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Kinetic and mechanistic study of oxidation of 1,2-propanediol by aqueous alkaline solution of N-bromosuccinimide in the presence of aquachloro-complex of ruthenium(III) as homogeneous catalyst

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Kinetics of Ru(III) catalysis in oxidation of 1,2-propanediol by N-bromosuccinimide in alkaline media has been studied in presence of mercuric acetate as bromide ions scavenger in the temperature range of 30–45 °C. The reaction follows complex kinetics, being first order with respect to both 1,2-propanediol and Ru(III). First order kinetics with respect to NBS at its lower concentrations shifts to zero order at its high concentrations. Variation of both [OH^-] and [KCl] shows a positive effect on the rate of reaction. Negligible effect of addition of succinimide (reduction product of NBS) is observed, while variation of both [$Hg(OAc)_2$] and ionic strength has no effect on rate of the reactions. Various activation parameters are calculated. The products of the reactions have been identified as acetic acid and formic acid. A suitable mechanism in conformity with the kinetic observations is discussed and rate law derived.

Keywords: Kinetics, Reaction mechanism, Oxidation, 1,2-Propanediol, N-Bromosuccinimide, Ruthenium

The use of NBS has been reported in various reactions of biological and industrial interest[1], viz., oxidation degradation of α-amino acids, oxidation of psychotropic drugs, in the study of peptides cleavage in fragmentation of peptides and proteins, etc. Utility of N-bromosuccinimide as an environmental friendly reagent for sensitive determination of olanzapine and aripiprazolein in pharmaceuticals is also reported[2,3]. NBS has been used for the study of kinetics and mechanism of oxidation of esters[4], alcohols[5,6] and ketones[7-9] in acidic media. Although oxidative capacity of NBS has been examined in several uncatalysed[4-9] and catalysed[10-14] reactions in acidic media, so far, its role as oxidant in alkaline media in the presence of Ru(III) is unknown in the literature.

The 1,2-propanediol functionality is found in a series of synthetic intermediate. 1,2-Propanediol is a non-toxic, antifreeze in breweries and dairies. It finds importance in a several areas[15,16] such as (a) in the production of unsaturated polyester resins, (b) as an additive in nutrition product, (c) non-ionic detergent, (d) cosmetics, (e) brake fluid or hydraulic fluid, and, (f) as an de-icing agent. 1,2-Propanediol derivatives also find use as central acting skeletal muscle relaxant. These characteristics of 1,2-propanediol interest us to study its oxidation kinetics.

Most ruthenium produced is used for wear-resistant electrical contacts and the production of thick-film resistors. A minor application of ruthenium is its use in some platinum alloys, and, like many elements located near platinum, it is used in automobile catalytic converters. Some ruthenium complexes absorb light throughout the visible spectrum and are being actively researched in various potential solar energy technologies. For example, ruthenium-based compounds have been used for light absorption in dye-sensitized solar cells, a promising new low-cost solar cell system.

In view of importance of propylene glycols, unprobed catalytic nature of Ru(III) and role of NBS as oxidant in the presence of alkaline solution of ruthenium trichloride, an attempt has been made in the present article to investigate the kinetics and mechanism of Ru(III) catalysed oxidation of propylene glycol by alkaline solution of N-bromosuccinimide.

Materials and Methods

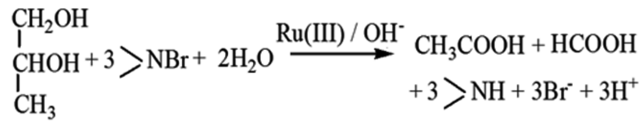
All the reagents used were of the highest purity available. NBS (CDH Lab) solution was always prepared afresh and its strength was checked iodometrically. The solution of sample of 1,2-propanediol (E. Merck) was prepared by dissolving its known amount in the desired volume of doubly distilled water. The solution of ruthenium(III) chloride (Loba Chem) was prepared by dissolving its 1 g sample in 200 mL of 0.01 *M* hydrochloric acid and diluting to 1000 mL with doubly distilled water. The strength of the thus prepared ruthenium(III) chloride solution was 3.824×10^{-3} *M*. It was used as the homogeneous catalyst in present investigation. Sodium perchlorate and sodium hydroxide were used to maintain the required ionic strength and alkalinity, respectively. A standard solution of mercuric acetate was acidified with 20% (*v/v*) acetic acid and solutions of all other reagents, viz., KCl, succinimide and sodium thiosulphate (all E. Merck) were prepared by dissolving their weighed samples in known volume of distilled water.

Kinetic investigations

All the kinetic measurements were carried out at constant temperature of 35 °C (±0.1 °C). Appropriate volumes of all reactants, NBS, Ru(III), $Hg(OAc)_2$, KCl, NaOH and $NaClO_4$ were taken in a reaction bottle (Jena glass). The requisite volume of doubly distilled water was added to the reaction mixture so that total volume of the reaction mixture was 100 mL after addition of requisite volume of 1,2-propanediol solution. The bottle containing the reaction mixture was placed in an electrically operated thermostat (maintained at 35 °C) for thermal equilibrium. Appropriate volume of solution of 1,2-propanediol, also equilibrated at 35 °C, was rapidly poured into the reaction mixture to initiate the reaction. The progress of the reaction was followed by estimating the amount of unconsumed [NBS] iodometrically in aliquots (5 mL) withdrawn from the reaction mixture at regular time intervals for about two half lives of the reaction.

