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Kinetics and mechanism of uncatalysed and ruthenium(III) catalysed oxidation of allyl alcohol by diperiodatoargentate(III) in aqueous alkaline medium

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ABSTRACT: The oxidation of allyl alcohol by diperiodatoargentate(III) (DPA) is carried out both in the absence and presence of ruthenium(III) catalyst in alkaline medium at 298 K and a constant ionic strength of 1.1 mol dm^{-3} was studied spectrophotometrically. The oxidation products in both the cases were acrolein and Ag(I), identified by spectral studies. The stoichiometry is same in both the cases, that is, [AA]/[DPA] = 1:1. The reaction shows first order in [DPA] and has less than unit order dependence each in both [AA] and [Alkali] and retarding effect of [IO_4^-] in both the catalysed and uncatalysed cases. The order in [Ru(III)] is unity. The active species of DPA is understood to be as monoperiodatoargentate(III) (MPA) in both the cases. The uncatalysed reaction in alkaline medium has been shown to proceed via a MPA–allyl alcohol complex, which decomposes in a rate determining step to give the products. In catalysed reaction, it has been shown to proceed via a Ru(III)-allyl alcohol complex, which further reacts with one molecule of MPA in a rate determining step to give the products. The reaction constants involved in the different steps of the mechanisms were calculated for both reactions. The catalytic constant (K_c) was also calculated for catalysed reaction at different temperatures. The activation parameters with respect to slow step of the mechanisms were computed and discussed for both the cases. The thermodynamic quantities were also determined for both reactions.

KEYWORDS: allylalcohol; diperiodatoargentate(III); Ru(III)catalysis; oxidation; kinetics

INTRODUCTION

Allyl alcohol (AA) finds a number of industrial applications in the preparation of resin, plasticizers, pharmaceuticals and many organic compounds. Kinetic studies on the oxidation of AA with different oxidants such as potassium permanganate, chromic acid, vanadium(V), chloramine-T, diperiodatonickelate(IV), and so on have been reported.[1–3] Different products were obtained with different oxidants[4,5] for the oxidation of AA.

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential[6] 1.74 V. It is widely used as a volumetric reagent for the determination of various organic and inorganic species.[7] Jaya Prakash Rao *et al*.[8] have used DPA as an oxidizing agent for the kinetics of oxidation of various organic substrates. They normally found that order with respect to both oxidant and substrate was unity and [OH$^-$] was found to enhance the rate of reaction. It was also observed that they did not arrive the possible active species of DPA in alkali and on the other hand they proposed mechanisms by generalizing the DPA as $[Ag(HL)L]^{(x+1)-}$. However, Kumar *et al*.[9] put an effort to give an evidence for the reactive form of DPA in the large scale of alkaline pH. In the present investigation, we have obtained the evidence for the reactive species for DPA in alkaline medium.

In recent years, the use of transition metal ions such as osmium, ruthenium and iridium, either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest.[10] The ruthenium(III) acts as a catalyst in the oxidation of many organic and inorganic substrates.[11] Ruthenium(III) catalysis in redox reactions involve different degrees of complexity, due to formation of different intermediate complexes, and to different oxidation states of ruthenium. The use of different catalysts, gave different oxidation products[12] in case of AA oxidation. We have observed that ruthenium(III) catalyses the oxidation of AA by DPA in alkaline medium in micro amounts. In order to understand the active species of oxidant and catalyst, and to propose the appropriate mechanisms, the title reaction is investigated in detail, in view of various mechanistic possibilities.

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EXPERIMENTAL

All chemicals used were of reagent grade and double distilled water was used throughout the work. The AA (Koch Light) was purified by standard procedure and its concentration in aqueous solution was checked[13] by addition of excess of chloramine-T followed by iodometric estimation of the excess. A standard stock solution of Ru(III) was prepared by dissolving $RuCl_3$ (S.D. Fine Chemicals) in $0.20\,mol\,dm^{-3}$ HCl and the concentration was ascertained[14] by EDTA titration. KNO_3 and KOH (BDH) were used to maintain ionic strength and alkalinity of the reaction, respectively. Aqueous solution of $AgNO_3$ was used to study the product effect, Ag(I). A stock standard solution of IO_4^- was prepared by dissolving a known weight of KIO_4 (Riedel-de Haen) in hot water and used after keeping for 24 h. Its concentration was ascertained iodometrically[15] at neutral pH maintained using phosphate buffer. The temperature was maintained constant to within ±0.10 °C.

Preparation of DPA

DPA was prepared by oxidizing Ag(I) in presence of KIO_4 as described elsewhere:[16] the mixture of 28 g of KOH and 23 g of KIO_3 in 100 cm^3 of water along with 8.5 g $AgNO_3$ was heated just to boiling and 20 g of $K_2S_2O_8$ was added in several lots with stirring then allowed to cool. It was filtered through a medium porosity fritted glass filter and 40 g of NaOH was added slowly to the filtrate, whereupon a voluminous orange precipitate agglomerates. The precipitate was filtered as above and washed three to four times with cold water. The pure crystals were dissolved in 50 cm^3 water and warmed to 80 °C with constant stirring thereby some solid was dissolved to give a red solution. The resulting solution was filtered when it was hot and on cooling at room temperature, the orange crystals separated out and were recrystallised from water.

The complex was characterized from its U.V. spectrum, exhibited three peaks at 216, 255 and 362 nm. These spectral features were identical to those reported earlier for DPA.[16] The magnetic moment study revealed that the complex is diamagnetic. The compound prepared was analyzed[17] for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess KI was added to the filtrate for IO_4^-. The aqueous solution of DPA was used for the required [DPA] in the reaction mixture. During the kinetics a constant concentration *viz.* $1 \times 10^{-5}\,mol\,dm^3$ of KIO_4 was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of AA by periodate was tested and found that there was no significant interference due to KIO_4 under experimental condition. The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under nitrogen and in presence of air was observed. In the view of ubiquitous contamination of CO_3^{2-}, its effect was also studied on the rate of reaction. Added carbonate had no effect on the reaction rate.

