Mechanistic study of palladium(II) catalysed oxidation of crotonic acid by periodate in aqueous perchloric acid medium

Ashish [b,1], Surya Prakash Singh [b,2], Ajaya K. Singh [a,*], Bharat Singh [b]

[a] *Department of Chemistry, Govt. V.Y.T.P.G. Autonomous College Durg, Chhattisgarh, India*
[b] *Department of Chemistry, University of Allahabad, Allahabad, UP, India*

Abstract

The Pd(II) homogeneous catalysis of periodates oxidation of crotonic acid (CA) in perchloric acid has been studied. The linear dependence of the reaction rate at lower $[IO_4^-]$ and [Pd(II)] tends towards zero order at their higher concentrations. The reaction exhibited zero order in [CA]. Negligible effect of change in $[H^+]$, ionic strength of medium and varying $[Cl^-]$ on rate of reaction is observed. $[Pd]^{2+}$ and $[IO_4^-]$ are assumed as the most reactive species of Pd(II) chloride and periodate, respectively. Acetaldehyde and glyoxylic acid have been identified as the main oxidation products of the reaction. Various activation parameters have also been calculated and recorded. On the basis of experimental findings, a suitable mechanism consistent with the observed kinetics was proposed. A comparative study was also made between the kinetic results of the present investigation and those of Pd(II) catalysed oxidation CA by chloramines-T in acidic medium.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Kinetics; Oxidation; Periodate; Pd(II) catalysis; Crotonic acid

1. Introduction

A study of literature indicated many possible fields of application for the acid and its derivative, most of which took advantage of the double bond in α,β-position, in resin modification, drying oil modifications plasticizers, perfumery and as a chemical intermediate. Crotonic acid, however, will undergo most of the additions and condensations peculiar to the ethylenic bond and the carboxylic group under the correct conditions. This myriad believe that crotonic acid could find an important place in the chemical world. The oxidation of crotonic acid by hexacyanoferrate(III) [1], by chloramine-T (CAT) [2] in perchloric acid and by potassium bromate [3] in alkaline medium has earlier been shown to result in the cleavage of the carbon–carbon bond. Earlier reports [4] show that the double bond of unsaturated acids is quite reactive, but its oxidative property is restricted towards one-electron oxidants. Periodate is widely employed as

a diol cleaving reagent [5], although it is less potent oxidant in alkaline than in acidic media. Earlier kinetics and mechanism of Pd(II) catalysed oxidation of some redox reactions have been reported [2,6–13]. In view of scant work on the periodate oxidation with industrially important substrates like α,β-unsaturated carboxylic acid, there seems to be much exciting chemistry in further probing the oxidative capacity of periodate in the oxidation of crotonic acid particularly in the presence of Pd(II). Pd(II) chloride is the most important Pd(II) salt in the homogeneous catalytic chemistry of palladium. Because of the industrial importance of the reaction, the kinetics of oxidation of ethylene by aqueous Pd(II) chloride were studied by Henry in 1964 [13]. Some interesting results in the homogeneous catalysis of reactions of organic compounds have contributed to this interest. In most of the studies Pd(II) is the catalytic species where palladium chloride [14] is employed, but nature of its active form in such reaction remains obscure. Hence, the effect of chloride ion on the reaction was studied in order to establish the active species of the catalyst, although the mechanism of catalysis depends on the nature of the substrate, the oxidant and other experimental conditions. In the present work, we report kinetics and mechanism of oxidation of crotonic acid by periodate in the presence of Pd(II) in aqueous homogenous acidic system at 313 K. Objectives of

---

* Corresponding author. Tel.: +91 788 2223421.
  E-mail address: ajayaksingh_au@yahoo.co.in (A.K. Singh).
[1] Present address: Samtel Center for Display Technologies, IIT Kanpur, India.
[2] Present address: Nano Material Laboratory, Indian Institute of Chemical Technology, Hyderabad, India.

the present study are to: (i) elucidate a plausible mechanism, (ii) identify the oxidation products, (iii) deduce an appropriate rate law, (iv) ascertain the various reactive species and (v) calculate activation parameters.

