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Kinetics and Mechanism of Ru(III) Catalyzed Oxidation of Butyl Digol by N-Bromosuccinimide

A.K. SINGH
Department of Chemistry
Magadh University, Bodh-Gaya-824 234, India

Kinetics and mechanism of Ru(III) catalyzed oxidation of butyl digol by N-bromosuccinimide (NBS) has been extensively studied at 35°C under Ostwald isolation condition. Kinetic findings indicate first order reaction kinetics in oxidants, substrates, H^+ ions and catalysts, respectively. There is no significant influence of successive addition of mercuric acetate, succinimide and sodium chlorate on redox reaction rate. On the other hand, it shows decreasing effect on addition of potassium chloride on reaction rate. On the basis of the experimental observed kinetic findings, the proposed rate expression is $\frac{-d[NBS]}{dt} = \frac{K[NBS][H^+][S][Ru(III)]}{K_1[H_2O] + [Cl^-]}$.

Key Words: Kinetics, Mechanism, Ru(III), Oxidation, Butyl digol, N-Bromosuccinimide.

INTRODUCTION

N-Bromosuccinimide (NBS) is a potential oxidising agent[1, 2] which has been extensively used in the estimation of several organic as well as inorganic compounds. Recently transition metal ions have been widely used as effective homogeneous catalysts in the oxidation of organic compounds in acidic as well as in alkaline medium[3–5]. The use of ruthenium(III) chloride as effective homogeneous catalyst has been reported by Tondon and Krishna[6]. In the present work, an attempt has been made to study the mechanism of Ru(III) catalyzed oxidation of butyl digol by N-bromosuccinimide.

EXPERIMENTAL

All the chemicals are of A.R. (E. Merck) or B.D.H. grade. The solution of NBS is always freshly prepared and stored in a black coated flask to prevent photochemical effect[7], and its strength was checked iodometrically[8]. The aqueous solution of ruthenium(III) choloride was prepared in 0.01 N HCl in double distilled water. The entire progress of the reaction is elucidated by estimating the unreacted N-bromosuccinimide iodometrically at 35°C under isolation condition.

RESULTS AND DISCUSSION

It is evident from Table-1 that the reaction follows first order reaction kinetics with respect to [NBS]. This finding has been further confirmed by k_1 (calculated) which is very close to each other as well as k_1 (graphical) values (not shown). It shows direct proportionality between k_1 values and [B. Digol] and k_2 (2nd order rate constant) do not change significantly, leading us to conclude first order dependence in [B. Digol]. This finding has been further confirmed graphically, *i.e.*, k_1 *vs.* [Digol] (not shown), a straight line passing through origin with a slope 4.96×10^{-1} mol^{-1}, min^{-1} directly gives the value of k_2; practically constant value confirms first order reaction kinetics in [B. Digol]. It shows direct proportionality in $[H^+]$, whereas it shows linear relationship between k_1 and [B. Digol] and k_2 values are practically constant supporting first order reaction kinetics in $[H^+]$ and [Ru(III)] (Table-2) respectively. It is evident from Table-3 that no significant effect of increasing the $[Hg(OAc)_2]$ [succinimide] and $[NaClO_4]$ observed whereas it shows decreasing effect on addition of [KCl] on redox reaction rate (Table-4) respectively. Finally the dependence of temperature on redox reaction rate has been extensively studied at three temperatures and important thermodynamical functions have been evaluated and found to be energy of activation (E_a) = 13.49 kcal/mol, frequency factor (A) = 3.17×10^9 mol^{-1}, sec^{-1}, entropy of activation $\Delta S^{\pm} = -16.01$ e.u., heat of activation ($\Delta H^{\pm}$) = 12.88 kcal/mol and free energy of activation ($\Delta F^{\pm}$) = 17.81 kcal/mol respectively.

