Indian Journal of Chemistry
Vol. 32A, December 1993, pp. 1060-1063

Kinetics and mechanism of palladium(II) catalysed oxidation of some hydroxyacids by N-bromosuccinimide in perchloric acid medium

Rashmi Saxena & S K Upadhyay*
Department of Chemistry, Harcourt Butler Technological Institute, Kanpur 208 002, India

Received 12 May 1993; revised and accepted 11 June 1993

The kinetics of oxidation of palladium(II) catalysed oxidation of some hydroxyacids, viz., malic, citric and tartaric acids by N-bromosuccinimide have been studied in perchloric acid medium in the presence of mercuric acetate. A first order dependence of rate each in [oxidant] and [catalyst] has been observed. The order of reaction in substrate decreases at higher [substrate]. A retarding effect of $[H^+]$ on the rate has also been observed. A suitable mechanism consistent with observed kinetic data is proposed and discussed.

The formation of a 1:1 complex between $[Pd(OH)Cl_3]^{2-}$ (reactive species of $PdCl_2$ in alkaline medium) and chloramine-T and its subsequent reaction with substrate has been observed[1] during palladium(II) catalysed oxidation of hydroxyacids by alkaline chloramine-T. However, the kinetic results for the palladium(II) catalysed oxidation of hydroxyacids by N-bromosuccinimide (NBS) in perchloric acid medium support the formation of an intermediate complex between substrate and the catalyst. The present paper incorporates the detailed results of the title investigation.

Materials and Methods

DL-Malic acid, citric acid, DL-tartaric acid, N-bromosuccinimide (E. Merck), succinimide, mercuric acetate, perchloric acid (70%, E. Merck) palladous chloride (Johnson Matthey) and other reagents employed were of AR grades. All solutions were prepared in doubly distilled water.

Solution of NBS was always prepared a fresh and its strength was checked by iodometric method.The solution of Pd(II) chloride was prepared by dissolving the sample in very dilute HCl, the final strength of palladium(II) chloride and HCl being kept at 22.5×10^{-3} and 1.0×10^{-2} mol dm^{-3} respectively. The stock solution of Pd(II) chloride was stored in a black coated bottle to prevent photochemical decomposition.

All solutions were equilibrated at the desired temperature (± 0.1°C) and the reaction was initiated by addition of NBS solution to a mixture of other reagents. The progress of the reaction was followed by determining NBS iodometrically in aliquots withdrawn after regular time intervals. The iodine liberated by palladium(II) was taken into account.

Stoichiometry

The reaction mixtures containing a known excess of [NBS] over [hydroxyacid] were kept in presence of $HClO_4$, $Hg(OAc)_2$ and $PdCl_2$ at 35°C for 72 hrs. After completion of the reactions, the unconsumed NBS was estimated iodometrically in different sets of experiments. Stoichiometry in general may be represented by Eq. (1).

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C(OH)COOH + >NBr \rightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C=O \quad >NH + HBr + CO_2 \quad \ldots (1)$$

However, in the case of tartaric acid, nearly two moles of NBS were consumed for each mole of tartaric acid.

The presence of carbonyl compound as the oxidation product was detected by spot tests[2]. For tartaric acid, glyoxylic acid and formic acid were detected as the products. The corresponding carbonyl compounds and CO_2 as the oxidation products of hydroxyacids[3] and C–C cleavage product in the case of tartaric acid are reported in the literature[1,3]. It is, therefore, likely that the corresponding carbonyl compound of tartaric acid may further be oxidised to give C–C cleavage products when oxidant is in excess.

Results and Discussion

The reactions were studied at various initial [reactant]. The log [NBS] versus time plots initially

showed a curvature up to 10-20% of the reactions then became linear and thereofre, pseudo-first order rate constant in NBS (k_{obs}) were evaluated from the slopes of these plots. The rate constants at different initial [NBS] are reported in Table 1. It is observed that an increase in initial [NBS] resulted in a decrease in the k_{obs} (Table 1).