The rate of the reaction (-*dc/dt*) in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of NBS, given as [NBS]*. The order of the reaction with respect to each reactant was determined by the relation between initial rate (-*dc/dt*) and initial [reactant].

Solutions of varying [NBS]:[1, 2- propanediol] ratios were equilibrated at 35 °C for 72 h under the condition [NBS] >> [1,2-propanediol]. Estimation of residual [NBS] in different sets showed that one mole of [1,2-propanediol] consumed three moles of NBS. Accordingly, the stoichiometric equation (A) can be formulated, where >NBr and >NH stand for NBS and succinimide (NHS), respectively.



…(A)

The main products of oxidation of 1, 2-propanediol are acetic acid and formic acid which were identified by spot test[17,18] and thin layer chromatography[19].

Results and Discussion

The kinetics of the oxidation of propylene glycol was investigated at several initial concentrations of the reactant and catalyst (Table 1).The value of first-order rate constant (k_{obs}) in each kinetic run was calculated as,

$$k_{obs} = (-dc/dt)/[NBS]^*$$

where [NBS]* represents the concentration of NBS at which tangents were drawn.

First order dependence in NBS at its low concentrations tending to zero order at its higher concentrations was observed. The shifting of order in NBS from first order to zero order is also obvious from the plot of (-*dc/dt*) versus [NBS] (Fig. 1).

The reaction was found to be dependent on the concentration of 1,2-propanediol. The rate of reaction was observed to be directly proportional to the [1,2-propanediol], indicating first order which is also evident from plot of (–*dc/dt*) versus [1,2-propanediol] (Fig. 2).

The rate of reaction (-*dc/dt*) increased linearly with increase in [Ru(III)], indicating first order dependence of the reactions on [Ru(III)] which is also obvious from the plot of (-*dc/dt*) versus [Ru(III)] (Fig. 3).

Table 2 shows the effects of variation of $[OH^-]$, [KCl] and addition of $[Hg(OAC)_2]$ on the rate of the reaction. A close examination of data given in Table 2 reveals the positive effect of $[OH^-]$ variation in the concentration range from $(0.50–1.33)\times10^{-2}$ mol dm^{-3} and after reaching a maximum, constant effect was observed from $(2.00–5.00)\times10^{-2}$ mol dm^{-3} $[OH^-]$ ions. This is also clear by the graph plotted between (-*dc/dt*) and $[OH^-]$ (Fig. 4).

Three-fold variation of mercuric acetate (from 1.11×10^{-3} to 3.34×10^{-3} mol dm^{-3}) did not influence the rate of reaction. Variation of ionic strength of the medium from 2.75×10^{-2} to 13.00×10^{-2} mol dm^{-3} showed negligible effect on the rate of the reaction (data not shown in table). Addition of chloride ions in the form of KCl to the reaction mixture under

Table 1 – Effect of variation of [NBS], [1, 2-propanediol] and [Ru(III)] on the rate at 35 °C.
{React. cond.: [NaOH] = 1.00×10^{-2} mol dm^{-3}; [KCl] = 1.00×10^{-2} mol dm^{-3}; [$Hg(OAc)_2$] = 2.50×10^{-3} mol dm^{-3}}

[NBS]$\times10^3$ (mol dm^{-3})	[1,2-propanediol]$\times10^2$ (mol dm^{-3})	Ru(III) $\times10^5$ (mol dm^{-3})	($-dc/dt$) $\times10^7$ (mol dm^{-3} s^{-1})	$k_{obs}\times10^4$ (s^{-1})
0.67	2.00	7.65	0.76	2.30
0.83	2.00	7.65	0.92	2.30
1.00	2.00	7.65	1.02	1.90
1.34	2.00	7.65	1.50	1.93
1.67	2.00	7.65	1.85	1.62
2.00	2.00	7.65	1.98	1.38
2.50	2.00	7.65	2.28	1.26
3.34	2.00	7.65	2.26	0.84
1.00	1.00	7.65	0.55	0.86
1.00	1.34	7.65	0.72	1.12
1.00	2.00	7.65	1.02	1.90
1.00	2.50	7.65	1.86	2.90
1.00	4.00	7.65	2.06	3.21
1.00	5.00	7.65	2.52	3.93
1.00	2.00	3.82	0.52	0.81
1.00	2.00	7.65	1.02	1.90
1.00	2.00	9.56	1.30	2.03
1.00	2.00	11.47	1.54	2.40
1.00	2.00	13.40	1.80	2.81
1.00	2.00	15.30	2.03	3.17

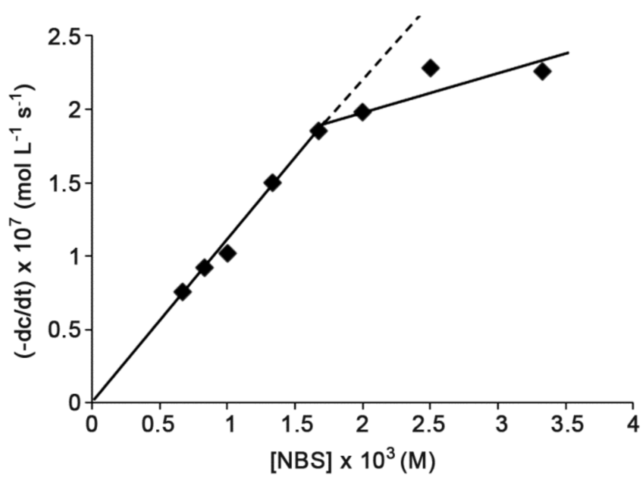


Fig. 1 – Plot of ($-dc/dt$) versus [NBS] at 35 °C under the conditions of Table 1.

