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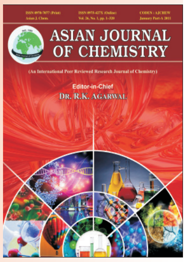

Kinetics and Mechanism of Ru(III) Catalyzed Periodate Oxidation of Methyl Glycol and Diacetone Alcohol in Perchloric Acid

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Kinetics of oxidation of methyl glycol (MG) and diacetone alcohol (DAA) by periodate in the presence of ruthenium(III) chloride as homogeneous catalyst have been studied in acidic medium. The results indicate zero order dependence of the reaction on [IO_4^-] while first order kinetics with respect to [Ru(III)] was observed. First order in both [MG] and [DAA] was observed while positive effect of [H^+] was exhibited. Variation of ionic strength of the medium and addition of potassium chloride did not bring about any significant change in the rate of the reaction. Showing thus zero effect of ionic strength and added chloride ions. A suitable mechanism consistent with kinetic results has been proposed and rate law has been deduced for the title reactions.

Keywords: Kinetics, Mechanism, Methyl glycol, Diacetone alcohol, Periodate.

INTRODUCTION

In recent years, the use of transition metals ions, such as osmium, iridium, palladium and ruthenium either alone or as binary mixtures as catalysts in the oxidation of several redox processes is of considerable interest of these reactions. Ruthenium(III) chloride utility as nontoxic and homogeneous catalyst has been known[1-7], but less attention has been paid to explore the catalytic role of Ru(III) with periodate[7-10] as an oxidant. Earlier, oxidation kinetics[11] of methyl glycol and diacetone alcohol by osmium tetroxide in alkaline medium have been reported. In view of less work on the periodate oxidation with industrically important substrates, there seems to be much exciting chemistry in further probing the oxidative capacity of periodate in the oxidation of methyl glycol and diacetone alcohol particularly in the presence of Ru(III) in perchloric acid medium. In present communication, a detailed kinetic studies based mechanistic steps in Ru(III) catalyzed periodate oxidation of methyl glycol (MG) and diacetone alcohol (DAA) have been reported.

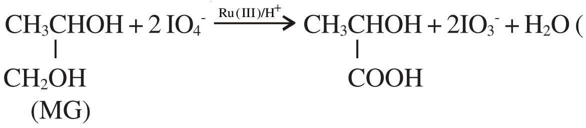
EXPERIMENTAL

Standard solutions of methyl glycol and diacetone alcohol (both of E. Merck) were prepared by directly weighing their samples and dissolving them in doubly distilled water. 1 g sample of ruthenium(III) chloride (Johnson & Matthey) was prepared in 100 mL of 0.01 mol dm^{-3} HCl solution and there after it was diluted to 1 L in which its final strength was noted. Sodium metaperiodate (Koch-Light) was used after recrystallization and its stock solution, prepared in doubly distilled water was standardized iodometrically. All other chemicals used were of AR grade. Perchloric acid (70 % of E. Merck) was used as source of H^+ ions and sodium perchlorate (E. Merck) was used to vary the ionic strength of the medium.

Kinetic measuremental: A thermostatic water bath was used to maintain the desired temperature within ± 0.1 °C. The appropriate volumes of methyl glycol or diacetone alcohol, $HClO_4$, Ru(III) chloride and required volume of water were taken in a black coated reaction vessel which was thermostated at 303 K for thermal equilibrium. After about 0.5 h when the reaction mixture had attained the temperature of the experiment, the requisite volume of periodate solution, also thermostated at the same temperature, was added rapidly into the reaction vessel to make the total volume of the reaction mixture 100 mL. Immediately 5 mL aliquot of reaction mixture was taken out and poured into acidified potassium iodide solution.

The iodine liberated in equivalent amount was estimated with standard solutions of sodium thiosulphate and the titre volume at zero time was noted. Similar reading were recorded at different intervals of time by estimating 5 mL of reaction mixture iodometrically and thus progress of the reaction was monitored periodate. Each kinetic run was studied for two half life of the reaction. The rate of the reaction (-dc/dt) was determined by the slope of the tangent drawn at a fixed [IO_4^-] in each kinetic run. The order of the reaction in each kinetic run was calculated by log-log plot of (-dc/dt) *versus* concentration of reactants.