The plots of (k_{obs}) versus [substrate] (Fig. 1) showed deviation from linearity at higher [substrate] while the plots of ($1/k_{obs}$) versus 1/[substrate] were linear with intercept indicating that order of reaction in substrate falls from unity at higher [substrate].

The effect of [H^+] on the reaction rate was studied at a fixed ionic strength ($\mu = 0.06$ mol dm^{-3}) maintained by the addition of sodium perchlorate. The amount of acid already present in the catalyst was taken into account. An increase in [$HClO_4$] lead to a decrease in the pseudo-first order rate constants (k_{obs}) (Table 1) and the plots of ($1/k_{obs}$) versus [$HClO_4$] were linear with intercepts (Fig. 2).

The plots of (k_{obs}) versus [$PdCl_2$] (Fig. 3) were linear with intercepts suggesting that rate $\alpha\{k' + k''[PdCl_2]\}$ where k' and k'' are rate constants for uncatalysed and catalysed paths respectively. It is also clear from Fig. 3 that rate for uncatalysed path is small.

The values of k' and k'' have also been evaluated with the help of intercepts and slopes of Fig. 3. The values of k' are 0.20, 0.50 and 0.15×10^{-4} s^{-1} in case of malic, citric and tartaric acids respectively while the values of k'' are 1.80, 2.00 and 0.55 s^{-1} mol^{-1} dm^3 for malic, citric and tartaric acids respectively under the experimental conditions as mentioned in Fig. 3.

The effect of ionic strength was studied by carrying out investigations in the presence of different amounts of sodium perchlorate (up to 20×10^{-2} mol dm^{-3}) which had no effect on the reaction rate. Addition of succinimide (reaction product of NBS) and mercuric acetate had also no effect on the reaction rate. Successive addition of acetic acid retarded observed rate constant (k_{obs}), Addition of sodium chloride resulted in an

Table 1—Effect of [N-bromosuccinide] and [$HClO_4$] on the rate constant at 35°C

[S] = 2.0×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 2.0×10^{-3} mol dm^{-3}, [Pd(II)] = 1.12×10^{-4} mol dm^{-3} for malic and citric acids and 2.25×10^{-4} mol dm^{-3} for tartaric acid. The effect of acid was studied at fixed ionic strength ($\mu = 0.06$ mol dm^{-3} maintained by $NaClO_4$).

[NBS] × 10^3 (mol dm^{-3})	[$HClO_4$] × 10^2 (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})		
		Malic acid A	Citric acid B	Tartaric acid C
1.5	2.0	2.68	5.37	0.92
2.0	2.0	2.11	2.30	0.76
2.5	2.0	1.91	1.89	0.67
3.0	2.0	1.42	1.54	0.57
2.0	0.4	3.45	4.79	1.82
2.0	1.0	2.49	3.26	1.00
2.0	2.0	1.91	2.11	0.69
2.0	3.0	1.45	1.61	0.56
2.0	4.0	1.18	1.34	0.46
2.0	6.0	0.87	0.95	0.34