2. Experimental

2.1. Material

The stock solution of palladous chloride (Johnson and Matthey) was prepared by dissolving the sample in dilute HCl $(1.00 \times 10^{-2} \, \text{mol dm}^{-3})$ was stored in black-coated bottle to prevent photochemical decomposition and standardized [15] against EDTA. For some kinetic observations in the absence of chloride ion, the chloride ion was precipitated with silver nitrate from the stock solution of palladium(II) chloride, and removed by repeated centrifugation. The resulting solution of palladium(II) contained less than $1.0 \times 10^{-6} \, \text{mol dm}^{-3}$ chloride and silver ions. Such extremely low concentrations of chloride and silver ions were found to have no significant effect on rate of reaction. The required chloride ion concentration between 1×10^{-5} and $10 \times 10^{-5} \, \text{mol dm}^{-3}$ was maintained with KCl. The reagents employed were crotonic acid (Kochlight), sodium perchlorate (E-Merck) and periodate (E-Merck). The solution of periodate was prepared by direct weighing and was standardized idometrically. Potassium iodate solution was prepared by dissolving a known amount of potassium iodate (AR) in double distilled water. Sodium perchlorate was used to maintain the required ionic strength of the medium and all other reagents employed during the reaction were of AR grade and their solutions were prepared in double distilled water.

2.2. Kinetic measurements

All the kinetic measurements were carried out in a black-coated vessel at constant temperature, $40\,^{\circ}\text{C}$ (± 0.1). The requisite volume of the solutions such as periodate, perchloric acid and Pd(II) chloride were taken in a reaction vessel and placed in electrically operated thermostatic water bath which was pre-equilibrated at $40\,^{\circ}\text{C}$. An appropriate volume of crotonic acid solution, also equilibrated at the desired temperature in same water bath, was rapidly poured into reaction vessel to initiate the reaction and progress of the reaction was monitored by iodometric determination of unconsumed $[\text{IO}_4^-]$ in known aliquots of the reaction mixture at different time intervals. The rate of reaction ($-\text{d}c/\text{d}t$) in each kinetic run was determined by the slope of the tangent drawn at a fixed $[\text{IO}_4^-]$. The order of reaction in each reactant was determined with the help of log–log plot of ($-\text{d}c/\text{d}t$) versus concentration of the reactants.

2.3. Stoichiometric result

Various ratios of periodate to crotonic acid, under the condition of $[\text{IO}_4^-] \gg [\text{CA}]$ were allowed to stand until the completion of the reaction for 72 h at $40\,^{\circ}\text{C}$. Estimation of residual $[\text{IO}_4^-]$ was assayed iodometrically [16]. The results revealed

that 2 mol of periodate were consumed per mole of CA. Accordingly, following stoichiometric equation could be formulated:

$$CH_3CH=CHCOOH + 2IO_4^- \xrightarrow{\text{Pd(II)/H}^+} \begin{array}{c} CHO \\ | \\ COOH \end{array} + CH_3CHO + 2IO_3^-$$
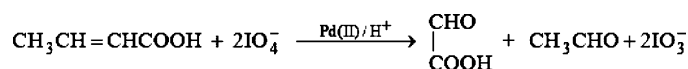
The concentration of the catalyst, Pd(II), remained unchanged at the end of the reaction, as found by estimating it as the palladium azide complex [17] at 315 nm ($\varepsilon = 12{,}000 \, \text{dm}^3 \, \text{mol}^{-1} \pm 10\%$). The products were analysed by NUCON gas chromatography using porapak Q101 Column and programmed oven temperature from 50 to $210\,^{\circ}\text{C}$, having FID detector. The major products were identified as glyoxylic acid and acetaldehyde in the oxidation of crotonic acid by periodate in aqueous perchloric acid medium catalysed by Pd(II), by comparison of retention time with the retention time of their standard solutions. The products were found to be identical under both stoichiometric and kinetic conditions and also by a spot test [18] and thin layer chromatography.

