Asian Journal of Chemistry Vol. 14, No. 2 (2002), 1091–1093

NOTE

Mechanistic Study of Induced Oxidation of Acetic Acid by As (III)

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The mechanistic study of induced oxidation by using As(III) as inductor and acetic acid as acceptor were investigated. A propable 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 acetic acid through anhydride formation.

Key Words: Mechanistic study, Induced, Oxidation, Acetic acid, As(III).

When two reactions proceed simiultaneously out of which one is spontaneous and other is non-spontaneous, the process is called chemical induction. Kessler[1] introduced the term induced oxidation. He studied the arsenite induced oxidation of magneous ion by chromic acid. Induced oxidation is very similar to catalysis the difference is that in catalysis, catalyst is recovered unchanged after the completion of reaction, whereas in induced reaction, inductor is consumed in the reaction in stoichiometric relation to the amount of product formed. In the present paper we report the induction factor and mechanism of induced oxidation of acetic acid by As(III).

All the solutions and the reagents required during the course of study were prepared and standardized using suitable methods. All chemical were of AnalaR grade and these were used as recieved without any further purification, variation of inductor, acceptor and salt effect was carried out as described earlier.[2]

The induction factor of As(III) induced oxidation of acetic acid does not appreciably change in the presence of salts like KNO_3, $NaNO_3$ or $LiNO_3$. It remains near to 1.5 in all cases which indicate negligible effect of cation on the oxidation process. Thus manganese is present in different oxidation state, *i.e.*, +7, +6, +5, +4, +3, +2. Each step is having its own induction factor It is possible to calculate induction factor (I.F.) theoritically. Thus calculated I.F. and experimental I.F. is compared to determine reactive intermediate species present in the system. In the present investigation, we have observed that if the oxidation of As(III) is carried out in presence of acetic acid, permanganate is consumed in excess of the

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amount required by As(III), when no acetic acid is present. Thus the over-consumption of permanganate is due to the induced oxidation of acetic acid involving an intermediate ion Mn^{5+}.

The inductor factor of acetic acid was observed to 1.47 (Table-1). It is more near to 1.5 with As(III) as an inductor. Therefore the formation of Mn^{5+} can be proposed by the following reaction sequence

$$Mn^{7+} + As^{3+} \longrightarrow Mn^{5+} + As^{5+}$$

$$Mn^{5+} + As^{3+} \longrightarrow Mn^{3+} + As^{5+}$$

$$Mn^{7+} + \text{Acetic acid} \longrightarrow Mn^{3+} + \text{Oxidation product of acetic acid}$$

$$3Mn^{5+} \longrightarrow 2\,Mn^{4+} + Mn^{7+}$$

TABLE-1
VARIATION OF ACCEPTOR

Inductor: Sodium arsenite (8×10^{-3}M); Actor: 0.0025 M; Temp.: 27 ± 0.5°C

10^{-1} (Acetic acid)	mmole of As	mmole of acetic acid	Induction factor
1	254.08	348	1.37
2		354	1.39
3		366	1.44
4		378	1.49
5		372	1.46
6		384	1.51
7		384	1.51
8		384	1.51
9		384	1.51
10		384	1.51

Mean induction factor = 1.47

TABLE-2
VARIATION OF INDUCTOR

Acceptor: Acetic acid Temp.: 27 ± 0.5°C; Actor: 0.01 M $KMnO_4$

10^3 (sodium arsenite)	mmoles of As	mmoles of acetic acid	Induction factor
10	74.9	114	1.52
20	149.8	198	1.32
30	224.7	306	1.36
40	299.6	414	1.38
50	374.5	510	1.36
60	449.4	606	1.35
70	524.3	702	1.34
80	599.2	774	1.29
90	674.1	900	1.34
100	749.0	936	1.25

Mean induction factor = 1.35

TABLE-3
EFFECT OF SALT

Salt	$NaNO_3$	$LiNO_3$	KNO_3
Induction factor	1.45	1.43	1.49

All these reactions are possible under the given experimental conditions. Acetic acid contains carboxylic group which can form an oxo-bridge with Mn^{+5}. The necessary condition is that both the reaction should have at least one –OH group. The mechanism can be written as

$$MnO_4 + H^+ \longrightarrow [O_3\,Mn^-\,OH]^{-2}$$

$$[O_3Mn^-OH]^{-2} + HO{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow{-H_2O} [O_3Mn{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3]^{-2}$$

anhydride

$$[Mn(V){-}O{-}\underset{\underset{O^-}{\|}}{C}{-}CH_3]$$

$$[Mn(V){-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3] \longrightarrow Mn\,(III) + CO_2 + 2H^+$$

$$2\,Mn\,(III) + CH_3COOH \longrightarrow 2Mn + CO_2 + 2H^+$$

$$2\,Mn\,(III) \longrightarrow Mn\,(II) + Mn\,(IV)$$

$$Mn\,(IV) + CH_3COOH \longrightarrow Mn\,(II) + CO_2 + 2H^+$$

Acetic acid reacts with Mn^{5+} and electron transfer takes place through anhydride formation. The possiblity of Mn^{6+} is least, because first it is stable only in the alkaline media and secondly MnO_4^{2-} inter change is vary rapid, presumbly by the transfer of 3d electron from MnO_4^{2-} to MnO_4^-

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(*Received*: 4 December 2001; *Accepted*: 15 February 2002) AJC-2647