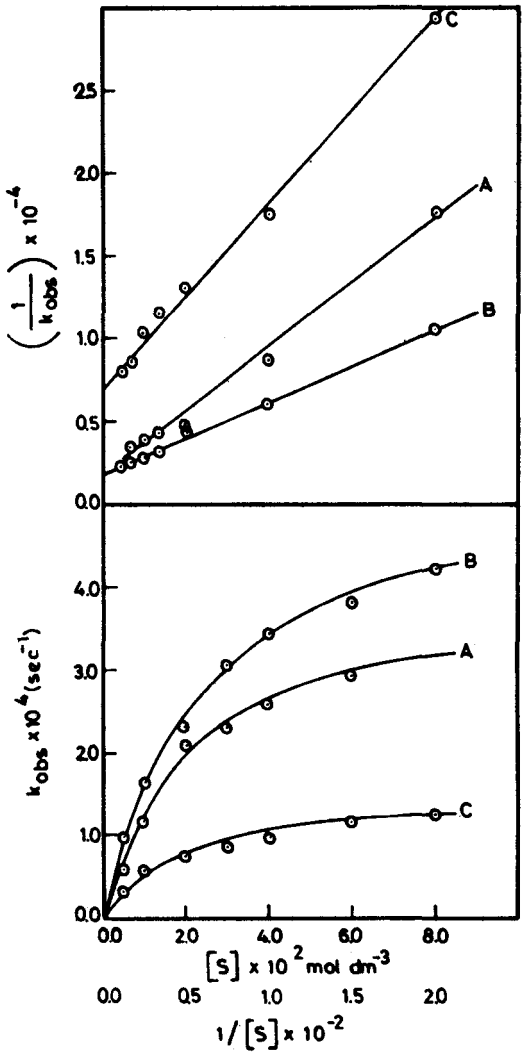


Fig. 1—Plot of (k_{obs}) versus [S] or ($1/k_{obs}$) versus (1/[S]) at 35°C. ([NBS] = 2.0×10^{-3} mol dm^{-3}, [$HClO_4$] = 2.0×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 2.0×10^{-3} mol dm^{-3} and [Pd(II)] = 1.12×10^{-4} mol dm^{-3} for malic and citric acids and 2.25×10^{-4} mol dm^{-3} for tartaric acid) A, malic acid; B, citric acid and C, tartaric acid.

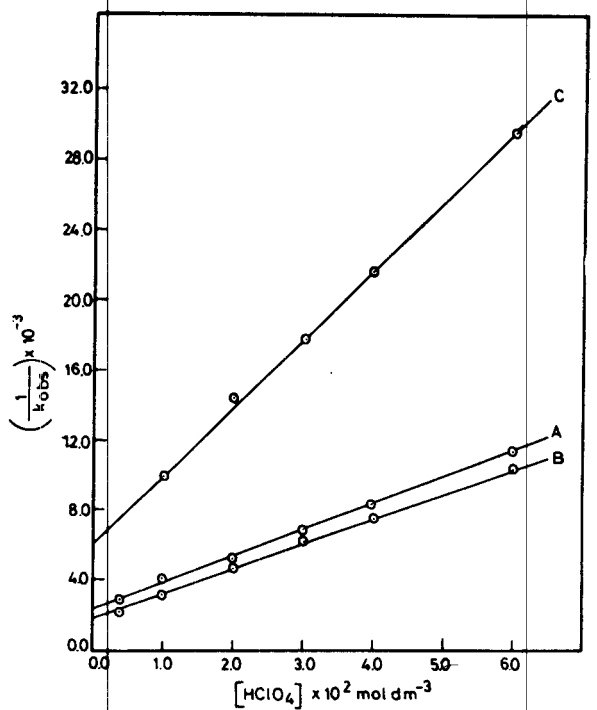


Fig. 2—Plots of $(1/k_{obs})$ versus $[HClO_4]$ at 35°C ([Substrate] = 2.0×10^{-2} mol dm^{-3}. Other conditions are same as in Fig. 1.)

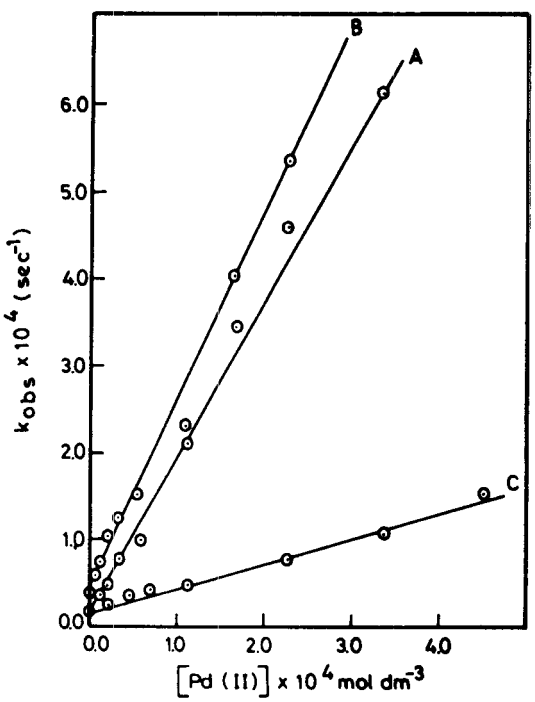


Fig. 3—Plots of (k_{obs}) versus [Pd(II)] at 35°C ([Substrate] = 2.0×10^{-2} mol dm^{-3}. Other conditions are same as in Fig. 1)