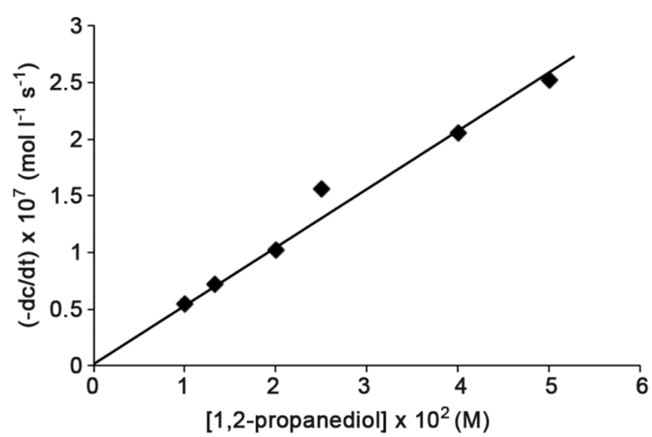


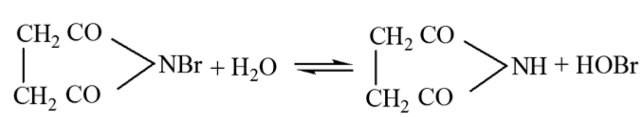
Fig. 2 – Plot of ($-dc/dt$) versus [1,2-propanediol] at 35 °C under the conditions of Table 1.

constant solution conditions increased the rate ($-dc/dt$) showing positive effect of [Cl^-] on the rate of reaction (Fig. not shown), while five-fold variation (0.50×10^{-3} to 2.5×10^{-3} mol dm^{-3}) in [Succinimide] showed negligible effect on the rate of reaction (data not shown in table).

The reaction was studied at different temperatures, i.e., 30, 35, 40 and 45 °C and activation parameters computed on the basis of rate measurement at 35 °C are recorded in Table 3.

Oxidising species of N-bromosuccinimide (NBS) in alkaline medium

In alkaline medium, NBS hydrolyses to give HOBr as shown by the following equilibrium.



NBS **Succinimide (NHS)**

HOBr is known to be stable in alkaline medium. Thus, the reactive species of NBS in alkaline medium may

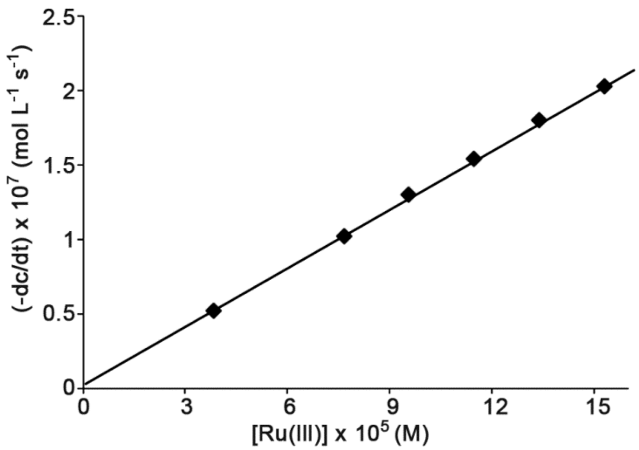


Fig. 3 – Plot of (*–dc/dt*) versus [Ru(III)] at 35 °C under the conditions of Table 1.

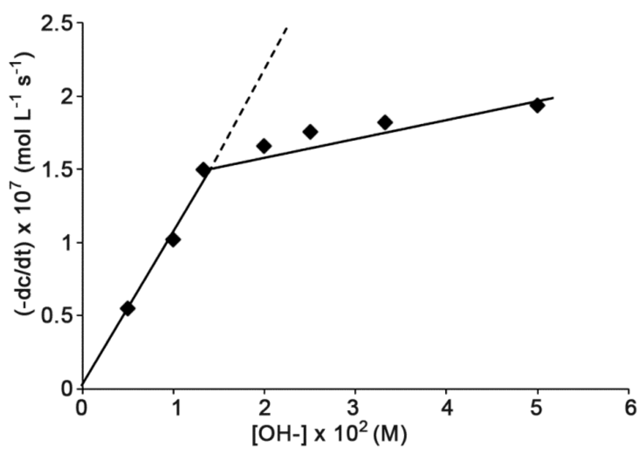


Fig. 4 – Plot of (-*dc/dt*) versus [OH^-] at 35 °C under the conditions of Table 2.

be either NBS itself or HOBr. If HOBr is taken as the reactive species then the rate law derived on its basis requires negative effect of addition of NHS contrary to the observed negligible effect of NHS on the reaction rate. This rules out the possibility of HOBr as the reactive species of N-bromosuccinimide in alkaline medium. Hence, under the circumstances the only choice left is to assume NBS as the oxidising species of N-bromosuccinimide in alkaline solution. The rate law derived on the basis of NBS also fully explains all the observed kinetic observations.

