



Oxidation of Poly Hydroxy Compounds by Tetravalent Cerium in Aqueous Acetic Acid - Perchloric Acid Media: A Kinetic Study

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Abstract : Kinetics of oxidation of glycerol and 1,2-propanediol by tetravalent cerium was studied in aqueous acetic acid-perchloric acid media. The reactions are first order in [oxidant], [substrate] and [H⁺]. The effect of Mn²⁺ and solvent variations are also studied. An increase in rate was observed with decrease in dielectric constant, pointing to the fact that these are the reactions between positive ion and dipole. Arrhenius parameters are calculated and a plausible mechanism is postulated based on experimental results.

Keywords : Glycerol, 1,2-propanediol, Cerium (IV), Acetic Acid medium, Oxidation, Kinetics.

Introduction:-

Oxidation of alcohols by Ce(IV) has been well studied¹. Kinetics of oxidation of vicinal glycols has been investigated by a no. of workers².

³Khanna and Behra studied the oxidation of butane 1, 4-diol and pentane 1,5-diol by ceric sulphate in aqueous sulphuric acid medium and reported no complexation between the oxidant and diol.

⁴Methotra and others after investigating the oxidation of series of diols by Mn(III) and Ce(IV), studied the oxidation of propane 1,3 and butane 1,4-diols by Ce(IV) and posulated C-H fission as the rate determining step.

⁵Wells investigated the oxidation of glycols by Mn(III) in aqueous perchloric acid medium and postulated Mn(III)-Pincacol-Complexes.

In view of conflicting observations it was found that worth while to investigate the oxidation of glycerol and 1,2-propanediol by Ce(IV) in aqueous acetic acid-perchloric acid medium. The present report deals with kinetic and mechanistic observations observed in the oxidation of glycerol and 1,2-propane diol.

Experimental:

All compounds used in the investigation are extrapure. A.R. acetic acid and perchloric acid are used for the present study.

Progress of Reaction: -

Aliquots of 5 c.c at various intervals of time are dumped into known excess of ferrous ammonium sulphate solution and the left over ferrous ammonium sulphate was titrated against standard dichromate with diphenylamine as an indicator.

Products have been identified glyceraldehyde for glycerol and 2-hydroxy propionaldehyde for 1,2-propane diol.

Results and Discussion:

Kinetics of Oxidation of Glycerol and 1,2-propanediol have been studied at various concentrations and results are given below.

Dependence on [Oxidant]:

It has been observed that the reaction is first order in oxidant.

The rate constants are unchanged with increase in concentration of oxidant.

Dependence on [Substrate]: Reaction is first order on substrate

Table-I Effect of Varying Substrate Concentration on the Reaction Rate**Conditions:-**

$[Ce^{+4}] = 0.005M$ $[HClO_4] = 0.5M$ Acetic acid=20% Temperature=35⁰c

Substrate	[Substrate] _M	K ₁ Min ⁻¹
Glycerol	0.0125	0.0008360
	0.0250	0.0035700
	0.1500	0.0105255
	0.2000	0.0255067
1,2-propanediol	0.05	0.0010431
	0.10	0.0019496
	0.15	0.0023763
	0.20	0.0122628

Dependence on [H^{*}] : It is found that the reaction is first order in [H^{*}]

Table-II Effect of Varying Acid Concentration on the Reaction Rate**Conditions:-**

[Substrate] =0.05M $[Ce^{+4}] = 0.005M$ $[HClO_4] = 0.5M$ Acetic acid =20% Temperature=35⁰c

Substrate	[HClO ₄] _M	K ₁ Min ⁻¹
Glycerol	0.50	0.003570
	0.75	0.005689
	1.00	0.009233
	1.50	0.016439
1,2 Propane diol	0.50	0.001043
	0.75	0.002025
	1.00	0.002838
	1.50	0.003129

Effect of Variation of solvent composition:

Table-III Effect of Varying Solvent Composition on the Reaction Rate**Conditions :-**[Substrate] =0.05M [Ce⁺⁴] =0.005M [HClO₄] =0.5M Temperature =35⁰c

Substrate	AcoH:H ₂ O	K ₁ Min ⁻¹
Glycerol	20:80	0.003570
	30:70	0.004693
	40:60	0.006250
	50:50	0.008191
1,2 –propanediol	20:80	0.001043
	30:70	0.001847
	40:60	0.003800
	50:50	0.005444

From the present study it is identified that the reaction is between positive ion and dipole. According to the theory postulated by Amis⁶, the rate of reaction increases with decrease in dielectric constant in these reactions. In this case the reactive cationic Ce (IV) species is important. Hence in these oxidations there is an increase in rate with decrease in dielectric constant.

Effect of addition of MnSO₄:-

As the concentration of MnSO₄ increases in case of Glycerol there is retardation observed. In case of 1,2 -propanediol as the concentration of MnSO₄ increases there is acceleration observed till [Mn²⁺] is 0.002M and later there is retardation.

