IJPAC
© Global Research Publications

Vol. 9 • No. 3 • July-September 2014
pp. 123-126

Mechanistic Study of Palladium (II) Catalyzed Oxidation of Aspirin by Sodium Per Iodate ($NaIO_4$): in Perchloric Acid Medium

Sheila Srivastava[*] **and Reena Patel**

Chemical laboratories, Feroze Gandhi College, Raebareli-229001, U. P., India

---

ABSTRACT: Kinetic investigation of Pd(II) catalyzed oxidation of Aspirin by sodium per iodate ($NaIO_4$) in acidic medium has been studied in the temperature range 30-45^{0}C. The reaction is carried out in the presence of mercuric acetate as a scavenger for iodide ion. The rate shows first order kinetics with respect to the catalyst i.e. Pd(II) while less than unit order with respect to substrate i.e. Aspirin is observed. Experimental result shows zero order kinetics with respect to oxidant i.e. [$NaIO_4$] and [H^+]. Negligible effect of mercuric acetate and ionic strength of the medium was observed and the reaction showed negative effect with respect to [Cl^-]. A suitable mechanism in conformity with the kinetic observations has been proposed and the thermodynamic parameters computed.

Keywords: Kinetics, Oxidation, Pd(II), Periodate, Aspirin.

INTRODUCTION

In recent years, the use of transition metal ion such as Osmium, Ruthenium and Iridium as catalyst in various redox processes has attracted considerable interest [1]. The catalyzed mechanism can be quite complicated due to the formation of different intermediate complexes, and different oxidation states of Pd(II). Sodium periodate has been used as an oxidizing agent for studying the kinetics of oxidation of various organic substrates. A number of oxidants like potassium bromated [2-5], N-bromo acetamide [6-7], N bromo succinimide [8-9] have been earlier used in oxidation of various compounds. Various oxidation products of the redox reactions having Aspirin as reductant are reported to have industrial and biological significance. Aspirin (acetyl salicylate) in one among the most used drugs worldwide. It is a non steroidal analgesic, anti inflammatory and antipyretic agent. Aspirin is also sometimes used to treat rheumatic fever(a serious condition that may develop after a strep throat infection may cause swelling of the heart valves) and Kawasaki disease (an illness that may cause heart problems in children). Very few kinetic studies of Aspirin oxidation have been reported [10]. A little attention has been paid to $NaIO_4$[11-12] as an oxidant for various catalysed reactions, therefore we have under taken a careful study of oxidation of Aspirin by Sodium periodate in acidic medium.

EXPERIMENTAL

A stock solution of Aspirin (C.D.H. Ltd. New Delhi India) was prepared by dissolving the appropriate amount of recrystallised sample in double distilled water. The purity of [ASP] sample was checked with its m.p. 135 °C (literature m.p.136 °C). The required concentration of [ASP] was used from its aqueous stock solution. Solution of Sodium periodate was prepared by dissolving its known weight in doubly distilled water and its concentration was estimated iodometrically. $Pd(CI_2)$ (S.D. fine chemicals) solution was prepared in HCI of known strength (0.018N). Other reagents used were A.R. Grade and their solutions were also prepared in doubly distilled water. The reaction vessels were also coated black from outside to avoid photochemical effects.

The kinetic runs were carried out at 35 °C. The reaction was initiated by mixing the already thermostated solution of Aspirin to the thermally equilibrated reaction mixture containing required volume of solution of sodium periodate, [H^+], Pd(II) and all other reagents.