Reactive species Ru(III) chloride in alkaline medium

Electrochemical and spectrophotometric measurements of Ru(III) in 0.1 *M* KCl in the *p*H range from 0.4–2.0 at 25 °C suggest four major species[20], viz., $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$, and $[RuCl(H_2O)_5]^{2+}$. Except for $[RuCl_2(H_2O)_4]^+$, the stability of the species decreases with increasing *p*H. The $[RuCl_2(H_2O)_4]^+$ species was, however, quite stable at *p*H 2.0, which is in equilibrium with its hydrolyzed form (C_1), i.e., $[RuCl_2(H_2O)_3OH]$ (Eq. 1)[21,22].

$$[RuCl_2(H_2O)_4]^+ + H_2O \rightleftharpoons \underset{(C_1)}{[RuCl_2(H_2O)_3OH]} + H_3O^+ \quad \ldots(1)$$

Table 2 – The effect of variation of [NaOH], [Cl^-] and [$Hg(OAc)_2$] on the rate at 35 °C. {React. cond.: [NBS] = 1.00×10^{-3} mol dm^{-3}; [Ru(III)] = 7.65×10^{-5} mol dm^{-3}; [1,2-propanediol] = 2.00×10^{-2} mol dm^{-3}

[KCl]×10^2 (mol dm^{-3})	[NaOH]×10^2 (mol dm^{-3})	[$Hg(OAc)_2$]×10^3 (mol dm^{-3})	(-*dc/dt*)×10^7 (mol $dm^{-3}s^{-1}$)
1.00	1.00	2.50	1.02
2.00	1.00	2.50	1.44
3.00	1.00	2.50	2.00
4.00	1.00	2.50	2.44
5.00	1.00	2.50	2.74
1.00	0.50	2.50	0.55
1.00	1.00	2.50	1.02
1.00	1.34	2.50	1.50
1.00	2.00	2.50	1.66
1.00	2.50	2.50	1.76
1.00	3.34	2.50	1.82
1.00	5.00	2.50	1.94
1.00	1.00	1.11	1.06
1.00	1.00	1.34	1.04
1.00	1.00	1.67	1.08
1.00	1.00	2.00	1.04
1.00	1.00	2.50	1.02
1.00	1.00	3.34	1.06

Table 3 – Effect of temperature and values of activation parameter for the oxidation of 1, 2-propanediol by NBS in the presence of Ru(III) chloride as catalyst in alkaline medium at 35 °C. {React. cond.: [NBS] = 10.00×10^{-4} mol dm^{-3}; [NaOH] = 1.00×10^{-2} mol dm^{-3}; [1,2-propanediol] = 2.00×10^{-2} mol dm^{-3}; [Ru(III)] = 7.65×10^{-5} mol dm^{-3}; [KCl] = 1.00×10^{-2} mol dm^{-3}; [$Hg(OAc)_2$] = 2.50×10^{-3} mol dm^{-3}}

Temp. (K)	$k_{obs}\times10^4$ (s^{-1})
303	1.08
308	1.90
313	2.17
318	3.28

Parameters	*Values*
$k_r\times10^{-2}$ (mol^{-3} dm^9 s^{-1})	2.15
E_a (kcal mol^{-1})	15.18
$\Delta S^\#$ (J K^{-1})	–2.80
$\Delta H^\#$ (kcal mol^{-1})	14.56
$\Delta G^\#$ (kcal mol^{-1})	14.77
$A\times10^{-13}$ (mol^{-3} dm^9 s^{-1})	1.24

With an increase in the concentration of chloride ion, the hydrolyzed form (C_1), may also form (C_2), i.e., $[RuCl_3(H_2O)_2OH]^-$ through equilibrium (Eq. 2).

$$[RuCl_2(H_2O)_3OH] + Cl^- \rightleftharpoons \underset{(C_2)}{[RuCl_3(H_2O)_2OH]^-} + H_2O \quad \ldots(2)$$

$[RuCl_2(H_2O)_3OH]$ seems to be the most likely reactive species in the catalyzed reaction of 1,2-propanediol with NBS, giving the positive increase in rate with increase in both $[OH^-]$ and $[Cl^-]$.