Stoichiometry and product analysis: Different sets of reaction mixture under the conditions $[IO_4^-] >> [Substrate]$ were equilibrated at 303 K for 72 h. Estimation of unconsumed IO_4^- in each set revealed that 2 and 4 moles of periodate were consumed in oxidation of each mole of methyl glycol and diacetone alcohol, respectively. Accordingly following stoichiometric equations can be formulated as (1) and (2).



$$\underset{\substack{|\\ CH_2OH \\ (MG)}}{CH_3CHOH} + 2\,IO_4^- \xrightarrow{Ru(III)/H^+} \underset{\substack{|\\ COOH}}{CH_3CHOH} + 2IO_3^- + H_2O \quad (1)$$

$$\underset{(DAA)}{(CH_3)C(OH)CH_2COCH_3} + 4IO_4^- \xrightarrow{Ru(III)/H^+} CH_3COCH_3 + CH_3COOH + CO_2 + 4IO_3^- + H_2O \quad (2)$$

The corresponding oxidation products of MG and DAA were identified by spot tests[12]. The presence of acetone in equation (2) was also confirmed by its 2,4-dinitrophenyl hydrazone derivative.

RESULTS AND DISCUSSION

The kinetics of oxidation of methyl glycol (MG) and diacetone alcohol (DAA) by periodic in the presence of little [Ru(III)] in aqueous acidic solution were investigated at several initial concentrations of all the reactants at 303 K. The value of initial rate (-dc/dt) in each kinetic run was calculated from the slope of the tangent of the straight line obtained on plotting unconsumed $[IO_4^-]$ *versus* time at, fixed $[IO_4^-]$ except in $[IO_4^-]$ variation when tangent has been drawn at a fixed time. The initial rate (-dc/dt) thus obtained was used to determine the order of reaction with respect to each reactant.

On varying $[IO_4^-]$ rate of reaction (-dc/dt) remains practically constant in oxidation of each of MG and DAA, showing thus zero-order kinetics in [periodate] (Table-1). At fixed concentrations of all other reagents, increase in [MG] and [DAA] increased the value of (-dc/dt) linearly, showing first-order in both [MG] and [DAA]. This was further confirmed by slopes (k_1) of straight lines (Fig. 1) obtained on plotting (-dc/dt) *versus* [MG] or [DAA], in agreement with experimental k_1 values (where $k_1 = (-dc/dt)/[Substrate]$). The value of (-dc/dt) also increased linearly with increase in [Ru(III)] in oxidation of both GM and DAA, indicating thus first-order in [Ru(III)]. The graphical k_1 values (obtained from the slope of the plot between (-dc/dt) and [Ru(III)] were found in close agreement with corresponding experimentally observed k_1 value (Table-1), showing and confirming first-order in [Ru(III)] in oxidation of both MG and DAA (Fig. not shown here).

Table-2 contains the results of variation of $[H^+]$ and temperature as well as effect due to addition of KCl. Increase in $[H^+]$ increased the rate non-linearly, showing positive effect of $[H^+]$ on the rate of oxidation of both MG and DAA. Addition of KCl to the reaction mixture was found to have no significant effect, indicating zero effect of $[Cl^-]$ on rate oxidations. Variation of ionic strength from 1.20×10^{-2} M to 6×10^{-2} M (in case of MG) and from 2.33×10^{-2} M to 7.33×10^{-2} M (in case of DAA) did not bring about significant change in oxidation of their rates, showing negligible effect of ionic strength on rate of

TABLE-1
EFFECT OF VARIATION OF [REACTANTS] ON RATE OF REACTION AT 30 °C
$[HClO_4] = 1.00 \times 10^{-2}$ mol dm^{-3} [MG] AND 2×10^{-2} mol dm^{-3} [DAA], $[KCl] = 1.00 \times 10^{-3}$ mol dm^{-3}