Kinetics

The kinetic measurements were performed on a Varian CARY 50 Bio UV-Vis spectrophotometer. The kinetics was followed under pseudo first order condition where [AA] > [DPA] both in uncatalysed and catalysed reaction at 25 ± 0.1 °C, unless specified. In the absence of catalyst the reaction was initiated by mixing the DPA to AA solution which also contained required concentration of KNO_3, KOH and KIO_4. The reaction in the presence of catalyst was initiated by mixing DPA to AA solution which also contained required concentration of KNO_3, KOH, KIO_4 and Ru(III) catalyst. The progress of reaction was followed spectrophotometrically at 360 nm by monitoring decrease in absorbance due to DPA with the molar absorbancy index, 'ε' to be $13{,}900 \pm 100\,dm^3\,mol^{-1}\,cm^{-1}$ in both catalysed and uncatalysed reaction. It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength.

The pseudo-first order rate constants, ('k_u or k_c'), in both the cases were determined from the log(absorbance) *versus* time plots. The plots were linear up to 85% completion of reaction (Fig. 1 for uncatalysed). The orders for various species were determined from the slopes of plots of log (k_u or k_c) *versus* respective concentration of species except for [DPA] in which non-variation of 'k_u or k_c' was observed as expected to the

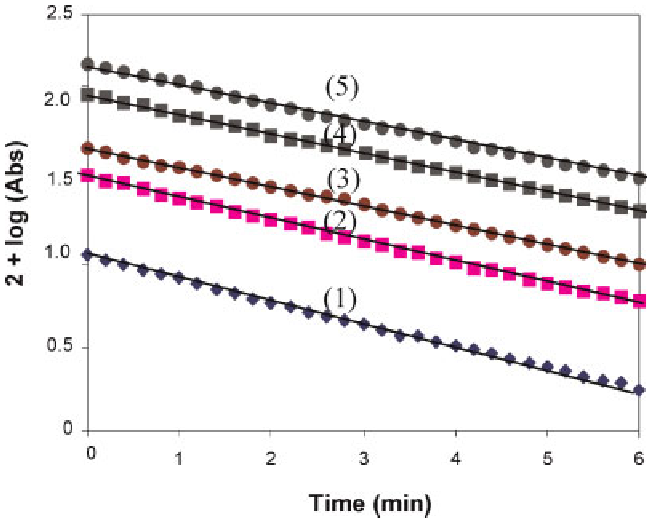


Figure 1. First order plots for the oxidation of allyl alcohol by DPA in aqueous alkaline medium at 25 °C. 10^5 [DPA] ($mol\,dm^{-3}$); (1) 1.0; (2) 3.0; (3) 5.0; (4) 8.0; (5) 10.0

reaction condition. The rate constants were reproducible to within ±5%. Regression analysis of experimental data to obtain regression coefficient r and the standard deviation *S*, of points from the regression line, was performed with the Microsoft office Excel-2003 programme.

RESULTS

Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPA to AA in presence of constant amount of OH^-, KNO_3 in uncatalysed reaction and a constant amount Ru(III) in catalysed reaction were kept for 3 h in closed vessel under nitrogen atmosphere. The remaining concentration of DPA was estimated by spectrophotometrically at 360 nm. Under the condition where $[AA] > [DPA]$ the unreacted AA was estimated[13] as mentioned above. The results indicate that 1:1 stoichiometry for both the reactions as given in Eqn (1).

$$\begin{aligned} &CH_2 = CH - CH_2OH + [Ag(H_2IO_6)(H_2O)] \\ &\quad + 2OH^- \xrightarrow{Ru(III)} CH_2 = CH - CHO \\ &\quad + Ag(I) + H_2IO_6^{3-} + 4H_2O \end{aligned} \qquad (1)$$

The stoichiometric ratio in both the cases suggests that the main product was acrolein, which was identified by spot test.[18] The nature of aldehyde was confirmed by its IR spectrum showed a carbonyl stretching at 1715 cm^{-1} and −CH stretching at 2854 cm^{-1} thus confirming the presence of acrolein.

Reaction orders

As the diperiodatoargentate(III) oxidation of AA in alkaline medium proceeds with a measurable rate in the absence of Ru(III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions, so $k_C = k_T - k_U$. Hence the reaction orders have been determined from the slopes of log k_C *versus* log (concentration) plots by varying the concentrations of AA, IO_4^-, OH^- and catalyst (Ru(III)), in turn, while keeping others constant. The order in DPA was unity between the concentration was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed AA, KOH and KNO3 in both cases of uncatalysed and catalysed reactions. Linearity of the plots of log (absorbance) *versus* time up to 85% completion of the reaction indicates a reaction order of unity in [DPA]. This was also confirmed by varying of [DPA], which did not result in any change in the pseudo first order rate constants, k_u (Table 1), k_c (Table 3; Ru(III)). In case uncatalysed reaction the AA concentration was varied in the range 1.0×10^{-3} to 1.0×10^{-2} mol dm^3 at 25 °C while keeping other reactant concentrations and conditions constant. The k_u values increased with the increase in concentration

Table 1. Effect of [DPA], [AA], $[OH^-]$ and $[IO_4^-]$ on the oxidation of allyl alcohol by DPA in alkaline medium at 25 °C, $I = 1.10$ mol dm^{-3}