Role of mercuric acetate in the present investigation

In the absence of mercuric acetate in the reaction mixture, bromide ions (reduction product of NBS) interact with NBS to form Br_2 which induces parallel oxidation of the substrate and thus creates complications in NBS oxidation. In order to prevent parallel Br_2 oxidation of the substrate, mercuric acetate has been used as bromide ions scavenger. Formation of the complex, $[HgBr_4]^{-2}$ ensures pure NBS oxidation of 1, 2-propanediol. Earlier, also it has been reported that Hg(II) acts as an oxidant[23] as well as co-catalyst[24]. Therefore, the role of $Hg(OAc)_2$ as oxidant and co-catalyst needs to be ascertained in the present investigation in addition to its role as Br^- ions scavenger. In preliminary experiments, it was observed that in the absence of NBS at constant concentration of all other reagents, e. g., 1,2-propanediol, $Hg(OAc)_2$, NaOH, Ru(III) and KCl, the reaction did not proceed at all, indicating non-involvement of $Hg(OAc)_2$ as oxidant. Further, in another experiment with NBS as oxidant and at constant concentrations of all other reagents, the rate of the reaction was not influenced with increase in $[Hg(OAc)_2]$, ruling out the role of mercuric acetate in the reaction as co-catalyst. These observations indicate that the role of Hg (II) is limited in the reaction as Br^- ion scavenger only.

Spectral evidence for the formation of complexes during the reaction

After deciding upon the reactive species of both N-bromosuccinimide and Ru(III)chloride in alkaline medium and also considering first-order kinetics with respect to 1,2-propanediol, efforts were made to ascertain the possibility of formation of a complex or complexes during the reaction. It is reported[25] that Ru(III)chloride forms complex with IO_3^- (oxidant) in a slow and rate determining step and with reducing sugars (glucose and fructose) in a fast step during their oxidation. It has been also recently reported[26] that in the slow and rate controlling step, 1,2-propanediol is not involved, although in the fast step it will react with the most reactive complex to form the reaction products along with regeneration of the catalyst for its further catalytic action. In the present investigation, first order kinetics observed during the five-fold variation of [1,2-propanediol] shows that in the slow and rate controlling step 1,2-propanediol is involved, and will react with the most reactive complex to form the reaction products along with regeneration of the catalyst for its further catalytic action.

In order to prove our case about the reactive species of Ru(III) chloride in alkaline medium, spectra of different solutions containing different compositions were recorded, which indicated that with the addition of OH^- ions and Cl^- ions to the solution of Ru(III) chloride, there is an increase in absorbance (Fig. 5). This increase in absorbance with the increase in $[OH^-]$ can be considered due to

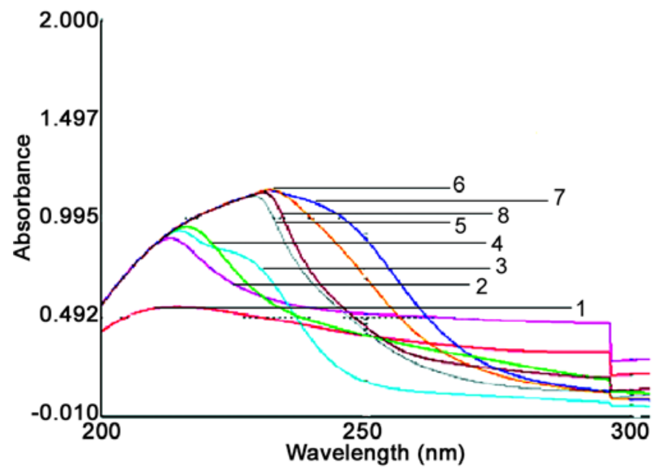
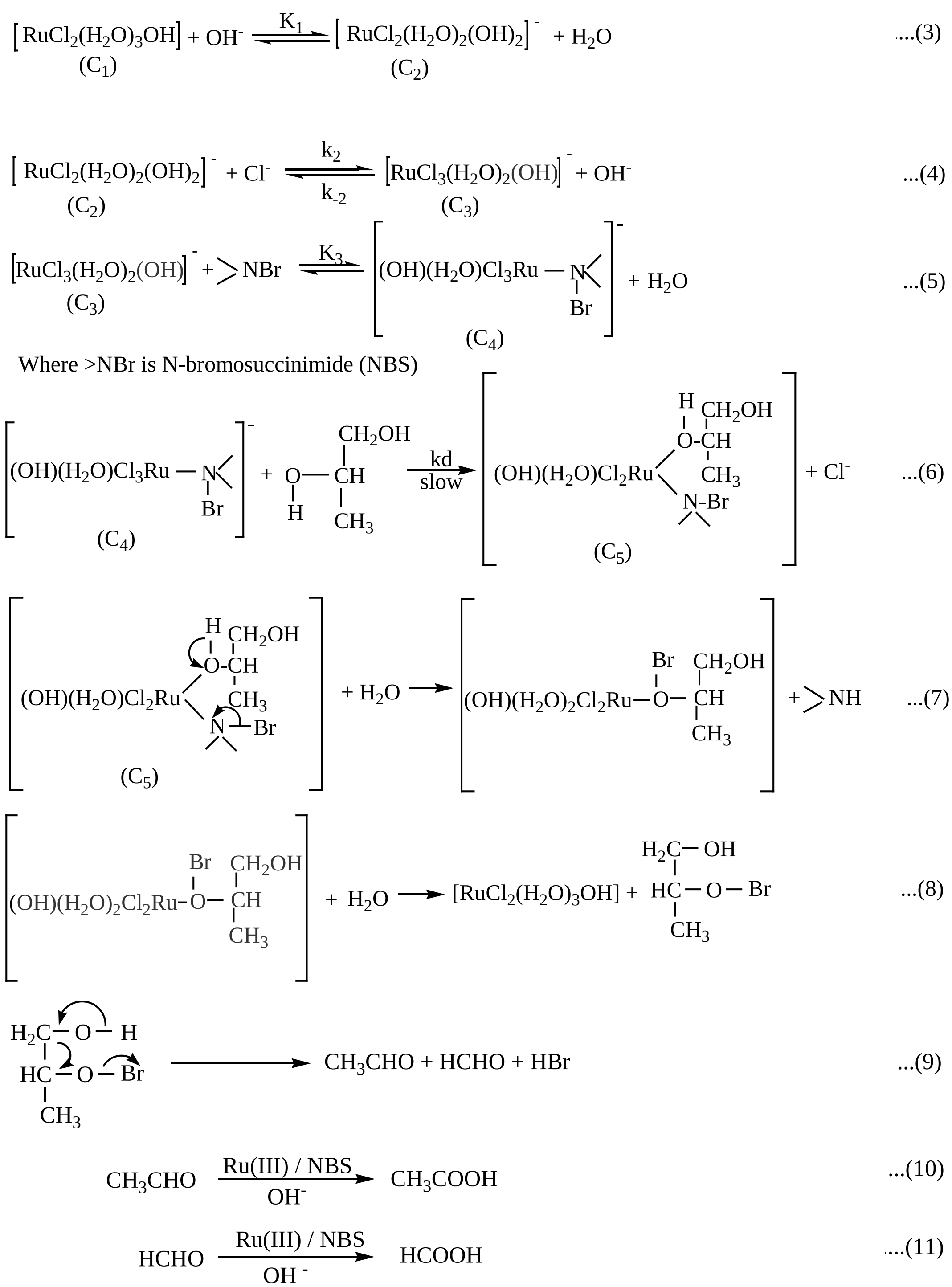