3. Kinetic results and discussion

The kinetics of the oxidation of CA by periodate ion in aqueous acid medium in the presence of Pd(II) chloride were investigated at several initial concentrations of all the reactants. The value of the initial rate in each kinetic run was calculated from the slope of the tangent of plot of unconsumed $[\text{IO}_4^-]$ versus time at fixed $[\text{IO}_4^-]$ except in $[\text{IO}_4^-]$ variation when a tangent has been drawn at a fixed time. The value of the first-order rate constant (k_1) in each run was calculated as:

$$k_1 = \frac{-\text{d}c/\text{d}t}{[\text{IO}_4^-]}$$

On varying [periodate] rate of reaction varies in the same proportion only in its lower concentration range but it deviates from linearity at its higher concentrations. This is also obvious from the plot of ($-\text{d}c/\text{d}t$) and $[\text{IO}_4^-]$ (Table 1; Fig. 1), indicating first order kinetics at lower concentrations and tending towards zero order kinetics in its higher concentrations. When a plot is made between pseudo first order rate constant (k_1) against [Pd(II)], straight line observed at lower concentrations deviates at its higher concentrations, indicating the order less than unity with respect to [Pd(II)] (Table 1; Fig. 1). This observation regarding order in [Pd(II)] was confirmed by the slope of log–log plot of k_1 versus [Pd(II)] and it is found as 0.62. The rate of the reaction ($-\text{d}c/\text{d}t$), were calculated at different [CA]. This was found to be same for all [CA], showing zero order kinetics in [CA]. Since order in CA is zero, in each kinetic run the rate of the reaction ($-\text{d}c/\text{d}t$), will always be equal to the standard zero order rate constant. Addition of reduced product of the oxidant, IO_3^- did not influence the rate of reaction significantly. A variation of ionic strength of the medium, addition of perchloric acid and addition of chloride ion had no significant effect on the rate of reaction (Table 2).

Measurements made at 35, 40, 45 and $50\,^{\circ}\text{C}$ led to calculate activation parameters such as energy of activation (E_a), entropy of activation ($\Delta S^{\#}$), Gibbs free energy of activation ($\Delta G^{\#}$) and Arrhenius factor, i.e. A, whose values are given in Table 3.

Table 1
Effect of variation of reaction on rate of reaction at 40 °C

$[NaIO_4] \times 10^4$ (mol dm^{-3})	$[CA] \times 10^2$ (mol dm^{-3})	$[Pd(II)] \times 10^5$ (mol dm^{-3})	$(-dc/dt) \times 10^7$ (mol dm^{-3} s^{-1})	$k_1 \times 10^4$ (s^{-1})
4.00	2.00	1.13	0.90	2.26
5.00	2.00	1.13	1.14	2.28
8.00	2.00	1.13	1.92	2.40
10.00	2.00	1.13	2.26	2.26
12.00	2.00	1.13	2.71	2.26
16.00	2.00	1.13	3.28	2.05
20.00	2.00	1.13	3.48	1.74
24.00	2.00	1.13	3.84	1.60
28.00	2.00	1.13	4.09	1.46
10.00	1.00	1.13	1.90	2.00
10.00	1.25	1.13	2.14	2.25
10.00	1.67	1.13	2.21	2.33
10.00	2.00	1.13	2.13	2.25
10.00	3.00	1.13	2.05	2.16
10.00	5.00	1.13	2.08	2.19
10.00	8.00	1.13	2.24	2.36
10.00	10.00	1.13	2.12	2.23
10.00	2.00	0.56	1.04	1.09
10.00	2.00	0.85	1.45	1.53
10.00	2.00	1.13	2.14	2.25
10.00	2.00	1.69	2.92	3.07
10.00	2.00	2.26	3.51	3.70
10.00	2.00	3.94	3.96	4.17
10.00	2.00	5.64	4.22	4.44

$[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}.

3.1. Test for free radical

The addition of the reaction mixture to an aqueous acrylamide monomer solution did not initiate polymerization indicating the absence of formation of free radical species in situ in the reaction sequence. The controlled experiments were also performed under the same reaction conditions but without periodate.

