

Kinetic and mechanistic study of n-bromosuccinimide oxidation of dimethyl digolin aqueous alkaline solution in the presence of aquachloro-complex of iridium (iii) used as homogeneous catalyst

Shipra Tripathi, Sandeep Kumar Mishra and Bharat Singh

Chemical Kinetics Laboratory, Department of Chemistry, University of Allahabad, Allahabad- 211 002, India,

Email: mishra@sandeep@gmail.com

Accepted : 10 November 2017

Abstract

Kinetics of Ir(III) catalysed oxidation of dimethyl digol (DMD) by N-bromosuccinimide (NBS) has been investigated in alkaline medium in the presence of mercuric acetate as Br⁻ ion scavenger in the temperature range of 30 to 45°C. The reaction follows complex kinetics, being first order in [NBS], zero order in DMD and first order in [Ir(III)]. Increase in [OH⁻] does not affect the rate of reaction, showing zero effect of [OH⁻] while addition of KCl increases the rate, showing positive effect of chloride ions on the rate of the reaction. Successive addition of mercuric acetate, succinimide (NHS) and variation of ionic strength of the medium did not bring about significant change in the rate of the reaction. [IrCl₃(OH)(H₂O)₂]⁻¹ and NBS itself have been postulated as the reactive catalytic species of iridium (III) chloride and N-bromosuccinimide in alkaline medium, respectively. Activation parameters for the slow and rate determining step of the proposed mechanism involving the formation of most activated complex, [Cl₃Ir NBS(OH)(H₂O)]⁻¹ have been obtained from the rate measurements at 30, 35, 40 and 45°C. The rate law conforming to the observed kinetic results has been derived as:

$$-\frac{d[NBS]}{dt} = \frac{k_d K_1' [Ir(III)]_T [NBS] [Cl^-]}{1 + K_1' [Cl^-]}$$

Keywords: Kinetics, Mechanism, Oxidation, Ir(III) catalysis, NBS, dimethyl digol

Introduction

The diverse nature of the chemistry of N-halo compounds¹⁻⁵ is due to their ability to act as a source of halogenonium cations, hypohalite and nitrogen anions species which act as both bases and nucleophiles. N-Halosuccinimides are sources of positive halogens and these reagents have been exploited as oxidant for a variety of substrates^{6,7}. N-bromosuccinimide (NBS) has been extensively used as an oxidizing agent and analytical reagent especially in acid medium^{8,9} in both uncatalysed and catalysed reactions. However, there are only a few reports on the oxidation reactions of NBS in alkaline medium¹⁰⁻¹². The role of NBS as an oxidant in the oxidation of a large number of substrates has been probed using Ru (III)¹³, Pd (II)¹⁴⁻¹⁶, Pt (IV)¹⁷ and Rh (III)^{18,19} as homogeneous catalyst. Although Ir (III) catalysed^{20, 21} NBS oxidation has been reported in aqueous acid, but no report is available on the role of Ir(III) chloride in NBS oxidation of any substrate in alkaline medium. Dimethyl digol having chemical formula (CH₃OCH₂CH₂)₂O is a water soluble, flammable, clear, colourless liquid with etheral odour. These characteristics of DMD interest us to study its oxidation by alkaline NBS in the presence of aquachloroiridium (III) complex as catalyst. Thus in view of biological and industrial importance of Ir (III) complexes, NBS and DMD and also in view of less information available in the literature on the role of aquachlorocomplex of Ir (III) in alkaline solution, an attempt has been made to study the kinetics and mechanism of Ir (III) catalysed oxidation of DMD by NBS in alkaline solution using mercuric acetate²² as bromide ions scavenger. The main objectives of the present study are to ascertain (i) the reactive species of NBS in alkaline medium, (ii) the real catalytic species of Ir (III) chloride in alkaline medium, (iii) the role of chloride ions in deciding the real catalytic species of iridium (III), (iv) the role of mercuric acetate in addition to its role as

bromide ions scavenger and finally (v) to elucidate the mechanistic steps and to discuss the rate law consistent with the observed kinetic results.

Materials and Method

The reagents employed in the present investigation are DMD (CDH Laboratory), N-bromosuccinimide of E. Merck grade, iridium(III)chloride (Johnson & Matthey), sodium hydroxide (E. Merck) and mercuric acetate (E. Merck). All other reagents used were of A. R. grade. All the solutions were prepared in doubly distilled water.