10^5 [DPA] (mol dm^{-3})	10^2 [AA] (mol dm^{-3})	$[OH^-]$ (mol dm^{-3})	10^5 $[IO_4^-]$ (mol dm^{-3})	10^3k_u (s^{-1}) Found	10^3k_u (s^{-1}) Calculated
1.0	1.0	0.5	1.0	2.70	2.71
3.0	1.0	0.5	1.0	2.72	2.71
5.0	1.0	0.5	1.0	2.81	2.71
8.0	1.0	0.5	1.0	2.70	2.71
10	1.0	0.5	1.0	2.72	2.71
5.0	0.1	0.5	1.0	0.73	0.69
5.0	0.3	0.5	1.0	1.60	1.55
5.0	0.5	0.5	1.0	2.10	2.05
5.0	0.8	0.5	1.0	2.54	2.51
5.0	1.0	0.5	1.0	2.81	2.71
5.0	1.0	0.05	1.0	1.47	1.44
5.0	1.0	0.08	1.0	1.79	1.79
5.0	1.0	0.1	1.0	1.96	1.95
5.0	1.0	0.3	1.0	2.52	2.55
5.0	1.0	0.5	1.0	2.81	2.71
5.0	1.0	0.5	1.0	2.81	2.71
5.0	1.0	0.5	3.0	2.30	2.23
5.0	1.0	0.5	5.0	2.01	1.90
5.0	1.0	0.5	8.0	1.70	1.62
5.0	1.0	0.5	10.0	1.51	1.45

Table 2. Thermodynamic activation parameters for the oxidation of allyl alcohol by DPA in alkaline medium with respect to the slow step of Scheme 1

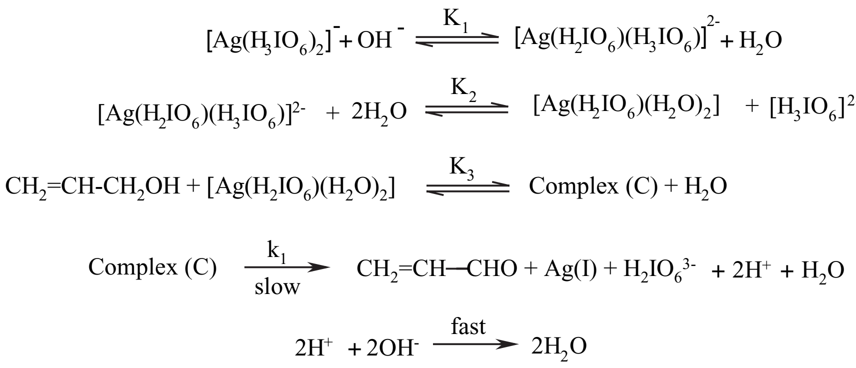
Temperature(K)	$10^3 k_1$ (s^{-1})	Parameters	Values
(A) Effect of temperature		(B) Activation parameters (Scheme 1)	
298	4.01	E_a (kJ mol^{-1})	53.6 ± 2.3
303	5.95	$\Delta H^{\#}$ (kJ mol^{-1})	51.1 ± 2.2
308	8.47	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	-118 ± 5
313	11.3	$\Delta G^{\#}$ (kJ mol^{-1})	86.5 ± 3.5
		log A	7.0 ± 0.3
Temperature (K)	**K_1 (dm^3 mol^{-1})**	**$10^4 K_2$ (mol dm^{-3})**	**$10^{-2} K_3$ (dm^3 mol^{-1})**
(C) Effect of temperature to calculate K_1, K_2 and K_3 for the oxidation of allyl alcohol by diperiodatoargentate (III) in alkaline medium			
298	0.17 ± 0.008	2.99 ± 0.12	3.14 ± 0.13
303	0.13 ± 0.006	7.29 ± 0.32	1.40 ± 0.05
308	0.11 ± 0.005	15.2 ± 0.60	0.87 ± 0.04
313	0.10 ± 0.004	25.3 ± 1.02	0.65 ± 0.03
Thermodynamic quantities	**Values from K_1**	**Values from K_2**	**Values from K_3**
(D) Thermodynamic quantities using K_1,K_2 and K_3			
ΔH (kJ mol^{-1})	-27.4 ± 1.2	111 ± 5.0	-80.6 ± 3.8
ΔS (JK^{-1} mol^{-1})	-107.1 ± 5.0	306 ± 14	-222 ± 10
ΔG_{298} (kJ mol^{-1})	4.4 ± 0.2	20.1 ± 0.8	-14.2 ± 0.5

[DPA] = 5.0×10^{-5}; [AA] = 1.0×10^{-2}; [OH$^-$] = 0. 5;[IO$_4$] = 1.0×10^{-5} mol dm^{-3}.

of AA indicating an apparent less than unit order dependence on [AA] (Table 1). In case catalysed reaction the AA concentration was varied in the range 5.0×10^{-4} to 5.0×10^{-3} mol dm^{-3} at 25 °C while keeping other reactant concentrations and conditions constant. The k_c values increased with the increase in concentration of AA indicating an apparent less than unit order dependence on [AA] (Table 3). The effect of alkali on the reaction has

Table 3. Effect of [DPA], [AA], [OH$^-$] and [IO$_4^-$] on the ruthenium(III) catalysed oxidation of allyl alcohol by DPA in alkaline medium at 25 °C, I = 1.10 mol dm^{-3}