3.2. Suggested mechanism

It has been reported earlier by several workers that in acidic medium [19] periodate [IO_4^-] exists in the following equilibria:
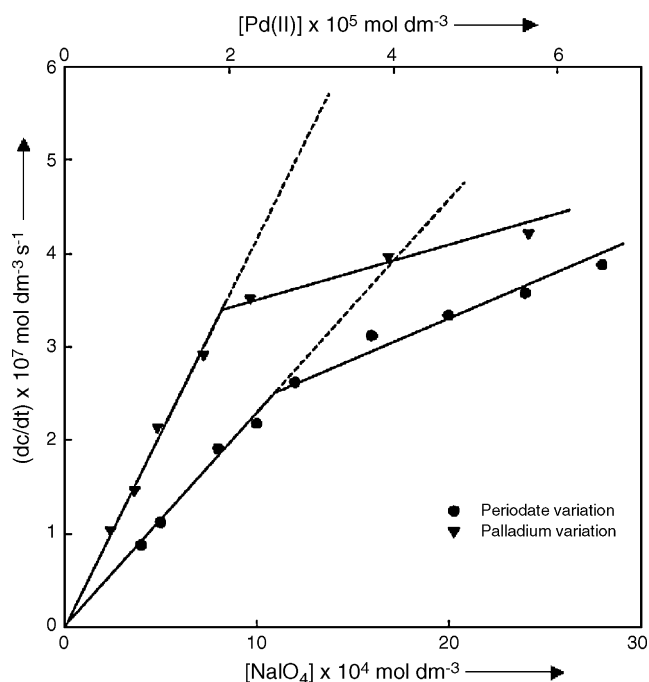
$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \tag{A}$$

Fig. 1. Plot between $(-dc/dt)$ and $[NaIO_4]$ and plot between $(-dc/dt)$ and $[Pd(II)]$ under the conditions of Table 1.

Table 2
Effect of variation of [KCl], [H$^+$] and [μ] on the rate constant at 40 °C

$[H^+] \times 10^2$ (mol dm^{-3})	$[Cl^-] \times 10^3$ (mol dm^{-3})	$[\mu] \times 10^2$ (mol dm^{-3})	$k_1 \times 10^4$ (s^{-1})
0.5			2.25
1.0			2.28
2.0			2.23
3.0			2.26
4.0			2.25
5.0		−	2.26
	1.0		2.27
	2.0		2.28
	4.0		2.25
	6.0		2.26
	8.0		2.27
	10.0		2.24
		2.0	2.26
		4.0	2.25
		8.0	2.28
		10.	2.28
		12.0	2.26

Solution conditions: $[CA] = 2 \times 10^{-2}$ mol dm^{-3}, $[IO_4^-] = 10 \times 10^{-4}$ mol dm^{-3} and $[Pd(II)] = 1.13 \times 10^{-5}$ mol dm^{-3}.

Table 3
Activation parameters of Pd(II) catalysed oxidation of CA by periodate in acidic medium at 40 °C

Parameter	Value
k_r (mol^{-1} dm^3 s^{-1})	4.36×10^{-2}
$\log A$	10.10
$\Delta H^{\#}$ (kcal mol^{-1})	13.93
$\Delta S^{\#}$ (e.u.)	-13.77
$\Delta G^{\#}$ (kcal mol^{-1})	19.94
E_a (kcal mol^{-1})	14.56

Temperature (K)	$k_1 \times 10^4$ (s^{-1})
308	1.51
313	2.26
318	3.31
323	4.57

Solution conditions: $[CA] = 2 \times 10^{-2}$ mol dm^{-3}, $[IO_4{}^-] = 10 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3} and $[Pd(II)] = 1.13 \times 10^{-5}$ mol dm^{-3}.

$$H_4IO_6{}^- \rightleftharpoons IO_4{}^- + 2H_2O \tag{B}$$

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

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

In acidic solutions, periodate is one of the most powerful known oxidizing agent and its activity [20] as an oxidizing agent varies greatly as a function of pH and hence it also affects the rate of oxidation of CA in the present investigation. Thus, there seems to be the three possible reactive species of periodate, i.e. H_5IO_6, $IO_4{}^-$ and $H_4IO_6{}^-$ under our experimental conditions. It might be possible that one or more than one may actively participate in the reaction. Under the conditions of experiments (pH $\approx$ 2) H_5IO_6 exists negligibly small and thus its involvement in reaction is ruled out. Now if $H_4IO_6{}^-$ is taken as reactive species of periodate there must be negative effect of $[H^+]$, contrary to observe zero effect of $[H^+]$ on the rate of reaction. Hence, it is reasonable to rule out the possibility of $H_4IO_6{}^-$ as a reactive species of periodate. Thus, in the light of the kinetic observations, especially the order with respect to $[IO_4{}^-]$, $IO_4{}^-$ can be assumed to be the main reactive species of periodate under our experimental conditions in oxidation of CA by periodate in perchloric acid medium catalysed by Pd(II) chloride.