Fig. 5 – Spectral evidence for the formation of complexes during the course of the reaction conditions. {(1) [Ru(III)] = 15.30×10^{-5} mol dm^{-3}; (2) [Ru(III)] = 15.30×10^{-5} mol dm^{-3} and [NaOH] = 2×10^{-2} mol dm^{-3}; (3) [Ru(III)] = 15.30×10^{-5} mol dm^{-3} and [NaOH] = 5×10^{-2} mol dm^{-3}; (4) [Ru(III)] = 15.30×10^{-5} mol dm^{-3}, [NaOH] = 5×10^{-2} mol dm^{-3} and [KCl] = 6×10^{-2} mol dm^{-3}; (5) [Ru(III)] = 15.30×10^{-5} mol dm^{-3}, [NaOH] = 5×10^{-2} mol dm^{-3}, [KCl] = 6×10^{-2} mol dm^{-3} and [NBS] = 1.00×10^{-3} mol dm^{-3}; (6) [Ru(III)] = 15.30×10^{-5} mol dm^{-3}, [NaOH] = 5×10^{-2} mol dm^{-3}, [KCl] = 6×10^{-2} mol dm^{-3} and [NBS] = 2.00×10^{-3} mol dm^{-3}; (7) [NBS] = 2.00×10^{-3} mol dm^{-3} and [NaOH] = 5×10^{-2} mol dm^{-3}; (8) [Ru(III)] = 15.30×10^{-5} mol dm^{-3}, [NaOH] = 5×10^{-2} mol dm^{-3}, [KCl] = 6×10^{-2} mol dm^{-3}, [NBS] = 2.00×10^{-3} mol dm^{-3}and [1,2-propanediol] = 5×10^{-2} mol dm^{-3}}.

increase in formation of complex between $[RuCl_2(H_2O)_3OH]$ and OH^- as follows:

$$[RuCl_2(H_2O)_3OH] + OH^- \rightleftharpoons [RuCl_2(H_2O)_2(OH)_2]^- + H_2O$$

The above equilibrium in the reaction is supported by the positive effect of $[OH^-]$ on pseudo-first-order rate constant (k_1). The complex species, $[RuCl_2(H_2O)_2(OH)_2]^-$, reacts with Cl^- ion to form another complex species $[RuCl_3(H_2O)_2(OH)]^-$ (Scheme 1).



Scheme 1

In view of the observed first-order tending to zero order kinetics in [NBS], it is evident that in the present investigation there seems to be a strong possibility of the formation of complex between the reactive species of Ru(III) chloride and NBS in alkaline medium. In order to verify the existence of this reactive complex species, spectra for NBS and OH^- solution (Fig. 5(g)), and Ru(III) chloride, Cl^-, OH^- with two different concentrations of NBS solution have been collected (Fig. 5(e, f)). From the recorded spectra, it was found that with the addition of NBS solution there is an increase in absorbance with a shift in λ_{max} towards longer wavelength. This increase in absorbance with the increase in [NBS] clearly indicates that there is a formation of the active complex species, $[RuCl_3(NBS)(OH)(H_2O)]^-$. The shift in λ_{max} towards longer wavelength is due to the combination of a chromophore, NBS, and an auxochrome, OH^-, to give rise to another chromophore (Scheme 1).