10^5 [DPA] (mol dm$^-$3)	10^3 [AA] (mol dm$^-$3)	[OH$^-$] (mol dm$^-$3)	10^5 [IO$_4$] (mol dm$^-$3)	10^6 [Ru(III)] (mol dm$^-$3)	10^2 k_T (s^{-1})	10^3 k_U (s^{-1})	10^2 k_C Found	10^2 k_C Found
1.0	1.0	0.5	1.0	3.0	1.10	1.08	0.99	0.95
3.0	1.0	0.5	1.0	3.0	1.10	1.15	0.98	0.95
5.0	1.0	0.5	1.0	3.0	1.08	1.16	0.96	0.95
8.0	1.0	0.5	1.0	3.0	1.09	1.17	0.97	0.95
10	1.0	0.5	1.0	3.0	1.09	1.18	0.97	0.95
5.0	0.5	0.5	1.0	3.0	0.68	0.55	0.62	0.64
5.0	0.8	0.5	1.0	3.0	0.93	0.88	0.84	0.85
5.0	1.0	0.5	1.0	3.0	1.08	1.16	0.96	0.95
5.0	3.0	0.5	1.0	3.0	1.51	1.40	1.37	1.42
5.0	5.0	0.5	1.0	3.0	1.70	1.85	1.52	1.58
5.0	1.0	0.05	1.0	3.0	0.41	0.65	0.34	0.34
5.0	1.0	0.08	1.0	3.0	0.55	0.78	0.47	0.47
5.0	1.0	0.1	1.0	3.0	0.63	0.86	0.54	0.53
5.0	1.0	0.3	1.0	3.0	0.92	0.95	0.82	0.84
5.0	1.0	0.5	1.0	3.0	1.08	1.16	0.96	0.95
5.0	1.0	0.5	0.5	3.0	1.22	1.45	1.08	1.06
5.0	1.0	0.5	0.8	3.0	1.11	1.25	1.00	0.99
5.0	1.0	0.5	1.0	3.0	1.08	1.16	0.96	0.95
5.0	1.0	0.5	3.0	3.0	0.78	0.98	0.68	0.68
5.0	1.0	0.5	5.0	3.0	0.60	0.95	0.50	0.52
5.0	1.0	0.5	1.0	0.8	0.38	1.16	0.27	0.27
5.0	1.0	0.5	1.0	1.0	0.48	1.16	0.36	0.35
5.0	1.0	0.5	1.0	3.0	1.08	1.16	0.96	0.95
5.0	1.0	0.5	1.0	5.0	1.55	1.16	1.43	1.42
5.0	1.0	0.5	1.0	8.0	2.36	1.16	2.24	2.23



$$[Ag(H_3IO_6)_2]^- + OH^- \overset{K_1}{\rightleftharpoons} [Ag(H_2IO_6)(H_3IO_6)]^{2-} + H_2O$$

$$[Ag(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \overset{K_2}{\rightleftharpoons} [Ag(H_2IO_6)(H_2O)_2] + [H_3IO_6]^{2-}$$

$$CH_2{=}CH\text{-}CH_2OH + [Ag(H_2IO_6)(H_2O)_2] \overset{K_3}{\rightleftharpoons} \text{Complex (C)} + H_2O$$

$$\text{Complex (C)} \xrightarrow[\text{slow}]{k_1} CH_2{=}CH{-}CHO + Ag(I) + H_2IO_6^{3-} + 2H^+ + H_2O$$

$$2H^+ + 2OH^- \xrightarrow{\text{fast}} 2H_2O$$

Scheme 1. Detailed scheme for the oxidation of allyl alcohol by alkaline diperiodatoargentate(III)

been studied for both the cases in the range of 0.05–0.50 mol dm^{-3} at constant concentrations of AA, DPA and a constant ionic strength of 1.10 mol dm^{-3} in uncatalysed reaction and at constant concentration of Ru(III) in catalysed reaction. The rate constants increased with increasing [alkali] and the order was found to be less than unity (Tables 1 and 3 Ru(III)) for both the cases.

Effect of periodate

In case of uncatalysed reaction periodate was varied from 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at constant [DPA], [AA] and ionic strength. It was observed that the rate constants decreased by increasing [IO_4^-] (Table 1).

In case of catalysed reaction periodate was varied from 5.0×10^{-6} to 5.0×10^{-5} mol dm^{-3} at constant [DPA], [AA] and ionic strength. It was observed that the rate constants also decreased by increasing [IO_4^-] (Table 3).

Effect of added products

Initially added products, Ag (I) and acrolein did not have any significant effect on the rate of reaction (for both the cases).

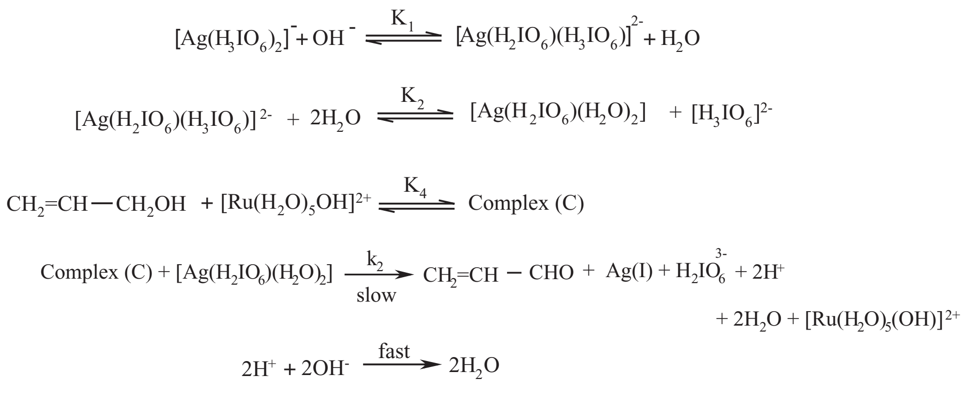
Effect of ionic strength (I) and dielectric constant of the medium (D)

It was found that ionic strength and dielectric constant of the medium have no significant effect on the rate of reaction in both the case of uncatalysed and catalysed reaction.

Effect of temperature

The influence of temperature on the rate of reaction was studied for uncatalysed reaction at 25, 30, 35 and 40 °C. The rate constants, (k_1), of the slow step of Scheme 1 were obtained from the slopes and the intercepts of the plots of $1/k_u$ *versus* 1/[AA], $1/k_u$ *versus* [$H_3IO_6^{2-}$] and $1/k_u$ *versus* 1/[OH^-] plots at four different temperatures. The values are given in Table 2. The activation parameters for the rate determining step were obtained by the least square method of plot of log k_1 *versus* $1/T$ and are presented in Table 2.