The solution of iridium(III) chloride was prepared by dissolving its 1g sample in HCl (3.6 mol dm^{-3}). The concentrations of iridium(III) chloride and HCl were noted in the final solution which was stored in a black coated bottle to prevent any photochemical decomposition. The solution of NBS was prepared by dissolving its weighed amount in known volume of distilled water and its strength was estimated iodometrically. The solution of DMD was prepared by dissolving its known amount in desired volume of distilled water. 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, sodium thiosulphate of E. Merck grade were prepared by dissolving their weighed samples in known volume of distilled water.

All the kinetic measurements were carried out at constant temperature $35^{\circ}\text{C} (\pm 0.1^{\circ}\text{C})$. Appropriate volumes of all reactants NBS, Ir(III), $\text{Hg}(\text{OAc})_2$, 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 would become 100 ml after addition of requisite volume of DMD solution. The bottle containing reaction mixture was placed in an electrically operated thermostat (maintained at 35°C) for thermal equilibrium. Appropriate volume of solution of DMD, 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 which is written as $[\text{NBS}]^*$. The order of the reaction with respect to each reactant was determined by the relation between initial rate $(-dc/dt)$ and initial [reactant].

Results

In order to study the role of reactants in the oxidation of DMD by NBS in the presence of aquachloroiridium(III) in alkaline medium, the oxidation kinetics was carried out at different initial concentrations of reactants at 308°K . Rate $(-dc/dt)$ of the reaction increases in direct proportionality with increase in the initial [NBS], showing first-order kinetics with respect to [NBS]. This is also obvious from the plot of $(-dc/dt)$ versus [NBS] (Fig.1). A straight line passing through origin shows that the reaction follows first order kinetics with respect to [NBS].

At constant [NBS], [NaOH], [Ir(III)], $[\text{Hg}(\text{OAc})_2]$, [KCl] and temperature, the first-order rate constant (k_{obs}) remains practically constant on varying six-fold initial [DMD], indicating zero-order dependence of the reaction on [DMD]. The reaction rate $(-dc/dt)$ and first-order rate constant (k_{obs}) both increase with increase in [Ir(III)] under constant solution conditions (Table 1, Fig. 2), indicating first order dependence of the reaction on [Ir(III)]

Variation of ionic strength of the medium from $1.23 \times 10^{-2} \text{ mol dm}^{-3}$ to $8.73 \times 10^{-2} \text{ mol dm}^{-3}$ did not change the rate of reaction, indicating zero effect of ionic strength on the rate. Addition of succinimide (NHS) from $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ to $5.00 \times 10^{-3} \text{ mol dm}^{-3}$ was found to have no effect on the rate, showing thus negligible effect of addition of NHS on the rate of the reaction.

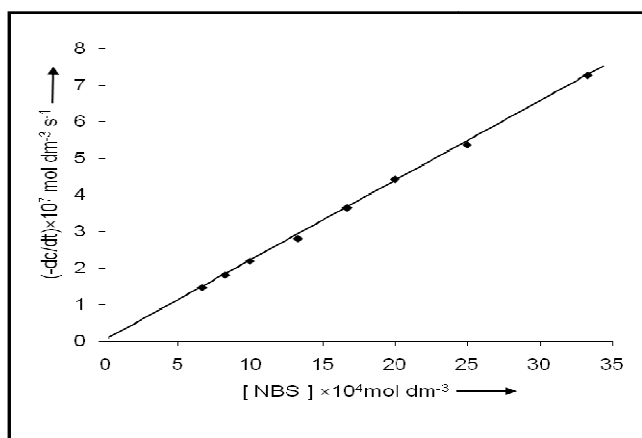


Fig.1 Plot of $-(dc/dt)$ vs. $[NBS]$ at $35^{\circ}C$ under the conditions of Table 1

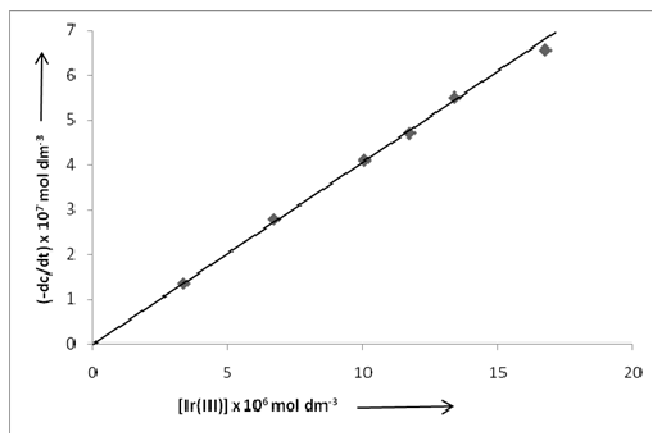


Fig. 2 Plot of $-(dc/dt)$ vs. $[Ir(III)]$ at $35^{\circ}C$ under the conditions of Table 1