When the solution of 1,2-propanediol was added to the mixed solution of NBS, Ru(III) chloride, OH^- and Cl^-, the spectra (Fig. 5(f)) disappeared immediately and another spectra (Fig. 5(h)) with decreased absorbance corresponding to the reaction products was obtained, which suggests that the reactive species $[RuCl_3(NBS)(OH)(H_2O)]^-$ attacks 1,2-propanediol molecule in the slow and rate determining step.

Reaction mechanism

In view of positive effect of chloride ion and initial tending to zero effect of hydroxide ion (OH^-) on the rate of Ru(III) chloride catalysed oxidation of 1,2-propanediol by alkaline solution of N-bromo-succcinimide (NBS or >NBr) and other kinetic results, the reaction steps shown in Scheme 1 are suggested.

Derivation of rate law

Considering the stoichiometry of the reaction the rate of the reaction may be expressed in terms of loss of [NBS] as Eq. (12).

$$\frac{-\mathrm{d}\,[\mathrm{NBS}]}{\mathrm{dt}} = 3\,\mathrm{k_d}\,[\mathrm{C_4}][1,2-\mathrm{propanediol}] \quad \ldots(12)$$

In step (3), $K_1 = \dfrac{[\mathrm{C_2}]}{[\mathrm{C_1}][\mathrm{OH^-}]}$

Therefore,

$$[\mathrm{C_2}] = K_1\,[\mathrm{C_1}][\mathrm{OH^-}] \quad \ldots(13)$$

Considering steps (4) and (5) and application of steady state approximation to $[C_3]$, we have

$$\frac{d[\mathrm{C_3}]}{dt} = 0$$

Therefore,

$$\frac{d[\mathrm{C_3}]}{dt} = 0 = k_2[\mathrm{C_2}][\mathrm{Cl^-}] - k_{-2}[\mathrm{C_3}][\mathrm{OH^-}] - k_3[\mathrm{C_3}][\mathrm{NBS}]$$

where $K_3 = k_3/k_{-3}$.

$$\text{Or } [\mathrm{C_3}] = \frac{k_2\,[\mathrm{C_2}][\mathrm{Cl^-}]}{k_{-2}[\mathrm{OH^-}] + k_3[\mathrm{NBS}]} \quad \ldots(14)$$

From Eqs (13) and (14) we have

$$[\mathrm{C_3}] = \frac{k_2 K_1\,[\mathrm{C_1}][\mathrm{Cl^-}][\mathrm{OH^-}]}{k_{-2}[\mathrm{OH^-}] + k_3[\mathrm{NBS}]} \quad \ldots(15)$$

Also, from step (5) we have

$$\mathrm{K_3} = \frac{[\mathrm{C_4}]}{[\mathrm{C_3}][\mathrm{NBS}]}$$

$$\text{Or } [\mathrm{C_4}] = K_3\,[\mathrm{C_3}][\mathrm{NBS}] \quad \ldots(16)$$

From Eqs (15) and (16) we have

$$[\mathrm{C_4}] = \frac{\mathrm{k_2 K_1\,K_3[C_1][NBS][Cl^-][OH^-]}}{\mathrm{k_{-2}[OH^-] + k_3[NBS]}} \quad \ldots(17)$$

Total concentration of Ru(III), i.e., $[Ru(III)]_T$ may be written as Eq. (18).

$$[\mathrm{Ru(III)}]_\mathrm{T} = [\mathrm{C_1}] + [\mathrm{C_2}] + [\mathrm{C_3}] + [\mathrm{C_4}] \quad \ldots(18)$$

Substituting $[C_2]$, $[C_3]$ and $[C_4]$ from Eqs (13), (15) and (17) in Eq. (18).

$$[\mathrm{Ru(III)}]_\mathrm{T} = [\mathrm{C_1}] + \mathrm{K_1}\,[\mathrm{C_1}][\mathrm{OH^-}] + \frac{\mathrm{k_2 K_1\,[C_1][Cl^-][OH^-]}}{\mathrm{k_{-2}[OH^-] + k_3[NBS]}} + \frac{\mathrm{k_2 K_1\,K_3[C_1][NBS][Cl^-][OH^-]}}{\mathrm{k_{-2}[OH^-] + k_3[NBS]}}$$

$$\text{Or } [\text{Ru(III)}]_T = [C_1]\left[\begin{array}{c} 1 + K_1[OH^-] \\ + \dfrac{k_2K_1[Cl^-][OH^-]}{k_{-2}[OH^-] + k_3[NBS]} \\ + \dfrac{k_2K_1K_3[NBS][Cl^-][OH^-]}{k_{-2}[OH^-] + k_3[NBS]} \end{array}\right]$$

$$= [C_1]\left[\dfrac{(1 + K_1[OH^-])\begin{pmatrix} k_{-2}[OH^-] \\ + k_3[NBS] \end{pmatrix} + k_2K_1[Cl^-][OH^-](1 + K_3[NBS])}{k_{-2}[OH^-] + k_3[NBS]}\right]$$

Or

$$[C_1] = \frac{[\text{Ru(III)}]_T(k_{-2}[OH^-] + k_3[NBS])}{(1 + K_1[OH^-])(k_{-2}[OH^-] + k_3[NBS]) + k_2K_1[Cl^-][OH^-](1 + K_3[NBS])} \quad \ldots(19)$$