TABLE-1

DEPENDENCE OF [OXIDANT], [SUBSTRATE] ON REACTION RATE

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, $[KCl] = 400 \times 10^{-2}$ M

$[NBS]^{\pm}$ $\times 10^{-4}$ M	[B. Digol] $\times 10^{-2}$ M	[Ru(III)] $\times 10^{-7}$ M	$[HClO_4]$ $\times 10^{-2}$ M	$k_1 \times 10^3$ min^{-1} (Calculated values)	$k_1 \times 10^3$ min^{-1} (Graphical values)
4.70	2.00	1.54	1.00	10.29	10.26
7.59	2.00	1.54	1.00	10.03	10.06
9.88	2.00	1.54	1.00	9.87	9.84
13.33	2.00	1.54	1.00	10.01	9.89
22.17	2.00	1.54	1.00	10.14	10.07
25.77	2.00	1.54	1.00	10.09	10.07
[B. Digol]$^{\pm}$ $\times 10^{-2}$ M	[NBS] $\times 10^{-4}$ M				$k_2 \times 10^1$ mol^{-1}, min^{-1}
1.00	9.88	1.54	1.00	4.98	4.99
1.25	9.88	1.54	1.00	6.20	4.96
2.00	9.88	1.54	1.00	9.87	4.94
2.50	9.88	1.54	1.00	12.56	5.02
4.00	9.88	1.54	1.00	19.85	4.96
5.00	9.88	1.54	1.00	24.86	4.97

B. digol = Butyl digol; NBS = N-bromosuccinimide; ± = Vriation of individual parameters.

TABLE-2
DEPENDENCE OF [$HClO_4$], [Ru(III)]
[$Hg(OAc)_2$] = 400 × 10^{-3} M, [KCl] = 4.00 × 10^{-2} M

[$HClO_4$]$^{\pm}$ × 10^{-2} M	[NBS] × 10^{-4} M	[B. Digol] × 10^{-2} M	[Ru(III)] × 10^{-7} M	k_1 × 10^3 min^{-1}	k_1 × 10^3 mol^{-1} min^{-1}
1.00	9.88	2.00	1.54	9.87	9.87
1.25	9.88	2.00	1.54	12.68	10.14
1.67	9.88	2.00	1.54	16.79	10.05
2.00	9.88	2.00	1.54	20.00	10.00
3.30	9.88	2.00	1.54	33.05	10.02
5.00	9.88	2.00	1.54	50.05	10.01
[Ru(III)]$^{\pm}$ × 10^{-7} M			[$HClO_4$] × 10^{-2} M		
0.44	9.88	2.00	1.00	2.97	6.95
0.88	9.88	2.00	1.00	5.63	6.39
1.32	9.88	2.00	1.00	6.56	6.48
1.53	9.88	2.00	1.00	9.87	6.41
1.76	9.88	2.00	1.00	11.44	6.50
2.00	9.88	2.00	1.00	14.15	6.43

TABLE-3
DEPENDENCE OF [$Hg(OAc)_2$] AND [SUCCINIMIDE]
[$HClO_4$] = 1.00 × 10^{-2} M, [KCl] = 4.00 × 10^{-2} M

[$Hg(OAc)_2$]$^{\pm}$ × 10^{-3} M	[NBS] × 10^{-4} M	[B. Digol] × 10^{-2} M	[Ru(III)] × 10^{-7} M	k_1 × 10^3 min^{-1}
4.00	9.88	2.00	1.54	9.87
6.00	9.88	2.00	1.54	9.92
9.00	9.88	2.00	1.54	9.85
12.00	9.88	2.00	1.54	9.95
15.00	9.88	2.00	1.54	9.86
18.00	9.88	2.00	1.54	9.84
24.00	9.88	2.00	1.54	9.88
[Succinimide]$^{\pm}$ × 10^{-4} M				
0.00	9.88	2.00	1.54	9.87
5.00	9.88	2.00	1.54	9.88
8.00	9.88	2.00	1.54	9.80
10.00	9.88	2.00	1.54	9.78
15.00	9.88	2.00	1.54	9.90
20.00	9.88	2.00	1.54	9.86
25.00	9.88	2.00	1.54	9.85