The complexes of platinum or palladium group metals are well known. The different possible mononuclear complexes of palladium(II), viz. $[PdLCl_3]^-$, $[PdL_2Cl_2]$, $[PdL_3Cl]^+$ and $[PdL_4]^{2+}$ (where L represents a ligand like amine, phosphine, sulphide) are reported [21]. In most of the studies using Pd(II) as a homogeneous catalyst; it has been employed in the form of Pd(II) chloride. Palladous chloride [13] is insoluble in aqueous solution but is dissolved in the presence of Cl^-. The stock solution of Pd(II) chloride was prepared by dissolving in aqueous hydrochloric acid (1.0×10^{-2} mol dm^{-3}) and the ratio of $[Cl^-]$ and $[Pd(II)]$ was always maintained as 2. Elding [22] reported that in the presence of chloride ion, palladium chloride exists as $[PdCl_4]^{2-}$ and in the aqueous solution it may be further hydrolyzed to $[PdCl_3(H_2O)]^-$. The equilibrium constants corresponding to the following equilibrium have been determined by several workers, and all are in good agreement with a value

of $\log \beta_4$ between 11 and 12 at 25 °C.

$$Pd^{2+} + Cl^- \underset{K_1}{\rightleftharpoons} PdCl^+ \tag{E}$$

$$PdCl^+ + Cl^- \underset{K_2}{\rightleftharpoons} PdCl_2 \tag{F}$$

$$PdCl_2 + Cl^- \underset{K_3}{\rightleftharpoons} PdCl_3{}^- \tag{G}$$

$$PdCl_3{}^- + Cl^- \underset{K_4}{\rightleftharpoons} PdCl_4{}^{2-} \tag{H}$$

It is also reported that K_4 is probably the most important stability constant for catalytic chemistry. The reported value of $\log K_1 - \log K_4$ are 4.47, 3.29, 2.41 and 1.37, respectively. According to the following equilibria (I) and (J):

$$Pd^{2+} + 4Cl^- \underset{\beta_4}{\rightleftharpoons} PdCl_4{}^{2-} \tag{I}$$

$$PdCl_4{}^{2-} + H_2O \underset{K_h}{\rightleftharpoons} [PdCl_3(H_2O)]^- + Cl^- \tag{J}$$

The reported value of $\log \beta_4$ is 11.54 (β_4 is the equilibrium constant) and value of hydrolytic constant (K_h) is 2.50×10^{-3}. The existence of Pd(II) chloride exclusively in the form of complex $[PdCl_4]^{2-}$ is also supported by Ayers [23]. In the reaction under study, the reaction is not influenced by chloride ions, to be expected in the palladium(II) catalysed reactions. Hence, the reactive species of palladium(II) chloride involved is Pd^{2+} [24] and not its chloride complex as in other cases.

On the basis of observed kinetic results and taking Pd^{2+} and $IO_4{}^-$ as the most active species of palladium chloride and sodium metaperiodate, respectively, the following reaction steps (Scheme 1) have been proposed in the oxidation of CA by periodate ion in the presence of catalyst, i.e. palladium(II) chloride.

Considering all the steps in Scheme 1 for the oxidation of crotonic acid and stoichiometry of the reaction rate of the reaction may be expressed as:

$$Rate = 2k[C_2] \tag{1}$$

considering equilibrium (I) we have

$$[C_2] = K_1[C_1][IO_4{}^-] \tag{2}$$

from Eqs. (1) and (2), we have

$$Rate = 2kK_1[C_1][IO_4{}^-] \tag{3}$$

The total concentration of $[Pd(II)]$, i.e. $[Pd(II)]_T$, can be obtained from the reaction Scheme 1.
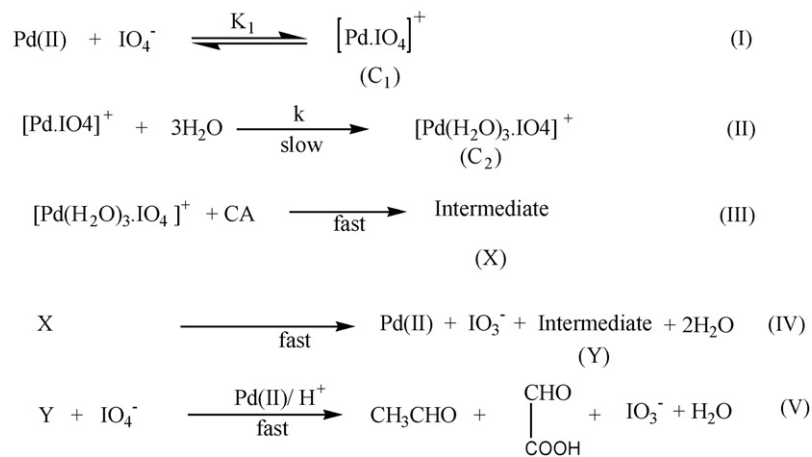
$$[Pd(II)]_T = [C_1] + [C_2] \tag{4}$$

From Eqs. (2) and (4)

$$[C_1] = \frac{[Pd(II)]_T}{1 + K_1[IO_4{}^-]} \tag{5}$$
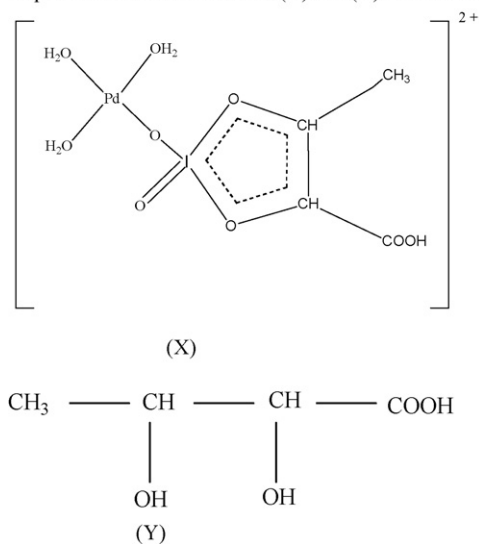
From Eqs. (3) and (5), we have

At very high concentration of Pd(II), $[IO_4{}^-]_T$ can be expressed as Eq. (6):

$$[IO_4{}^-]_T = [IO_4{}^-] + [C_2] \tag{6}$$

$$Pd(II) + IO_4^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Pd.IO_4]^+ \qquad (I)$$
$$(C_1)$$

$$[Pd.IO4]^+ + 3H_2O \xrightarrow[\text{slow}]{k} [Pd(H_2O)_3.IO4]^+ \qquad (II)$$
$$(C_2)$$

$$[Pd(H_2O)_3.IO_4]^+ + CA \xrightarrow{\text{fast}} \text{Intermediate} \qquad (III)$$
$$(X)$$

$$X \xrightarrow{\text{fast}} Pd(II) + IO_3^- + \text{Intermediate} + 2H_2O \quad (IV)$$
$$(Y)$$

$$Y + IO_4^- \xrightarrow[\text{fast}]{Pd(II)/H^+} CH_3CHO + \underset{COOH}{\overset{CHO}{|}} + IO_3^- + H_2O \quad (V)$$

Representation of intermediate (X) and (Y) are as follows:

(X)

(Y)

Scheme 1.

On substituting the value of [C$_2$] from Eq. (2) in above equation,

$$[IO_4^-] = \frac{[IO_4^-]_T}{1 + K_1[C_1]} \qquad (7)$$

Since C$_1$ is free concentration of Pd(II) hence it can be replaced by [Pd(II)]$_f$. Now Eq. (7) will be written as Eq. (8).

$$[IO_4^-] = \frac{[IO_4^-]_T}{1 + K_1[Pd(II)]_f} \qquad (8)$$

Eq. (8) clearly shows that at very high concentration of Pd(II), denominator of Eq. (7) will have some significant value as result of which there will be decrease in the free concentration of IO_4^-. This decrease in free [IO_4^-] will ultimately result in the form of deviations observed for the oxidation of CA at very high concentration of Pd(II).

From Eqs. (6) and (8), we have

$$\text{Rate} = \frac{2kK_1[Pd(II)]_T[IO_4^-]_T}{1 + K_1[IO_4^-]_T + K_1[Pd(II)]_f} \qquad (9)$$

Eq. (9) clearly explains the deviations from straight lines observed at higher concentration of Pd(II).