---

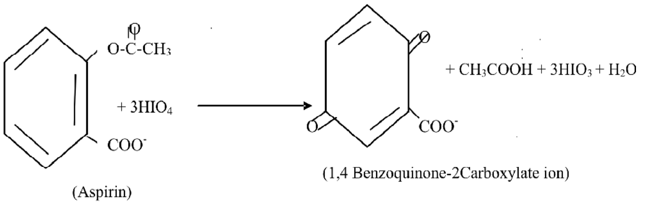
* *To whom correspondence be made:*
E-mail: she_ila72@yahoo.com, patel.reena14@gmail.com

METHOD

Aliquots (5ml) of the reaction mixture were pipetted out at regular intervals of time and poured into a conical flask containing 5ml of 4% KI solution and 5ml of dilute sulfuric acid. The rates were obtained from slope of concentration vs. time graph in the initial stages of the reactions by plane mirror method.

STOICHIOMETRY OF PD(II) CATALYZED OXIDATION OF ASPIRIN BY PERIODATE

The stoichiometry of the reaction was determined by equilibrating varying ratios of Periodate to [ASP] at 35 °C for 48h. under kinetic condition. Estimation of unconsumed periodate revealed that, one mole of [Aspirin] consumes three moles of sodium periodate. This result shows 1:3 stoichiometry. According to this above reaction the oxidation product of Aspirin is 1, 4 benzoqunone 2-carboxylate ion.



RESULT AND DISCUSSION

It is necessary to study the effect of variation in concentration of different reactants on the rate of reaction. The kinetic results were collected at several initial concentration of Sodium periodate, Substrate [ASP], Pd(II) and displayed in (Table-1). Zero order kinetics were observed with respect to the oxidant sodium periodate in case of Aspirin. A plot of (-dc/dt) versus [Pd(II)] (fig-1), gives a slope of 3.34 x 10^{-2} s^{-1} which is close to the average value of first order rate constants, i.e k_1= (-dc/dt)/[Pd(II) = 3.32 x $10^{-2}s^{-1}$ for Aspirin at 35 °C. Plot of –dc/dt versus [KCl] indicates negative order. The order of substrate was computed from slope of log (-dc/dt) versus log [Substrate] plot. This established that reaction follows fractional positive order which is obvious from the kinetic data in Table 1. Negligible effect of mercuric acetate excluded the possibility of its involvement either as a catalyst or as an oxidant hence, the function of mercuric acetate is to act as scavenger, for any iodide ion formed during the reaction. Experimental data showed negligible effect of ionic strength of the medium on the rate. Kinetic results obtained on varying concentrations of hydrogen ions indicate negligible effect of hydrogen ion variation, which means that the rate of the reaction is not affected by increase or decrease in [H^+] concentrations (Table 2).

Table 1
Effect of variation of oxidant, Aspirin, Pd(II) at 35°

[NaIO4]X103 (Mol dm^{-3})	*[Substrate]x10^2 (Mol dm^{-3}s^{-1})*	*[Pd(II)]x10^{-6} (mol dm^{-3})*	*(-dc / dt)x10^6 (mol dm^{-3})*
0.83	1.00	3.35	3.5
1.00	1.00	3.35	2.2
1.25	1.00	3.35	5.7
1.67	1.00	3.35	3.1
2.05	1.00	3.35	1.6
5.00	1.00	3.35	6.5
1.00	0.20	3.35	0.5
1.00	0.33	3.35	0.7
1.00	0.40	3.35	0.9
1.00	0.50	3.35	1.7
1.00	0.60	3.35	2.0
1.00	1.00	3.35	2.2
1.00	1.00	1.67	1.6
1.00	1.00	3.35	2.2
1.00	1.00	5.02	2.6
1.00	1.00	6.67	3.2
1.00	1.00	8.34	3.4
1.00	1.00	10.05	3.9