TABLE-4
DEPENDENCE OF [KCl], [NaClO$_4$]

[KCl]$^{\pm}$ $\times 10^{-2}$ M		[NBS] $\times 10^{-4}$ M	[B. Digol] $\times 10^{-2}$ M	Ru(III) $\times 10^{-7}$ M	[HClO$_4$] $\times 10^{-2}$ M	$k_1 \times 10^3$ min^{-1}
0.04		9.88	2.00	1.54	1.00	9.87
0.06		9.88	2.00	1.54	1.00	8.46
0.08		9.88	2.00	1.54	1.00	8.02
0.16		9.88	2.00	1.54	1.00	6.82
0.20		9.88	2.00	1.54	1.00	5.73
0.30		9.88	2.00	1.54	1.00	5.57
0.40		9.88	2.00	1.54	1.00	5.27
[NaClO$_4$]$^{\pm}$ $\times 10^{-4}$ M	$\mu \times$ M					
0.00	0.05	9.88	2.00	1.54	1.00	9.87
0.05	0.10	9.88	2.00	1.54	1.00	9.88
0.10	0.15	9.88	2.00	1.54	1.00	9.92
0.20	0.25	9.88	2.00	1.54	1.00	9.90
0.30	0.35	9.88	2.00	1.54	1.00	9.86
0.40	0.45	9.88	2.00	1.54	1.00	9.89
0.45	0.50	9.88	2.00	1.54	1.00	9.82

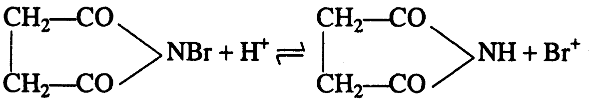
TABLE-5
DEPENDENCE OF [TEMPERATURE]
[Hg(OAc)$_2$] = 4.00×10^{-3} M, [KCl] = 4.00×10^{-2} M

[Temp]$^{\pm}$ (°C)	[NBS] $\times 10^{-4}$ M	[B. Digol] $\times 10^{-2}$ M	Ru(III) $\times 10^{-7}$ M	[HClO$_4$] $\times 10^{-2}$ M	$k_1 \times 10^3$ min^{-1}
30	9.88	2.00	1.54	1.00	6.98
35	9.88	2.00	1.54	1.00	9.87
40	9.88	2.00	1.54	1.00	13.89
45	9.88	2.00	1.54	1.00	19.77
30	13.33	2.00	1.54	1.00	7.09
35	13.33	2.00	1.54	1.00	10.01
40	13.33	2.00	1.54	1.00	14.10
45	13.33	2.00	1.54	1.00	20.07

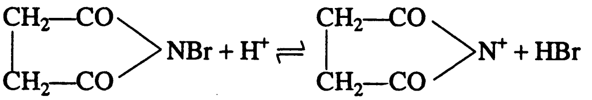
Insignificant effect of addition of mercuric acetate indicates that it itself is not involved in NBS oxidation, but only acts as a scavenger[9] for any Br formed in the reaction. The actual reactive species of Ru(III) chloride[10, 11] in this reaction is $[RuCl_5 \cdot H_2O]^{2-}$ supported by negative effect of chloride ion and the following equilibria in right direction.

$$[RuCl_6]^{3-} + H_2O = [RuCl_5 \cdot H_2O]^{2-} + Cl^- \qquad \ldots (1)$$

In acidified solution of NBS the following equilibria exist:



. . . (2)



. . . (3)

Thus NBS itself or Br^+ or N^+BSH is the possible oxidising species. Neither NBS itself nor Br^+ is the real oxidising species is ruled out because of hydrogen ion dependence and zero effect of succinimide on reaction rate. Under these circumstances, the only choice, *i.e.*, protonated NBS, *i.e.*, N^+BSH are the most predominant and real oxidising species of NBS.