$[NaIO_4] \times 10^3$ (mol dm^{-3})	$[Substrate] \times 10^2$ (mol dm^{-3})	$[Ru(III)] \times 10^6$ (mol dm^{-3})	$[-dc/dt] \times 10^7$ (mol dm^{-3} s^{-1})		$k_1^a \times 10^6$ (s^{-1})	
			MG	DAA	MG	DAA
0.80	2.00	9.60	0.65	1.72	–	–
1.00	2.00	9.60	0.64	1.68	–	–
1.25	2.00	9.60	0.67	1.70	–	–
1.67	2.00	9.60	0.63	1.74	–	–
2.50	2.00	9.60	0.68	1.64	–	–
4.00	2.00	9.60	0.64	1.72	–	–
1.00	0.50	9.60	0.17	0.42	3.40	8.40
1.00	1.00	9.60	0.33	0.86	3.30	8.60
1.00	1.50	9.60	0.49	1.29	3.26	8.60
1.00	2.00	9.60	0.66	1.74	3.30	8.70
1.00	2.50	9.60	0.84	2.12	3.36	8.48
1.00	3.00	9.60	1.02	2.60	3.40	8.66
1.00	2.00	1.20^b	–	0.22	–	18.33^c
1.00	2.00	1.60^b	0.11	–	6.87	–
1.00	2.00	1.80^b	–	0.32	–	17.78^c
1.00	2.00	2.40^b	–	0.44	–	18.33^c
1.00	2.00	3.20^b	0.21	–	6.56	–
1.00	2.00	3.60^b	–	0.63	–	17.50^c
1.00	2.00	4.80^b	0.31	0.85	6.46	17.71^c
1.00	2.00	6.00^b	–	1.08	–	18.00^c
1.00	2.00	6.40^b	0.42	–	6.40	–
1.00	2.00	8.00^b	0.53	–	6.62	–
1.00	2.00	9.60^b	0.64	–	6.67	–

a → $k_1 \times 10^6 = \frac{(-dc/dt)}{[Substrate]} = k_1 \times 10^6\ s^{-1}$, b → $k_1 \times 10^3 = \frac{(-dc/dt)}{[Ru(III)]} = k_1 \times 10^3\ s^{-1}$ and c → $[HClO_4] = \frac{(-dc/dt)}{[Ru(III)]} = 1.00 \times 10^{-2}$ mol dm^{-3}

oxidation. Rate measurements at 298, 303, 308 and 313 K in oxidation of MG and DAA led to calculate energy of activation (E_a), entropy of activation ($DS^{\#}$), free energy of activation ($\Delta G^{\#}$) whose values are given in Table-3.

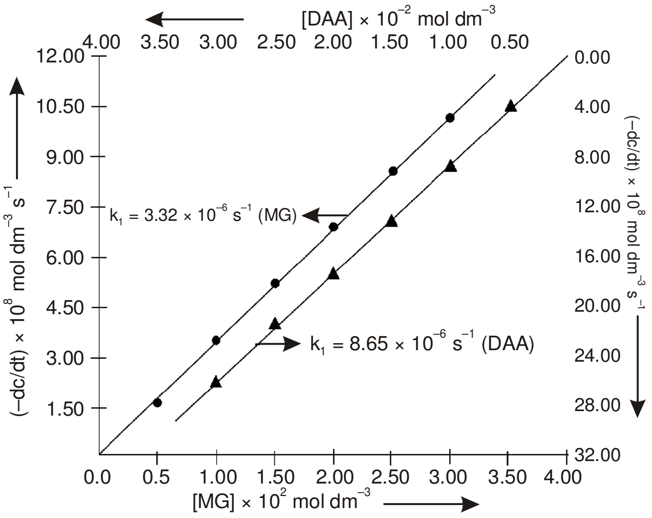


Fig. 1. Plot of (-dc/dt) *vs.* [MG] or [DAA] under the condition of Table-1

In aqueous solution (pH = 0 to 7) of acid periodic acid exists as equilibrium between free acid (H_5IO_6) and its various ions.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \qquad (a)$$