Table – IV : Effect of [MnSO₄] on the Reaction Rate**Conditions :-**[Substrate] =0.05M [Ce⁺⁴] =0.005M [HClO₄] =0.5M Acetic acid =20% Temperature =35⁰c

Substrate	[MnSO ₄]M	K ₁ Min ⁻¹
Glycerol	Without Mn ⁺²	0.003570
	0.002	0.038016
	0.008	0.020518
1,2 – Propanediol	Without Mn ⁺²	0.001043
	0.001	0.016282
	0.002	0.022145
	0.004	0.014409

This has been observed by Radha Krishna Murti and others in the oxidation of lactic acid by Ce (IV). The acceleration may be ascribed in the reaction between Mn²⁺ and 1,2-propane diol, which later break down by Ce (IV) to form Mn³⁺ and 1,2-propane diol complex which is a slow step and leads to formation of products.

Effect of temperature :-

To determine the effect of temperature and to evaluate the activation parameters, reactions are carried out at 35⁰ C, 40⁰ C, 45⁰ C, 50⁰ C and rate constants are recorded.

Table-V Effect of Temperature on the Reaction Rate**Conditions :-**[Substrate]= 0.05M [Ce⁺⁴] = 0.005M [HClO₄] = 0.5M Acetic Acid = 20%

Substrate	Temperature (K)	K ₁ Min ⁻¹
Glycerol	308	0.00357
	313	0.02122
	318	0.02857
	323	0.06230
1,2 – Propanediol	308	0.00104
	313	0.00532
	318	0.01253
	323	0.01527

Nature of Ce (IV) species :

Ce (IV) in perchloric acid may exist as [Ce(H₂O)₈]⁴⁺, [Ce(OH)(H₂O)₇]⁺⁵ and [CeO Ce (H₂O)₇]⁺⁶. The first species seems to be an active oxidant. Such a reasoning has been done earlier by Ardon⁷ in the studies of oxidation of ethanol by Ce (IV).

In Ce(IV) oxidations the alcohol and Ce(IV) are quite stable. There are plenty of evidences postulated earlier regarding complex formation in alcohols by Ce(IV).

Activation Parameters**Glycerol – Ceric Ammonium Nitrate**

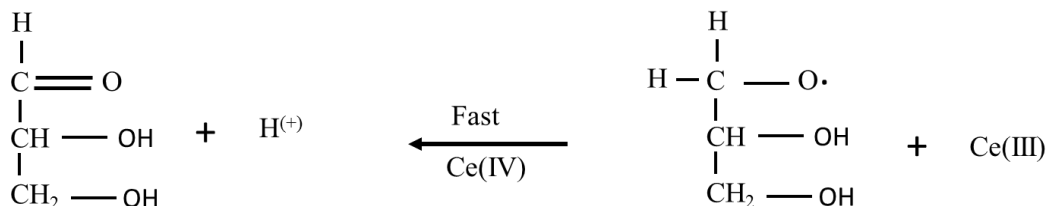
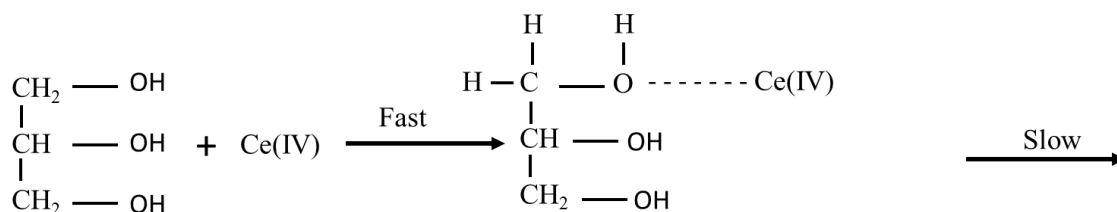
ΔE^\ddagger (K.cal/mole)	$\log_{10}A$	ΔH^\ddagger	ΔS^\ddagger
28.60038	17.84488	27.98838	-9.32358

1,2 – Propane diol – Ceric Ammonium Nitrate

ΔE^\ddagger (K.cal/mole)	$\log_{10}A$	ΔH^\ddagger	ΔS^\ddagger
20.59224	11.62870	19.98027	-9.6155

The observed reactivity is Glycerol > 1,2-propane diol. The difference is due to the end hydroxy methyl groups in glycerol and methyl group in 1,2-propane diol. Hydroxy methyl group is an electron attracting and favours O-H bond cleavage easily compared to methyl group which is an electron releasing.

The experimental data indicates that the reaction is first order in oxidant, in substrate and in [H⁺]. Solvent effect indicates reaction rate increases with decrease in D (Dielectric constant).

Mechanism: -

Similar mechanism holds good for 1,2-propanediol also.

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