The influence of temperature on the rate of reaction was studied for catalysed reaction at 25, 30, 35 and 40 °C. The rate constants, (k_2), of the slow step of Scheme 2 were obtained from the slopes and the intercepts of the plots of [Ru(III)]/k_C *versus* 1/[AA], [Ru(III)]/k_C *versus* 1/[OH^-]



$$[Ag(H_3IO_6)_2]^- + OH^- \overset{K_1}{\rightleftharpoons} [Ag(H_2IO_6)(H_3IO_6)]^{2-} + H_2O$$

$$[Ag(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \overset{K_2}{\rightleftharpoons} [Ag(H_2IO_6)(H_2O)_2] + [H_3IO_6]^{2-}$$

$$CH_2{=}CH{-}CH_2OH + [Ru(H_2O)_5OH]^{2+} \overset{K_4}{\rightleftharpoons} \text{Complex (C)}$$

$$\text{Complex (C)} + [Ag(H_2IO_6)(H_2O)_2] \xrightarrow[\text{slow}]{k_2} CH_2{=}CH - CHO + Ag(I) + H_2IO_6^{3-} + 2H^+ + 2H_2O + [Ru(H_2O)_5(OH)]^{2+}$$

$$2H^+ + 2OH^- \xrightarrow{\text{fast}} 2H_2O$$

Scheme 2. Detailed scheme for the Ru(III) catalysed oxidation of allyl alcohol by alkaline diperiodatoargentate(III)

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Table 4. Thermodynamic activation parameters for the ruthenium(III) catalysed oxidation of allyl alcohol by DPA in aqueous alkaline medium with respect to the slow step of Scheme 2

Temperature (K)	10^{-3} k_2 ($dm^3 mol^{-1} s^{-1}$)	Parameters	Values
(A) Effect of temperature		(B) Activation parameters (Scheme 2)	
298	6.11	E_a ($kJ mol^{-1}$)	36.9 ± 1.4
303	8.55	$\Delta H^{\#}$ ($kJ mol^{-1}$)	34.4 ± 1.3
308	10.2	$\Delta S^{\#}$ ($JK^{-1} mol^{-1}$)	-56.5 ± 2.4
313	12.7	$\Delta G^{\#}$ ($kJ mol^{-1}$)	51.3 ± 2.3
		log A	10.2 ± 0.4
Temperature (K)	K_1 ($dm^3 mol^{-1}$)	$10^5 K_2$ ($mol dm^{-3}$)	$10^{-3} K_4$ ($dm^3 mol^{-1}$)
(C) Effect of temperature to calculate K_1, K_2 and K_3 for the Ru(III) catalysed oxidation of allyl alcohol by diperiodatoargentate (III) in alkaline medium			
298	0.34 ± 0.014	7.2 ± 0.3	2.11 ± 0.09
303	0.45 ± 0.020	3.8 ± 0.2	1.89 ± 0.08
308	0.52 ± 0.022	2.2 ± 0.1	1.52 ± 0.06
313	0.64 ± 0.028	1.4 ± 0.04	1.22 ± 0.05
Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_4
(D) Thermodynamic quantities using $K_{1,}K_2$ and K_4			
ΔH ($kJ mol^{-1}$)	30.7 ± 1.2	-83.7 ± 3.8	-28.8 ± 1.2
ΔS ($JK^{-1} mol^{-1}$)	94.9 ± 4.2	-361 ± 14	-33.1 ± 1.4
ΔG_{298} ($kJ mol^{-1}$)	2.6 ± 0.11	23.6 ± 1.0	-18.9 ± 0.7

$[DPA] = 5.0 \times 10^{-5}$; $[AA] = 1.0 \times 10^{-3}$; $[OH^-] = 0.5$; $[Ru(III)] = 3.0 \times 10^{-6} mol dm^{-3}$; $[IO_4] = 1.0 \times 10^{-5} mol dm^{-3}$.

and [Ru(III)]/k_C *versus* [$H_3IO_6^{2-}$] plots at four different temperatures. The values are given in Table 4. The activation parameters for the rate determining step were obtained by the least square method of plot of log k_2 *versus* 1/T and are presented in Table 4.

Test for free radicals (polymerisation study)

To test the intervention of free radicals, for both uncatalysed and catalysed reactions, the reaction mixture was mixed with acrylonitrile monomer and kept for 8 and 2 h, respectively, under nitrogen atmosphere. On dilution with methanol no precipitate resulted, suggesting the AA dehydrogenation is faster than a hypothetic radical interception.

Effect of [Ru(III)]

The [Ru(III)] concentrations was varied from 8.0×10^{-7} to 8.0×10^{-6} mol dm^{-3} range, at constant concentration of diperiodatoargentate(III), AA, alkali and ionic strength. The order in [Ru(III)] was found to be unity from the linearity of the plots of log k_C *versus* log [Ru(III)].

Catalytic activity

It has been pointed out by Moelwyn–Hughes[19] that in presence of the catalyst, the uncatalysed and catalysed reactions proceed simultaneously, so that

$$k_T = K_U - K_C[\text{catalyst}]^x \qquad (2)$$

Here k_T is the observed pseudo first-order rate constant in the presence Ru(III) catalyst, k_U the pseudo first-order rate constant for the uncatalysed reaction, K_C the catalytic constant and 'x' the order of the reaction with respect to [Ru(III)]. In the present investigations, x values for the standard run were found to be unity for Ru(III). Then the value of K_C is calculated using the equation,

$$K_C = \frac{k_T - k_U}{[\text{Catalyst}]^x} = \frac{k_C}{[\text{Catalyst}]^x} \quad (\text{Where, } k_T - k_U = k_C) \qquad (3)$$

The values of K_C were evaluated for Ru(III) catalyst at different temperatures and found to vary at different temperatures. Further, plots of log K_C *versus* 1/T were linear and the values of energy of activation and other activation parameters with reference to catalyst were computed. These results are summarized in Table 5. The value of K_C is 7.98×10^2 at 298 K.