$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O \qquad (b)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{-2} + H^+ \qquad (c)$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{-3} + H+ \qquad (d)$$

The mono anion $H_4IO_6^-$ is largly dehydrated to tetrahedral IO_4^-. The activity of periodate ion as an oxidizing agent varies greatly as the function of pH and this is expected because of accompanying change in the degree of ionization of periodate[13,14]. Thus in acidic solution H_5IO_6, $H_4IO_6^-$, IO_4^-, $H_3IO_6^{-2}$ and $H_2IO_6^{-3}$ can act as oxidizing species. Of these species, possibility of $H_4IO_6^-$, $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ as oxidizing species is ruled out as these will require negative effect of $[H^+]$ contrary to the observed positive effect of $[H^+]$ on the rate. H_5IO_6 will also require decreasing effect of $[H^+]$ and hence it is also ruled out as oxidizing species. Now the only choice left is IO_4^- which when taken as oxidizing species explains all the observed kinetic results. Since order in [periodate] is zero which requires its involvement in fast reaction after slow and rate determining step, hence it matters little which one of the aforesaid species is involved in fast step.

It has been reported[15] that in dilute HCl solution ruthenium(III) chloride exists as $[RuCl_6]^{3-}$, which is involved in the following equilibrium.

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5(H_2O)]^{2-} + Cl^- \qquad (e)$$

Thus either of $[RuCl_6]^{3-}$ or $[RuCl_5(H_2O)]^{2-}$ may be effective catalytic species. It has also been reported that in acidic medium periodate ion rapidly converts[16] Ru(III) to Ru(VIII) according to the reaction given below which is faster than periodate oxidations.

$$2\,Ru(III) + 5\,IO_4^- + 10\,H^+ \rightarrow 2\,Ru(VIII) + 5IO_3^- + 5H_2O \quad (f)$$

TABLE-2
EFFECT OF VARIATION OF [HClO$_4$], TEMPERATURE AND ADDITION OF KCl ON THE RATE OF OXIDATION OF MG AND DAA AT 30 °C (UNLESS OTHERWISE STATED) $[NaIO_4] = 1 \times 10^{-3}$ mol dm^{-3}, [Substrate] = 2×10^{-2} mol dm^{-3}, & [Ru(III)] = 9.60×10^{-6} mol dm^{-3}

Temperature (°C)	[HClO$_4$] × 10^{2} (mol dm^{-3})	[KCl] × 10^{3} (mol dm^{-3})	[–dc/dt] × 10^{7} (mol dm^{-3} s^{-1})	
			MG	DAA
25	1.00	1.00	0.40	1.02[a]
30	1.00	1.00	0.64	1.70[a]
35	1.00	1.00	1.08	2.36[a]
40	1.00	1.00	1.38	3.96[a]
30	0.50	1.00	0.48	0.76
30	1.00	1.00	0.64	1.08
30	1.50	1.00	0.84	1.36
30	2.00	1.00	1.04	1.70
30	2.50	1.00	1.26	1.84
30	3.00	1.00	1.48	2.16
30	1.00	0.50	0.64	1.72[a]
30	1.00	1.00	0.67	1.66[a]
30	1.00	1.50	0.62	1.70[a]
30	1.00	2.00	0.68	1.68[a]
30	1.00	2.50	0.65	1.72[a]
30	1.00	3.00	0.66	1.74[a]

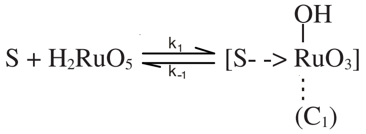
a → [HClO$_4$] = 2×10^{-2} mol dm^{-3}

TABLE-3
ACTIVATION PARAMETERS IN Ru(III) CATALYSED OXIDATION OF METHYL GLYCOL (MG) AND DIACETONE ALCOHOL (DAA) BY ACIDIC SOLUTION OF SODIUM METAPERIODATE AT 30 °C

Substrate	k_r (mol^{-2} L^{2} s^{-1})	log A	E_a (kcal/mol)	$\Delta H^{\#}$ (kcal/mol)	$\Delta S^{\#}$ eu	$\Delta G^{\#}$ (kcal/mol)
MG	6.03	12.78	16.65	16.04	–2.07	16.67
DAA	19.95	12.59	15.74	15.13	–2.94	16.02

Ru(VIII) is reported[17] to be present in the form of H_2RuO_5 or $RuO_3(OH)_2$ in the acidic medium. Hence, here H_2RuO_5 is assumed to be effective catalytic species in the present investigation. Thus catalytic action of Ru(III) occurs through Ru(VIII) centre.