increase in k_{obs} (Table 2) and a plot of (k_{obs}) versus $[Cl^-]^2$ was linear with an intercept. The rates were also studied at 35°, 40°, 45° and 50°C and the activation parameters (Table 3) have been evaluated.

In acidic media NBS, protonated NBS (i.e. $>N^+HBr$ or NBSH) and Br^+ are the possible reactive species[4-6] of NBS. Added mercuric acetate acts as a scavenger for any Br^- formed in the reaction and its negligible effect on the reaction rate rules out its involvement in NBS oxidation. Retarding effect of $[H^+]$ on the rate rules out the possibility of $>N^+HBr$ as the reactive species of NBS.

Negligible ionic strength effect suggests involvement of atleast one neutral molecule in the rate-determining step. The retardation of rate by added acetic acid (+ve dielectric effect) indicates anion-dipole or dipole-dipole interaction in the rate determining step. Involvement of Br^+ in the rate determining step also is ruled out as its involvement should give a negative dielectric effect. Thus NBS itself seems to be the reactive species.

Stock solution of Pd(II) chloride was prepared in dil. HCl in which it is known to exist[7] as $[PdCl_4]^{2-}$ as follows,

$$PdCl_2 + 2\,Cl^- \rightleftharpoons [PdCl_4]^{2-}$$

Table 2—Effect of [acetic acid] and [sodium chloride] on the rate constant at 35°C

[NBS] = 2.0×10^{-3} mol dm^{-3}, [S] = 2.0×10^{-2} mol dm^{-3}, $[HClO_4] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[Hg(OAc)_2] = 2.0 \times 10^{-3}$ mol dm^{-3} and [Pd(II)] = 1.12×10^{-4} mol dm^{-3} for malic and citric acids and 2.25×10^{-4} mol dm^{-3} for tartaric acid.

$[CH_3COOH]$ (%, v/v)	$[NaCl] \times 10^3$ (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})		
		Malic acid A	Citric acid B	Tartaric acid C
Nil	—	2.11	2.30	0.76
5	—	1.19	1.84	0.57
10	—	1.53	1.26	0.47
15	—	1.34	0.99	0.40
20	—	1.15	0.69	0.38
—	0.5	—	2.49	0.95
—	1.0	2.20	3.07	1.53
—	1.5	2.30	3.26	2.49
—	2.0	2.87	3.83	3.26
—	3.0	3.64	4.60	4.40
—	4.0	4.41	—	5.75

A positive effect of Cl^- on the rate of reaction suggests $[PdCl_4]^{2-}$ as the reactive species of $PdCl_2$. A complex formation[7,8] between $[PdCl_4]^{2-}$ and various organic substances, viz., amines, aminoalcohols, etc. has also been observed. The presence of Michaelis-Menton reciprocal relationship[9] in

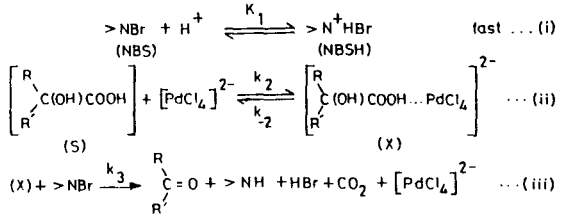
Table 3—Thermodynamic parameters

$[NBS] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[S] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[HClO_4] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[Hg(OAc)_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, and $[Pd(II)] = 1.12 \times 10^{-4}$ mol dm^{-3} for malic and citric acids and 2.25×10^{-4} mol dm^{-3} for tartaric acid.