DISCUSSION

In the later period of 20th century the kinetics of oxidation of various organic and inorganic substrates have been studied by Ag(III) species which may be due to its strong versatile nature of two electrons oxidant. Among the various species of Ag(III), $Ag(OH)_4^-$, diperiodatoargen-

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Table 5. Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values

Temperature (K)	$10^{-2}K_C$
298	7.98
303	10.9
308	14.0
313	16.0
E_a (kJ mol^{-1})	36.2
$\Delta H^{\#}$ (kJ mol^{-1})	33.7
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−75
$\Delta G^{\#}$ (kJ mol^{-1})	56
log A	9.2

$[DPA] = 5.0 \times 10^{-5}$; $[AA] = 1.0x10^{-3}$;$[OH^-] = 0.5$ mol dm^{-3}; $[IO_4] = 1.0 \times 10^{-5}$ mol dm^{-3}; $[Ru(III)] = 3.0 \times 10^{-6}$ mol dm^{-3}.

tate(III) and ethylenebis (biguanide), (EBS), silver(III) are of maximum attention to the researchers due to their relative stability.[20] The stability of $Ag(OH)_4^-$ is very sensitive towards traces of dissolved oxygen and other impurities in the reaction medium whereupon it had not drawn much attention. However, the other two forms of Ag(III)[8,9,21] are considerably stable; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

The literature survey[16] reveals that the water soluble diperiodatoargentate(III) (DPA) has a formula $[Ag(IO_6)_2]^{7-}$ with dsp^2 configuration of square planar structure, similar to diperiodatocopper(III) complex with two bidentate ligands, periodate to form a planar molecule. When the same molecule is used in alkaline medium, it is unlike to be existed as $[Ag(IO_6)_2]^{7-}$ as periodate is known to be in various protonated forms[22] depending on pH of the solution as given in following multiple equilibria (4–6).

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \tag{4}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \tag{5}$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \tag{6}$$

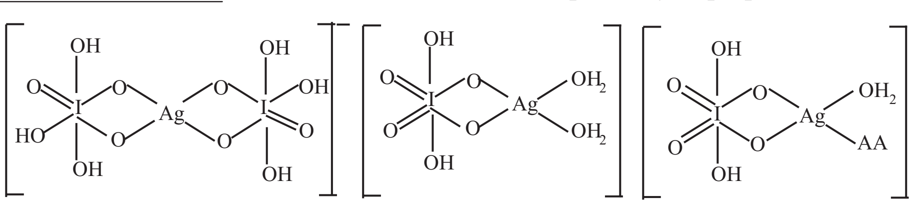
Periodic acid exists as H_5IO_6 in acid medium and as $H_4IO_6^-$ at pH 7. Thus, under the present alkaline conditions, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3}$. At higher concentrations, periodate also tends to dimerise.[23] On contrary, the Jayaprakash Rao *et al*.[8] in their recent past studies have proposed the DPA as $[Ag(HL)_2]^{x-}$ in which 'L' is a periodate with uncertain number of protons and 'HL' is a protonated periodate of uncertain number of protons. This can be ruled out by considering the alternative form[22] of IO_4^- at pH > 7 which is in the form $H_3IO_6^{2-}$ or $H_3IO_6^{3-}$. Hence, DPA could be as $[Ag(H_3IO_6)_2]^-$ or $[Ag(H_2IO_6)_2]^{3-}$ in alkaline medium. Therefore, under the present condition, diperiodatoargentate(III), may be depicted as $[Ag(H_3IO_6)_2]^-$. The similar speciation of periodate in alkali was proposed[24] for diperiodatonickelate(IV).

Mechanism for uncatalysed reaction

The reaction between DPA and AA in alkaline medium presents a 1:1 stoichiometry of oxidant to reductant. Since, the reaction was enhanced by $[OH^-]$, added periodate retarded the rate and first order dependency in [DPA] and fractional order in [AA] and $[OH^-]$, the following mechanism has been proposed which also explains all other experimental observations (Scheme 1).

Monoperiodatoargentate(III) (MPA) is considered to be the active species in view of the observed experimental results. In the prior equilibrium step 1, the $[OH^-]$ deprotonates the DPA to give a deprotonated diperiodatoargentate(III); in the second step, displacement of a ligand, periodate from deprotonated DPA takes place to give free periodate which is evidenced by decrease in the rate with increase in [periodate] (Table 1). It may be expected that lower Ag (III) periodate species such as MPA will be more important in the reaction than the DPA. The inverse fractional order in $[H_3IO_6^{2-}]$ might also be due to this reason. In the pre rate determining stage, MPA, combines with a molecule of AA molecule to give a complex, which decomposes in a slow step to form the products, acrolein and Ag(I). Thus, all these results indicate a mechanism of the type as in Scheme 1.

On the basis of square planar structure of DPA, the structure of MPA and complex may be proposed as below:



Spectroscopic evidence for the complex formation between oxidant and AA was obtained from UV-Vis spectra of AA ((1.0×10^{-2}), $[OH^-] = 0.50$ mol dm^{-3}) and a mixture of both. A hypsochromic shift of about 6 nm from 307 to 301 nm in the spectra of DPA to mixture of DPA and AA was observed. The Michaelis–Menten plot proved the complex formation between oxidant and substrate, which explains less than unit order in [AA]. Such a complex between a oxidant and a substrate has also been observed in other studies.[25]

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The rate law for Scheme 1 could be derived as

$$\text{Rate} = -\frac{\mathrm{d[DPA]}}{\mathrm{d}t} = \frac{k_1K_1K_2K_3[\mathrm{DPA}][\mathrm{AA}][\mathrm{OH^-}]}{[\mathrm{H_3IO_6^{2-}}] + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6^{2-}}] + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3[\mathrm{OH^-}][\mathrm{AA}]} \tag{7}$$

$$k_\mathrm{u} = \frac{k_1K_1K_2K_3[\mathrm{AA}][\mathrm{OH^-}]}{[\mathrm{H_3IO_6^{2-}}] + K_1[\mathrm{OH^-}][\mathrm{H_3IO_6^{2-}}] + K_1K_2[\mathrm{OH^-}] + K_1K_2K_3[\mathrm{OH^-}][\mathrm{AA}]} \tag{8}$$

which explains all the observed kinetic orders of different species.