Table 2
Effect of variation of $HClO_4$, KCl, $NaClO_4$ at 35 °C

[$HClO_4$] X 10^3M	*[KCl]X 10^3M*	*[$NaClO_4$]X 10^3M*	*(-dc / dt)x 10^7*
0.8	1.00	1.00	2.0
1.00	1.00	1.00	2.2
1.25	1.00	1.00	1.6
1.67	1.00	1.00	1.3
2.50	1.00	1.00	1.0
5.00	1.00	1.00	0.6
1.00	0.8	1.00	1.6
1.00	1.00	1.00	2.2
1.00	1.25	1.00	2.0
1.00	1.67	1.00	1.2
1.00	2.50	1.00	2.0
1.00	5.00	1.00	1.2
1.00	1.00	0.80	5.4
1.00	1.00	1.00	5.6
1.00	1.00	1.25	4.9
1.00	1.00	1.67	5.0
1.00	1.00	2.5	6.2
1.00	1.00	5	2.0

The kinetic studies were also made in the temperature range of 30-45 °C and the obtained specific rate constant were used to draw a plot of log k versus 1/T (fig. 2) which was linear. Values of the activation parameters were calculated (table 3). Moderate ΔH* and ΔE* values are favorable for electron transfer reaction. The high value of ΔG* has been due to energy of solution changes in the transition state. The negative value of ΔS* suggest that the intermediate complex is more ordered than the reactants.

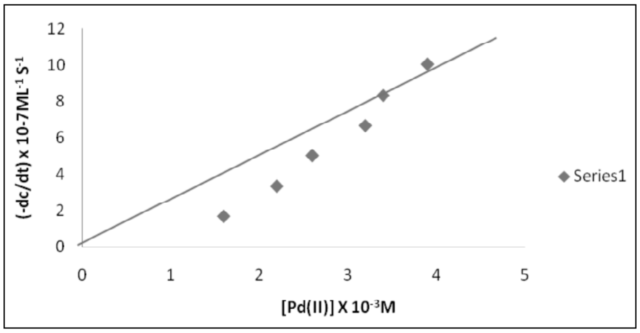


Figure 1

(Plot between [Pd(II) X 10^{-3}M vs. (-dc/dt) x 10 ML-1S^{-1})

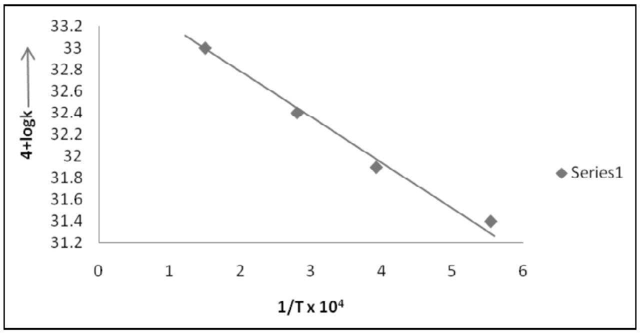


Figure 2

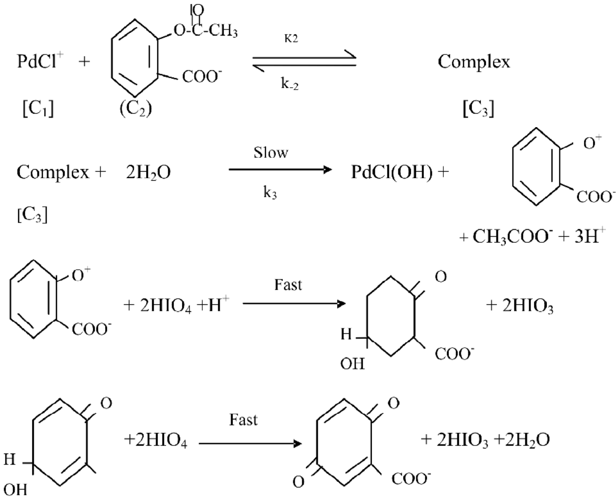
(Plot between log k vs 1/T for oxidation of Aspirin)

Table 3
Activation parameters at 35 °C

Parameter	*Temperature°c*	*Aspirin*
k_1x10^4s^{-1}	30	1.54
k_1x10^4s^{-1}	35	2.2
k_1x10^4s^{-1}	40	3.92
k_1x10^4s^{-1}	45	5.54
log A		11.11
ΔE_a*(kJmol^{-1})	35	63.58
ΔG*(kJmol^{-1})	35	52.41
ΔH*(kJmol^{-1})	35	25.99
ΔS*(JK^{-1} mol-----$_{----}^{-1}$)	35	-8.61

The observed modest enthalpy of activation indicates that oxidation presumably occurs via an inner sphere mechanism. This conclusion is supported by earlier observations. The activation parameters evaluated for the catalyzed reaction explain the catalytic effect on the reaction.

