.A.: Formic Acid.

TABLE-2
VARIATION OF INDUCTOR

Actor: KMnO_4 0.01 M Temp: $27 \pm 0.5^\circ\text{C}$
 Acceptor: Formic acid 1 M Inductor: S.A.

10^3 [S.A.]	B.R. (mL)	mmols of As(III)	mmols of F.A.	I.F.
10.0	4.6	74.90	165.60	2.21
20.0	8.7	149.80	308.20	2.06
30.0	12.7	224.70	446.20	1.99
40.0	15.7	299.60	538.20	1.80
50.0	20.0	374.50	690.00	1.84
60.0	22.6	449.40	763.60	1.70
70.0	26.8	524.30	910.80	1.74
80.0	30.1	599.20	1016.60	1.70
90.0	34.1	674.10	1154.60	1.71
100.0	37.6	749.00	1269.60	1.70

Mean I.F. value: 1.84

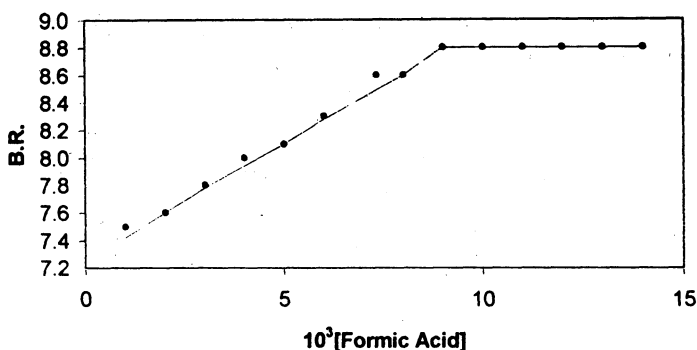


Fig. 1 Variation of acceptor.

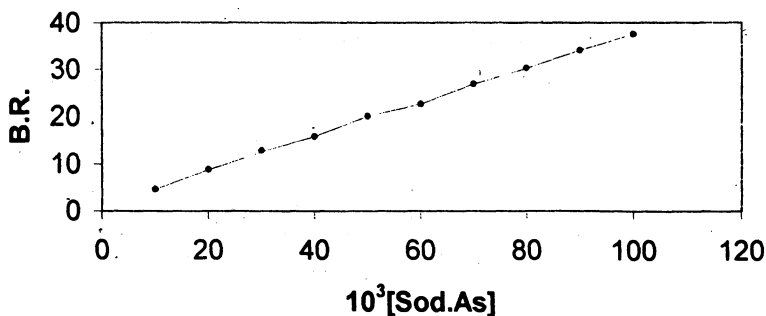
Temp.: $27 \pm 0.5^\circ\text{C}$; $[\text{KMnO}_4] = 0.002 \text{ M}$; $[\text{Sod. As}] = 5 \times 10^{-3} \text{ M}$ 

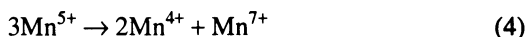
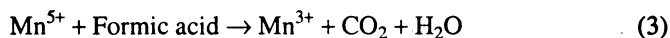
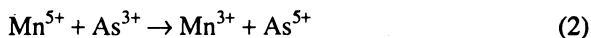
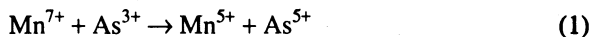
Fig. 2 Variation of Inductor.

Temp.: $27 \pm 0.5^\circ\text{C}$; $[\text{KMnO}_4] = 0.001 \text{ M}$; $[\text{Formic Acid}] = 1 \text{ M}$

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. Identification of intermediate species is possible if theoretical value of I.F. compared with experimental value⁵. We have observed that if the oxidation of As^{3+} is carried out in the presence of formic acid, permanganate is consumed in excess of the amount required by As^{3+} , 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 the absence of formic acid, As^{3+} reduces permanganate ion very rapidly to a mixture of Mn^{3+} and Mn^{4+} , the presence of formic acid in the reaction system will reduce both Mn^{3+} and Mn^{4+} to Mn^{2+} as no evidence regarding the formation of Mn^{4+} [black precipitate of MnO_2] was observed under experimental conditions. It is clear that whatever amount of Mn^{4+} is formed through either disproportionation of Mn^{3+} or in a direct step (the possibility is least). If Mn^{3+} is considered to be the end product in the acid conditions employed in the reaction, these are not sufficient to keep Mn^{3+} intact in the solution. Thus, as soon as it is formed,

it disproportionate to Mn^{2+} and Mn^{4+} species immediately reacts with the substrate. With the increasing concentration of acceptor the induction factor remains virtually 1.5; for this the mode of formation of Mn^{5+} can be proposed by the following reaction sequence.