The rate law (8) can be rearranged into the following form which is suitable for verification.

$$\frac{1}{k_\mathrm{u}} = \frac{[\mathrm{H_3IO_6^{2-}}]}{k_1K_1K_2K_3[\mathrm{OH^-}][\mathrm{AA}]} + \frac{[\mathrm{H_3IO_6^{2-}}]}{k_1K_1K_2K_3[\mathrm{AA}]} + \frac{1}{k_1K_3[\mathrm{AA}]} + \frac{1}{k_1} \tag{9}$$

The plots of $1/k_\mathrm{u}$ *versus* $1/[\mathrm{AA}]$, $1/k_\mathrm{u}$ *versus* $[\mathrm{H_3IO_6^{2-}}]$, $1/k_\mathrm{u}$ *versus* $1/[\mathrm{OH^-}]$ and were linear with an intercept supporting the MPA-AA complex, as verified in Fig. 2. From the intercept and slope of such plots, the reaction constants K_1, K_2, K_3 and k_1 were calculated as $(0.17 \pm 0.008)\,\mathrm{dm^3\,mol^{-1}}$, $(2.99 \pm 0.12) \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, $(3.14 \pm 0.13) \times 10^{2}\,\mathrm{dm^3\,mol^{-1}}$, $(4.01 \pm 0.2) \times 10^{-3}\,\mathrm{s^{-1}}$, respectively. The K_1 value is in near agreement with earlier work.[26] These constants were used to calculate the rate constants and compared with the experimental values and found to be in reasonable agreement with each other (Table 1) which fortifies the Scheme 1.The equilibrium constant K_1 is far greater than K_2 which may be attributed to the greater tendency of DPA to undergo deprotonation compared to the formation of hydrolysed species in alkaline medium.

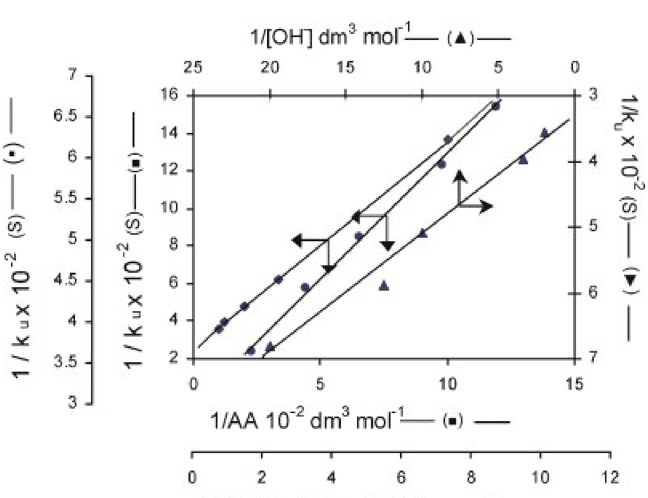

Figure 2. Verification of rate law (8) in the form of (9) for the oxidation of allyl alcohol by diperiodatoargentate(III) at 25 °C

The thermodynamic quantities for the different equilibrium steps, in Scheme 1 can be evaluated as follows. The AA and hydroxide ion concentrations (Table 1) were varied at different temperatures. The plots of $1/k_\mathrm{u}$ *versus* $1/[\mathrm{AA}]$ ($r \geq 0.9982$, $S \leq 0.00122$) and $1/k_\mathrm{u}$ *versus* $1/[\mathrm{OH^-}]$ ($r \geq 0.9997$, $S \leq 0.00084$) should be linear as shown in Fig. 2. From the slopes and intercepts, the values of K_1 were calculated at different temperatures. A van't Hoff's plot was made for the variation of K_1 with temperature [i.e. log K_1 *versus* $1/T$ ($r \geq 0.9894$, $S \leq 0.1108$)] and the values of the enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated. These values are given in Table 2. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step is fairly slow and involves high activation energy.[27] In the same manner, K_2 and K_3 values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 2.

A high negative value of $\Delta S^{\#}$ ($-118\,\mathrm{JK^{-1}\,mol^{-1}}$) suggests that intermediate complex is more ordered than the reactants.[28]

Mechanism for Ru(III) catalysed reaction

It is interesting to identify the probable ruthenium(III) chloride species in alkaline media. Electronic spectral studies[29] have confirmed that ruthenium chloride exists in hydrated form as $[\mathrm{Ru(H_2O)_5OH}]^{2+}$. In the present study, it is quite probable that the $[\mathrm{Ru(III)(OH)}_x]^{3-X}$, the x-value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The remainder of the coordination sphere would be filled by water molecules. Hence, under the conditions employed, for example, $[\mathrm{OH^-}] >> [\mathrm{Ru(III)}]$, ruthenium(III) is mostly present as the hydroxylated species,[30] $[\mathrm{Ru(H_2O)_5OH}]^{2+}$.

Since, the reaction was enhanced by $[\mathrm{OH^-}]$, added periodate retarded the rate and first order dependency in

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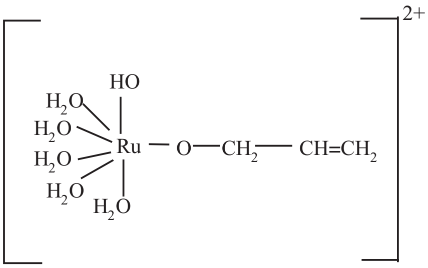
[DPA] and catalyst (Ru(III)) and fractional order in [AA] and [OH$^-$], the following Scheme 2 has been proposed, which also explains all other experimental observations.

In the prior equilibrium step 1, the [OH$^-$] deprotonates the DPA to give a deprotonated diperiodatoargentate(III); in the second step displacement of a ligand, periodate takes place to give free periodate which is evidenced by decrease in the rate with increase in [periodate] (Table 3). It may be expected that lower Ag (III) periodate species such as MPA is more important active species in the reaction than the DPA. The inverse fractional order in [$H_3IO_6^{2-}$] might also be due to this reason. In the pre rate determining stage, the hydroxylated species of Ru(III) combines with a molecule of AA to give an intermediate complex, which further reacts with 1 mole of MPA in a rate determining step to give the products as given in Scheme 2.