The dominance of PdCl$^+$ Species in aqueous acidic medium depends on [Cl$^-$].Considering the above kinetic observations, the following reaction scheme gives the details of the various steps in the reaction.



(1,4 Benzoquinone-2 Corboxylation)

Considering the above steps and applying the steady state treatment with reasonable approximation, the rate law may be written as follows-

$$\text{Rate} = k_3\,[C_3]$$

$$\text{Rate} = \frac{k_2\,k_3[\text{Pd(II)}]_T\,k_2[s]}{(k_{-1}+k_3)(1+k_1[\text{Cl}^-])+k_2[s]}$$

CONCLUSION

It is concluded from the present investigation HIO_4 and PdCl$^+$ are the reactive species of Sodium Periodate and Pd(II) chloride in an acidic medium respectively.

Acknowledgement

One of the authors Reena Patel thanks U.G.C., New Delhi for financial assistance.

References

[1] DAS, A.K. Kinetic and mechanistic aspects of metal ion Catalyst in Cerium Oxidation.Coord Chem. 213, 307-325, **(2001)**.

[2] K. RECZ. M. GURGER, Z. S. NAGY UNGVARAI: Int. Kinetics, 38(8), 503, **(2006).**

[3] Sh. SRIVASTAVA, R. K. SHARMA: Kinetics and mechanism of Irridium(III) Catalysed Oxidation of some Cyclic Ketones by Acid Bromate. Oxid. Commun., 29(2), 343, **(2006).**

[4] ASHISH, S. SINGH, A. SINGH, B. SINGH: Mechanistic study of Osmium(VIII) Promoted Oxidation of Crotonic Acid by Aqueous Alkaline Solution of Potassium Bromate. Trans. Metal Chem., 30(5), 610, **(2005)**.

[5] A. IFTHIKHAR, C. MOHAMMAD, D. ASHRAF: Kinetics and Mechanism of Palladium(II) Chloride Catalysed Oxidation of Allyl Alcohol by potassium Hexacynoferrate(III). Int J Chem.kinet., 11, 813 (2004).

[6] Sh. SRIVASTAVA, S. SINGH: Mechanistic study of Ruthenium(III) Catalysed Oxidation of Leucine by alkaline N-Bromoacetamide. Oxidation Commun., 29(3), 708, **(2006)**.

[7] Sh. SRIVASTAVA, A. AWASTHI, K. SINGH: Ruthenium (III)- catalysed Oxidation of Cyclopentanol and Cyclohexanol by N-Bromoacetamide. *Int. J. Chem. Kinet.*, 37, 275, **(2005)**.

[8] A. K. SINGH, DEEPTI CHOPRA; Oxidation commun., 20(3), 450-464, **(1997)**.

[9] K. SUREKHA MAVLANG, NIRMAL, N. HALLIGUDI, T. SHARANAPPA NANDIBEWOOR, Reaction Kinetic and Catalysis Letters, 72(2), 391-398, **(2001)**.

[10] D. KUMAR, HARI SINGH, *et al.* 17th+Annual Conf. Mat. Res. Soc. Ind. Lucknow **(2006)**.

[11] SRIVASTAVA S., SINGH K, SHUKLA M., PANDEY N., Oxidation Communication, 24(4), 558-562, **(2001)**.

[12] GUPTA N., RAHMANI S., SINGH A.K., Oxidation Communication 22(2), 243-273, **(1999)**.