Hence from the aforesaid discussion it was calculated that Eq. (9) is the final rate law, which is valid for all the variations, made to study the effect of [IO_4^-][CA], [H^+] and [Cl^-] on the rate of reaction and it is also valid for low concentration of Pd(II) in oxidation of CA.

Eq. (9) can also be written as Eq. (10):

$$\frac{1}{\text{Rate}} = \frac{1}{2kK_1[Pd(II)]_T[IO_4^-]} + \frac{1}{2k[Pd(II)]_T} \qquad (10)$$

According to Eq. (10) if a plot is made between 1/rate versus 1/[IO_4^-] a straight line with positive intercept on y-axis should be obtained. When a plot was made between 1/rate versus 1/[IO_4^-] straight line (Fig. 2) with positive intercept was obtained and from the values of intercept and slope of the plot equilibrium constant (K_1) and rate determining constant (k) were calculated. The values of K_1 and k were obtained as 1.8×10^{-2} mol^{-1} dm^3 and 5.9×10^{-2} s^{-1} from 1/rate versus 1/[IO_4^-] plot, respectively.
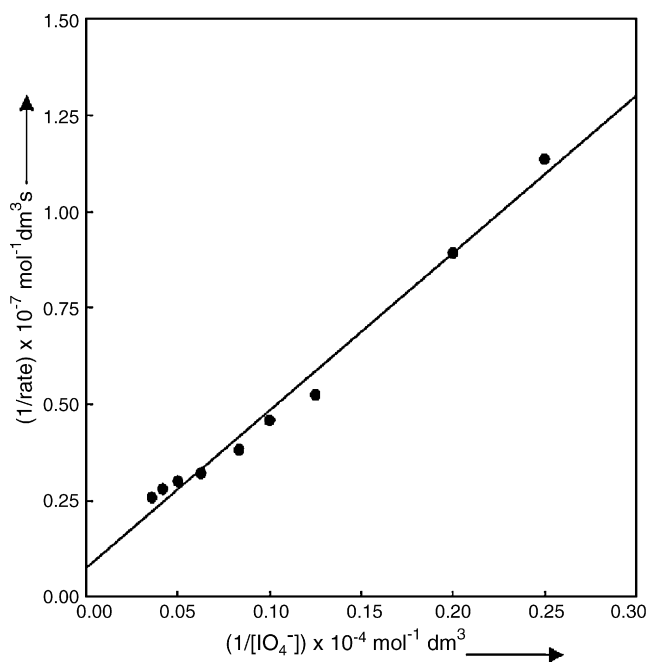
Fig. 2. Plot between 1/rate and $1/[IO_4^-]$ under the condition of Table 1.

According to rate determining step (II) in Scheme 1 that involves ion dipole interaction negligible effect of variation of ionic strength of the medium on the rate of oxidation of CA is well explained. Zero effect of [CA] can be viewed in a different way by neglecting the possibility of the formation of an active complex between the reactive species of Pd(II) and CA.

Entropy of activation plays an important role in the case of reaction between ions or between an ion and a neutral molecule or a neutral molecule forming ions. When reaction takes place between two ions of opposite charges, their union will results in a lowering of the net charge, and due to this some frozen solvent molecules will be released with an increase of entropy. But on the other hand, when reaction takes place between two similarly charged species, the transition state will be a more highly charged ion, and due to this, more solvent molecules will be required than for the separate ions, leading would lead to a decrease in entropy. On the basis of this information, observed negative entropy of activation in the oxidation of CA by periodate in the presence of Pd(II) supports the rate determining step of the proposed Scheme 1. The proposed mechanism is also supported by the moderate values of energy of activation and other activation parameters. The high positive values of $\Delta G^{\#}$ and $\Delta H^{\#}$ indicate that the transition state is highly solvated. The large negative value of $\Delta S^{\#}$ reflect a more ordered, rigid transition state for substrate.