The probable structure of the complex (C) is given below:



Spectroscopic evidence for the complex formation between catalyst and substrate was obtained from UV-Vis spectra of AA (1.0×10^{-3}), Ru(III) (3.0×10^{-6}, [OH$^-$] = 0.50 mol dm^{-3}) and mixture of both. A bathochromic shift of about 5 nm from 313 to 318 nm in the spectra of ruthenium(III) was observed and hyperchromicity was observed at 318 nm. The Michaelis–Menten plot also proved the complex formation between catalyst and reductant, which explains less than unit order in [AA]. The rate law for the Scheme 2 could be derived as,

$$\text{Rate} = \frac{-\text{d[DPA]}}{\text{d}t} = \frac{k_2K_1K_2K_4[\text{DPA}][\text{AA}][\text{OH}^-][\text{Ru(III)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_4[\text{OH}^-][\text{AA}]} \tag{10}$$

$$\frac{\text{Rate}}{[\text{DPA}]} = \text{k}_\text{C} = \text{k}_\text{T} - \text{k}_\text{U} = \frac{\text{k}_2K_1K_2K_4[\text{AA}][\text{OH}^-][\text{Ru(III)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_4[\text{OH}^-][\text{AA}]} \tag{11}$$

Equation (11) can be rearranged to Eqn (12), which is suitable for verification.

$$\frac{[\text{Ru(III)}]}{k_\text{C}} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{k_2K_1K_2K_4[\text{AA}][\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{k_2K_2K_4[\text{AA}]} + \frac{1}{k_2K_4[\text{AA}]} + \frac{1}{k_2} \tag{12}$$

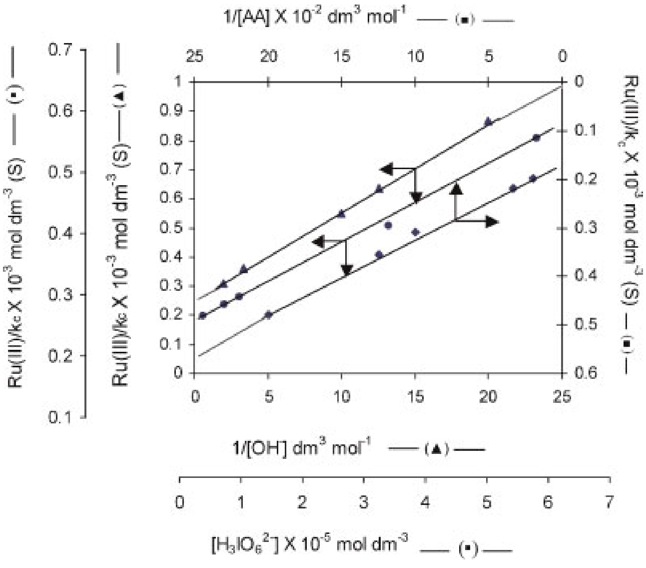


Figure 3. Verification of rate law (11) in the form of (12) for the Ru(III) catalysed oxidation of allyl alcohol by diperiodatoargentate(III) at 25 °C

The plots of [Ru(III)]/k_c *vrersus* 1/[AA], 1/[OH$^-$] and [$H_3IO_6^{2-}$], were linear (Fig. 3). From the intercepts and slopes of such plots, the reaction constants K_1, K_2, K_4 and k_2 were calculated as (0.34 ± 0.014) dm^3 mol^{-1}, $(7.23 \pm 0.36) \times 10^{-5}$ mol dm^{-3}, $(2.11 \pm 0.10) \times 10^3$ dm^3 mol^{-1}, $(6.11 \pm 0.30) \pm 10^3$ dm^3 mol^{-1} s^{-1}, respectively. These constants were used to calculate the rate constants and compared with the experimental k_c values and found to be in reasonable agreement with each other (Table 3), which fortifies the Scheme 2.

The thermodynamic quantities for the different equilibrium steps, in Scheme 2 can be evaluated as follows. The AA and hydroxide ion concentrations (Table 3) were varied at different temperatures. The plots of [Ru(III)]/k_C *versus* 1/[AA] ($r \geq 0.9993$, $S \leq 0.00132$), [Ru(III)]/k_C *versus* 1/[OH$^-$]($r \geq 0.9995$, $S \leq 0.00088$) and [Ru(III)]/k_C *versus* [$H_3IO_6^{2-}$] ($r \geq 0.9992$, $S \leq 0.00131$), should be linear as shown in Fig. 3. From the slopes and intercepts, the values of K_1 are calculated at different temperatures. A van't Hoff's plot was made for the variation of K_1 with temperature [i.e. log K_1 *versus* $1/T$ ($r \geq 0.9993$, $S \leq 0.1105$)] and the values of the enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated. These values are also given in Table 4. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step is fairly slow and involves a high activation energy.[27] In the same manner, K_2 and K_4 values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 4.

Negligible effect of ionic strength and dielectric constant in both uncatalysed and catalysed reaction might be due to involvement of neutral substrate in the reaction (Schemes 1 and 2). The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants.[28] The observed higher rate constant for the slow step indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observation.[31] The activation parameters evaluated for the catalysed and uncatalysed reaction explain the catalytic effect on the reaction. The catalyst, Ru(III) form the complex (C) with substrate which enhances the reducing property of the substrate than that without catalyst, Ru(III). Further the catalyst Ru(III) modifies the reaction path by lowering the energy of activation.

CONCLUSION

The comparative study of uncatalysed and ruthenium(III) catalysed oxidation of AA by diperiodatoargentate(III) was studied. Oxidation products were identified. Among the various species of Ag(III) in alkaline medium, MPA is considered to be the active species for the title reaction. Active species of Ru(III) is found to be $[Ru(H_2O)_5OH]^{2+}$. Activation parameters were evaluated for both uncatalysed and catalysed reactions with respect to slow step of reaction schemes. Catalytic constants and activation parameters with respect to catalyst were also computed.

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