On the basis of IO_4^- and H_2RuO_5 as oxidizing and catalytic species, respectively and considering other kinetic results and stoichiometric data, the following reaction mechanism is suggested for oxidation of MG and DAA as both exhibit common kinetic results. Here, S stands for substrates (MG and/or DAA).



$$S + H_2RuO_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [S\text{-}\text{-}> \overset{\overset{OH}{|}}{\underset{\underset{(C_1)}{\vdots}}{RuO_3}}] \qquad (i)$$

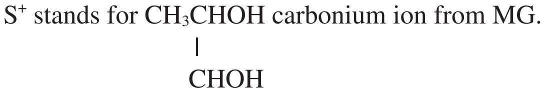
$$C_1 + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [C_2]^+ \qquad (ii)$$

$$[C_2]^+ \xrightarrow[\text{slow}]{k_d} [OH\text{-}RuO_3(H)] + S^+ + H_2O \qquad (iii)$$

$$[OH\text{-}RuO_3(H)] + IO_4^- \longrightarrow H_2RuO_5 + IO_3^- \qquad (iv)$$

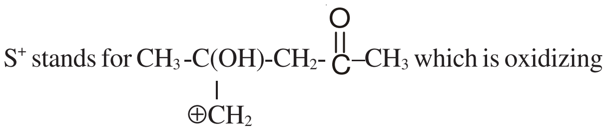
$$S^+ + IO_4^- \longrightarrow RCOOH + IO_3^- + H^+ \qquad (v)$$

where R is CH_3CHOH - group in MG and in step (v)



S^+ stands for $CH_3\underset{\underset{CHOH}{|}}{CHOH}$ carbonium ion from MG.

In case of DAA,



S^+ stands for $CH_3\text{-}\underset{\underset{\oplus CH_2}{|}}{C(OH)}\text{-}CH_2\text{-}\overset{\overset{O}{||}}{C}\text{–}CH_3$ which is oxidizing

in step (vi)

$$S^+ + 3IO_4^- \longrightarrow CH_3COCH_3 + CH_3COOH + 3IO_3^- + H^+ + CO_2 \qquad (vi)$$

Thus in oxidation of MG and DAA, n moles of IO_4^- are consumed where n = 2 in MG and 4 in DAA oxidation.

Considering aforesaid reaction steps and stoichiometry of the reactions, rate of reactions can be written in term of rate of loss of $[IO_4^-]$ as eqn (1) -

$$-\frac{d[IO_4^-]}{dt} = nk_d\,[C_2]^+ \qquad (1)$$

By applying the law of equilibrium in step (II) -

$$[C_2] = K_2\,[C_1]\,[H]^+ \qquad (2)$$

On applying steady state to $[C_1]$ and considering steps (i) and (ii),

$$[C_2] = \frac{k_1[S][H_2RuO_5]}{k_{-1} + k_2[H]^+} \qquad (3)$$

On substituting the value of $[C_1]$ from eqn (3) in eqn (2)

$$[C_2] = \frac{k_1K_2[S][H_2RuO_5][H]^+}{k_{-1} + k_2[H]^+} \qquad (4)$$

where $K_2 = k_2/k_{-2}$

By considering eqn (1) and (4) together

$$-\frac{d[IO_4^-]}{dt} = \frac{nk_dk_1K_2[S][H]^+[H_2RuO_5]}{k_{-1} + k_2[H]^+} \qquad (5)$$

The rate law (5) satisfies and explains all the observed kinetic results. It explains positive effect of $[H]^+$ and zero effect of $[Cl^-]$ on the rate of the reaction.

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