	ΔE_a (kJ mol^{-1})	log A	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
Malic acid	68.90	8.00	66.34	− 92.12	94.72
Citric acid	65.07	7.39	62.51	−103.76	94.48
Tartaric acid	86.16	10.49	80.60	− 44.40	94.28

the case of hydroxyacids (Fig. 1) suggests a complex formation between the substrate and the catalyst. The complex formation between hydroxyacid and $PdCl_2$ in perchloric acid medium has also been confirmed spectrophotometrically. The absorbance was measured (at 420 nm) for a series of solutions containing varying amount of hydroxyacid with a fixed amount of $PdCl_2$ and $HClO_4$. It is observed that addition of increasing amount of hydroxyacid decreases the absorbance due to $PdCl_2$ until the [hydroxyacid]: $[PdCl_2]$ ratio becomes 1:1 thereafter, there is no further decrease in absorbance. The absorbance due to hydroxyacid at 420 nm was negligible.

On the basis of above facts and experimental results a common mechanism for the oxidation of hydroxyacids by NBS in presence of $PdCl_2$ may be proposed as given in Scheme 1.



where >NH represent succinimide. R and R′ represent −H and $-CH_2COOH$ for malic acid, $-CH_2COOH$ and $-CH_2COOH$ for citric acid and −H and −CH(OH)COOH for tartaric acid.

Scheme 1

According to Scheme 1, the rate of disappearance of NBS may be given as,

$$-\frac{d[NBS]}{dt} = \frac{K_2 k_3 [Pd(II)]_T [S] [NBS]_T}{\{1 + K_1[H^+]\}\{1 + K_2[S] + k'[NBS]_T\}} \quad \ldots (2)$$

where $k' = k_3/k_{-2}$

$[NBS]_T$ and $[Pd(II)]_T$ represent the total concentrations of NBS and palladium(II) at any time t and may be given as,

$$[NBS]_T = [NBS] + [NBSH]$$

and

$$[Pd(II)]_T = [X] + [PdCl_4]^{2-}$$

The experimental results, i.e. first order dependence of rate on [NBS] during a particular kinetic run, decrease in the value of k_{obs} with an increase in $[NBS]_0$, decrease in order of reaction in substrate at higher [substrate], first order dependence of rate on [catalyst] (steps responsible for uncatalyzed path have not been included in the mechanism) and retarding effect of $[H^+]$ on the rate are in agreement with rate law Eq. (2).

The values of K_1 for step (i) (Scheme 1) have also been obtained with the help of intercepts and slopes of the plots of $(1/k_{obs})$ versus $[HClO_4]$ (Fig. 2). The values of K_1 were 66.0, 70.0 and 66.0 dm^3 mol^{-1} for malic, citric and tartaric acids respectively, i.e. nearly identical within the experimental error.

Acknowledgement

One of us (RS) gratefully acknowledges the award of SRF by the CSIR, New Delhi.

References

1 Shukla Anju & Upadhyay S K, *Indian J Chem*, 30A (1991) 154.
2 Feigl F, *Spot tests in organic analysis*, (1975) 191, 195.
3 Bishnoi M L, Negi S C & Banergi K K, *Indian J Chem*, 25A (1986) 660.
4 Reddy P G, Ramesh Y & Kandlikar S, *Oxid Commun*, 7 (1984) 89.
5 Sharma J P, Singh R N P, Singh A K & Singh Bharat, *Tetrahedron*, 42 (1986) 2739.
6 Saxena Rashmi, Gupta Sushma & Upadhyay S K, *Indian J Chem*, 29A (1990) 847.
7 Cotton F A & Wilkinson G, *Advanced inorganic chemistry* (John Wiley, New York) (1967), p. 1026.
8 Shukla Anju, Gupta Sushma & Upadhyay S K, *Int J chem Kinet*, 23 (1991) 279.
9 Michaelis L & Menton M L, *Biochem Z*, 49 (1913) 333.