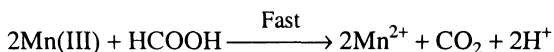
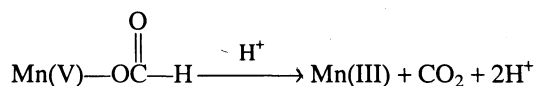
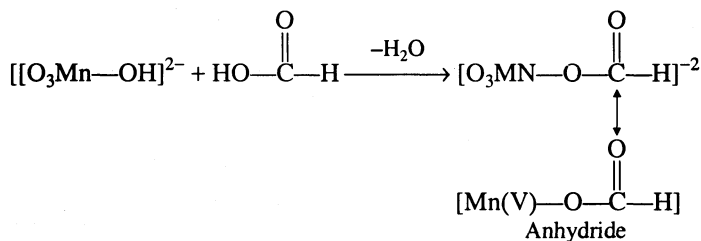
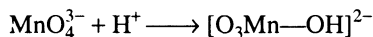
The step (4) has no experimental justification so far as our perusal of permanganate related reaction studies are concerned. Also this step experimentally does not appear feasible in the light of non-observation of MnO_2 in the reaction system.

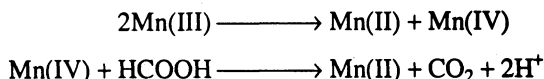
Under the experimental conditions formic acid selectively reduces the transient Mn^{5+} thereby providing a means of detection of this elusive intermediate (Mn^{5+} has not, yet, been reported in any such induced system).

Virtually the lifetime of Mn^{5+} is very short; the affective intermediate, therefore, should be either Mn^{3+} or Mn^{4+} as is observed from step (4), or the former is obtained from step (3). However, as stated earlier the disproportionate of Mn^{3+} from step (3) might also be responsible for the formation of Mn^{4+} . It appears that whatever little amount of Mn^{4+} is formed, it immediately reacts without precipitating as MnO_2 .^{6,7}

Apparently oxidation by Mn^{5+} may occur by electron transfer *via* the oxo-bridge of the anhydride intermediate. The reason why this Mn^{5+} species is selectively reduced by formic acid in the presence of MnO_4^- seems to be its ability to form an anhydride in which oxo-bridge may readily occur.⁸⁻¹⁰

For anhydride formation to take place, at least one —OH group must be available in both formic acid and Mn^{5+} species. This is possible because MnO_4^{3-} is a stronger base than MnO_4^- species. A tentative proposal for modelling the reaction events can be suggested as follows:





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^{5+} . As the life of Mn^{5+} is short lived, the oxygen bridge provides a facile pathway for the transport of electron from the substrate to the oxygen. Thus this bridge in the presence of acid due to protonation ruptures to Mn^{3+} species. Since the solution after titration does not indicate any presence of Mn(III) or precipitated MnO_2 , 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^{2+} .

REFERENCES

1. K.K. Saha, M.C. Ghosh and P. Banerjee, *J. Chem. Soc. Dalton Trans.*, 1301 (1986).
2. Deepa Suri, Seema Kothari and K.K. Benerjee, *Indian J. Chem.*, **37B**, 448 (1998).
3. F.C. Tompkins, *Trans Faraday*, **38**, 131 (1942).
4. I.M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, Wiley, New York, p. 97 (1857).
5. R.Y. Drummond and W.A. Waters, *J. Chem. Soc.*, 440 (1953); 497 (1955).
6. Kessler F. Pogg, *Ann.*, **119**, 218 (1863).
7. R. Stewart, in: K.B. Wiberg (Ed.), *Oxidation in Organic Chemistry*, Part A, Academic Press, New York (1965).
8. L.I. Simandi, M. Jaky and Z.A. Sehelly, *J. Am. Chem. Soc.*, **106**, 6866 (1984).
9. L.I. Simandi, M. Jaky, C.R. Sarage and Z.A. Sahelly, *J. Am. Chem. Soc.*, **107**, 4220 (1985).
10. P. Budo Zahenyi and L.I. Simandi, *Inorg. Chim. Acta*, **149** (1991).

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