An effort has also been made to compare our experimental findings with the results earlier reported for Pd(II) catalysed oxidation of CA by chloramine-T[2] in acidic medium. In the present study behavior of oxidant, i.e. IO_4^- is somewhat different from that of CAT. In the earlier reported work results show zero order dependence in [CAT], but in the present investigation first order at lower concentration range of IO_4^- tends towards zero order at its higher concentration range. In CAT oxidation of CA variation of [Cl$^-$] shows positive effect on the rate of the reaction and effect of [Cl$^-$] thus observed plays important role in deciding the reactive species of palladium(II) chloride, while present studies show zero effect of [Cl$^-$]. In the present work there is fractional order with respect to IO_4^- and Pd(II) species showing the greater possibility of forming a complex between them before the slow step but in the CAT oxidation of CA, Pd(II) species forms a complex with CA before disproportionation.

4. Conclusion

Oxidation of crotonic acid by periodate in aqueous perchloric acid medium is very sluggish, but it becomes facile in the presence of Pd(II) catalyst. On the basis of our study for Pd(II) catalysed oxidation of crotonic acid by periodate in the presence of $HClO_4$, the reactive species involed of palladium(II) chloride is Pd^{2+} not its chloride complex. Oxidation products have been identified. Activation parameters were calculated for the oxidation reaction. The observed results have been explained by a plausible mechanism and the related law has been deduced. It can be concluded that Pd(II) acts as an efficient catalyst in the oxidation of crotonic acid by periodate in aqueous perchloric acid medium.

Acknowledgement

References

[1] A.K. Bhattacharjee, M.K. Mahanti, Ind. J. Chem. 21A (1982) 770–772.
[2] Ashish, A.K. Singh, A.K. Singh, B. Singh, Ind. J. Chem. 43A (2004) 1645–1653.
[3] Ashish, S.P. Singh, A.K. Singh, B. Singh, Transition Met. Chem. 30 (2005) 610–615.
[4] J.S. Littler, J. Chem. Soc. (A) (1962) 382.
[5] C.A. Bunton, in: K.B. Wiberg (Ed.), Oxidation in Organic Chemistry, Part A, Academic Press, New York, 1965, p. 368.
[6] A.K. Singh, T. Gupta, V.K. Singh, S. Rahmani, D. Kesarwani, B. Singh, Oxid. Commun. 23 (4) (2000) 609–616.
[7] A.K. Singh, T. Gupta, V.K. Singh, D. Kesarwani, B. Singh, Oxid. Commun. 23 (3) (2000) 416–422.
[8] A.K. Singh, V. Singh, S. Rahmani, A.K. Singh, B. Singh, J. Mol. Catal. 197 (2003) 91–100.
[9] A.K. Singh, D. Chopra, S. Rahmani, B. Singh, Carbohydr. Res. 314 (1998) 157–160.
[10] A.K. Singh, J. Srivastava, S. Rahmani, V. Singh, Carbohydr. Res. 341 (2006) 397–409.
[11] A.K. Singh, V. Singh, Ashish, J. Srivastava, Ind. J. Chem. 45A (2006) 599–608.
[12] A. Shukla, S. Gupta, S.K. Upadhayay, Int. J. Chem. Kinet. 23 (1991) 279–288.
[13] P.M. Henry, Palladium(II) Catalysed Oxidation of Hydrocarbons, vol. 2, D. Reidal Publishing Company, Dordecht, 1980, pp. 11–12.
[14] G.P. Tikhonova, S.N. Bovkovets, Russ. J. Inorg. Chem. 23 (1978) 1687.
[15] A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, fourth ed., 325 ELBS, New York, 1978.
[16] G.P. Panigrahi, P.K. Misra, Ind. J. Chem. 15A (1977) 1066.

[17] G.S. Ray, E.H. Huffman, Analyt. Chem. 37 (1965) 86.

[18] F. Feigl, Spot Tests in Organic Analysis, seventh ed., Elsevier, Amsterdam, 1966, pp. 438–439, 482–484.

[19] C.E. Crouthmel, H.V. Mech, D.V. Martin, J. Am. Chem. Soc. 73 (1951) 82.

[20] G.A. Hiremath, P.L. Timmanagoudar, S.T. Nandibewoor, J. Phys. Org. Chem. 11 (1998) 31–35.

[21] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fifth ed., Wiley, New York, 1988, p. 1026.

[22] L.I. Elding, Inorg. Chim. Acta 6 (1972) 647.

[23] G.H. Ayres, Anal. Chem. 24 (1953) 1622–1627.

[24] V.A. Miss, S.T. Morab, Nandibewoor, React. Catal. Lett. 53 (1) (1994) 25–31.