Considering the above facts and kinetic findings the following reaction mechanism has been proposed:

$$NBS + H^+ \rightleftharpoons N^+BSH \qquad \ldots (I)$$

$$\underset{C_1}{[RuCl_6]^{3-}} + H_2O \overset{k_1}{\rightleftharpoons} \underset{C_2}{[RuCl_5{\cdot}H_2O]^{2-}} + Cl^- \qquad \ldots (II)$$

$$C_2 + N^+BSH \underset{Slow}{\overset{k_2}{\rightleftharpoons}} C_3 \text{ Complex} \qquad \ldots (III)$$

$$C_3 + RCH_2CH_2OH \xrightarrow[Slow]{k_2} C_3(RCH_2H_2CH^+OH) + C_2 \qquad \ldots (IV)$$

$$R = C_4H_9CH_2CCH_2O^- \text{ (B. Digol)}$$

$$NBSH_2 \xrightarrow[fast]{k_3} M + HBr \qquad \ldots (V)$$

$$RCH_2C^+HOH + H_2O \underset{fast}{\overset{k_4}{\rightleftharpoons}} RCH_2CHO + H_3O^+ \qquad \ldots (VI)$$

The rate of the reaction in terms of consumption of NBS may be

$$\frac{-d[NBS]}{dt} = k_2[S][C_3] \qquad \ldots (VII)$$

where S = butyl digols.

The total concentration of Ru(III) may be

$$[Ru(III)]_{-T} = [C_1] + [C_2] + [C_3] \qquad \ldots (VIII)$$

From steps (II) and (III) we have

$$[C_1] = \frac{[C_2][Cl^-]}{k_1[H_2O]} \qquad \ldots (A)$$

and

$$[C_2] = \frac{[C_3]}{k_2[N^+BSH]} \qquad \ldots (B)$$

From equations (A), (B), we have

$$[C_1] = \frac{[Cl^-][C_3]}{k_1k_2[H_2O][N^+BSH]} \qquad \ldots(C)$$

On substituting the value of $[C_1]$ and $[C_2]$ in equation (VIII), we have

$$[Ru(III)]_T = \frac{[C_3][Cl^-]}{k_1k_2[H_2O][N^+BSH]} + \frac{[C_3]}{k_2[N^+BSH]} + C_3$$

$$[C_3] \times \left\{ \frac{\{[Cl^-] + k_1[H_2O] + k_1k_2[H_2O][N^+BSH]\}}{k_1k_2[H_2O][N^+BSH]} \right\} \qquad \ldots(C)$$

Now from step (1), we have

$$[N^+BSH] = k[NBS][H^+]$$

On putting the value of $[N^+BSH]$ in equation (D), we have

$$[C_3] = \frac{kk_1k_2[H_2O][NBS][H^+][Ru(III)]_T}{k_1[H_2O] + [Cl^-] + k_1k_2k[H_2O][NBS][H^+]}$$

On comparing equation, $$\frac{-d[NBS]}{dt} = \frac{k_1[S]kk_1k_2[H_2O][NBS][H^+][Ru(III)]_T}{K_1[H_2O] + [Cl^-] + k_1k_2k[H_2O][NBS][H^+]}$$

or $$\frac{-d[NBS]}{dt} = \frac{kk_1k_2k_2[H_2O][S][NBS][H^+][Ru(III)]_T}{k_1[H_2O]\{1 + kk_2[NBS][H^+]\} + [Cl^-]}$$

on assuming $1 \gg k_1k_2[NBS][H^+]$. Thus

$$\frac{-d[NBS]}{dt} = \frac{kk_1k_2k_2[H_2O][NBS][H^+][S][Ru(III)]_T}{k_1[H_2O] + [Cl^-]} = \frac{k[NBS][H^+][S][Ru(III)]_T}{k_1[H_2O] + [Cl^-]} \qquad \ldots(X)$$

where $k = kk_1k_2k_2[H_2O]$.

The above rate expression is in complete agreement with our observed experimental kinetic findings. Thus the proposed mechanism is valid.

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