Considering Eqs (17) and (19) we have

$$[C_4] = \frac{\dfrac{k_2K_1K_3[NBS][Cl^-][OH^-][\text{Ru(III)}]_T}{(k_{-2}[OH^-] + k_3[NBS])}}{\dfrac{(k_{-2}[OH^-] + k_3[NBS])}{\left\{\begin{array}{c}(1 + K_1[OH^-])(k_{-2}[OH^-] + k_3[NBS]) \\ + k_2K_1[Cl^-][OH^-](1 + K_3[NBS])\end{array}\right\}}}$$

$$\text{Or } [C_4] = \frac{k_2K_1K_3[NBS][\text{Ru(III)}]_T[Cl^-][OH^-]}{\begin{array}{c}k_{-2}[OH^-] + k_3[NBS] + k_{-2}K_1[OH^-]^2 \\ + k_3K_1[OH^-][NBS] + k_2K_1[Cl^-][OH^-] \\ + k_2K_1K_3[Cl^-][OH^-][NBS]\end{array}} \quad \ldots(20)$$

Further, on assuming the inequality,

$$(k_{-2}[OH^-] + k_3[NBS] + k_2K_1[OH^-][Cl^-]) \gg k_{-2}K_1[OH^-]^2 + k_3K_1[OH^-][NBS] + k_2K_1K_3[Cl^-][OH^-][NBS]$$

we have

$$[C_4] = \frac{k_2K_1K_3[NBS][\text{Ru(III)}]_T[Cl^-][OH^-]}{k_3[NBS] + [OH^-](k_{-2} + k_2K_1[Cl^-])}$$

Further on assuming the inequality, $k_{-2} \ll k_2K_1[Cl^-]$, we have Eq. (21).

$$[C_4] = \frac{k_2K_1K_3[NBS][\text{Ru(III)}]_T[Cl^-][OH^-]}{k_3[NBS] + k_2K_1[OH^-][Cl^-]} \quad \ldots(21)$$

On substituting the value of $[C_4]$ from Eq. (21) in Eq. (12) we have

$$\frac{-d[NBS]}{dt} = \text{rate}$$

$$= \frac{\dfrac{3\,kd\,k_2K_1K_3[NBS][\text{Ru(III)}]_T}{[Cl^-][OH^-][1,2-\text{propanediol}]}}{k_3[NBS] + k_2K_1[OH^-][Cl^-]} \quad \ldots(22)$$

The rate law (22) shows all the observed kinetics with respect to all the reactants. It also shows first order in NBS and Ru(III), positive effect of chloride ions, positive effect of hydroxide ion and zero effect of addition of each of succinimide (the reduction product of NBS) and mercuric acetate (used as bromide ion scavenger).

Further on reversing Eq. (22) we have Eq. (23),

$$\frac{1}{\text{rate}} = \frac{k_3}{3kd\,k_2K_1K_3[\text{Ru(III)}][Cl^-][OH^-][S]} + \frac{1}{3\,kd\,K_3[NBS][S][\text{Ru(III)}]} \quad \ldots(23)$$

where [S] is concentration of 1, 2-propanediol.
On plotting 1/rate versus 1/ [NBS]

$$\text{Slope} = X = \frac{1}{3kd\,K_3[S][\text{Ru(III)}]} = 5.04 \times 10^3 \quad \ldots(24)$$

$$\text{and intercept} = Y = \frac{k_3}{\dfrac{3kd\,k_2K_1K_3[\text{Ru(III)}]}{[Cl^-][OH^-][S]}} = 4.50 \times 10^6 \quad \ldots(25)$$

$$\frac{X}{Y} = \frac{k_2K_1[Cl^-][OH^-]}{k_3} \quad \ldots(26)$$

On substituting the values of X, Y, $[Cl^-]$ and $[OH^-]$ in Eq. 26, we have

$$\frac{k_2K_1}{k_3} = 11.2 \quad \ldots(27)$$

Similarly, on plotting 1/rate versus 1/ $[OH^-]$ from Eq. (23)

$$X_1 = \frac{k_3}{3kd\,k_2K_1K_3[\text{Ru(III)}][Cl^-][S]} = 4.37 \times 10^2 \quad \ldots(28)$$

$$\mathrm{Y_1} = \frac{1}{\mathrm{3kd\ K_3\,[NBS][S][Ru(III)]}} = 4.50 \times 10^6 \qquad \ldots(29)$$

Further,

$$\frac{\mathrm{Y_1}}{\mathrm{X_1}} = \frac{\mathrm{k_2K_1[Cl^-]}}{\mathrm{k_3[NBS]}} \qquad \ldots(30)$$

On substituting the values of X_1, Y_1, $[Cl^-]$ and $[NBS]$ in Eq. (30), we have

$$\frac{\mathrm{k_2K_1}}{\mathrm{k_3}} = 10.26 \qquad \ldots(31)$$

The values of $\frac{k_2K_1}{k_3}$ from Eq. (27) (obtained by the plot of 1/rate versus 1/[NBS]) and from Eq. (31) (obtained by the plot of 1/ rate versus 1/ [OH]) are quite close to each other, thus proving the validity of the suggested mechanism.

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