Table 1 Effect of variation of $[NBS]$, $[1, 2\text{-propanediol}]$ and $[Ir(III)]$ on the rate at $35^{\circ}C$ under the solution conditions: $[NaOH] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[KCl] = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$ and $[Hg(OAc)_2] = 2.50 \times 10^{-3} \text{ mol dm}^{-3}$

$[NBS] \times 10^4$ (mol dm^{-3})	$[DMD] \times 10^2$ (mol dm^{-3})	$[Ir(III)] \times 10^6$ (mol dm^{-3})	$(-dc/dt) \times 10^7$ ($\text{mol dm}^{-3}\text{s}^{-1}$)	$k_{\text{obs}} \times 10^4$ s^{-1}
0.67	2.00	13.40	3.62	-----
0.80	2.00	13.40	4.46	-----
1.00	2.00	13.40	5.50	-----
1.34	2.00	13.40	7.20	-----
1.67	2.00	13.40	9.24	-----
3.34	2.00	13.40	18.40	-----
1.00	0.66	13.40	5.46	10.92
1.00	1.00	13.40	5.52	11.04
1.00	2.00	13.40	5.50	11.00
1.00	2.50	13.40	5.48	10.96
1.00	3.34	13.40	5.54	11.08
1.00	4.00	13.40	5.44	10.88
1.00	5.00	3.35	1.33	2.70
1.00	2.00	6.70	2.78	5.56
1.00	2.00	10.05	4.10	8.20
1.00	2.00	11.72	4.70	9.40
1.00	2.00	13.40	5.50	11.0
1.00	2.00	16.75	6.56	13.12

The data of summarized in Table- 2 shows that on increasing the concentration of OH^- the value of $(-dc/dt)$ remain almost constant thus shows zero-order with respect to $[OH^-]$. While successive addition of $Hg(OAc)_2$ to the reaction mixture indicated negligible effect on the rate of the reaction. Addition of chloride ions in the form of KCl to the reaction mixture under constant solution conditions increases the rate $(-dc/dt)$ and a plot of $\log k_{\text{obs}}$ vs. $\log [Cl^-]$ was linear (Fig.3) with slope (0.19), indicating positive effect of $[Cl^-]$ on the rate of the reaction (\log

Shipra Tripathi, Sandeep Kumar Mishra and Bharat Singh

k_{obs} & $\log [\text{Cl}^-]$ value not given in table 2).

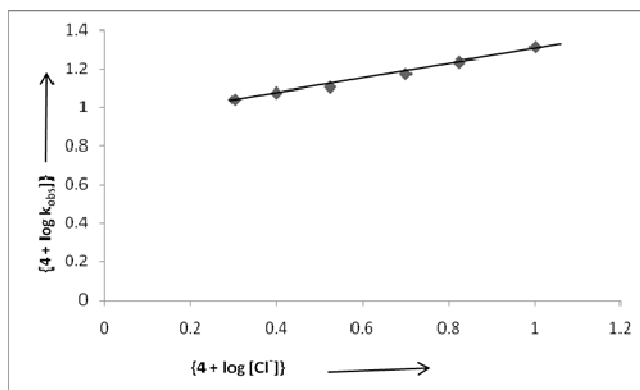


Fig. 3: Plot of $\log k_{\text{obs}}$ vs. $\log [\text{Cl}^-]$ at 35°C under conditions of Table 2.

Table 2 Effect of variation of $[\text{NaOH}]$, $[\text{Cl}^-]$ and $[\text{Hg}(\text{OAc})_2]$ on the rate at 35°C under the solution conditions $[\text{NBS}] = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Ir}(\text{III})] = 13.4 \times 10^{-6} \text{ mol dm}^{-3}$ and $[\text{DMD}] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$

$[\text{KCl}] \times 10^4$ (mol dm^{-3})	$[\text{NaOH}] \times 10^2$ (mol dm^{-3})	$[\text{Hg}(\text{OAc})_2] \times 10^3$ (mol dm^{-3})	$(-dc/dt) \times 10^7$ ($\text{mol dm}^{-3}\text{s}^{-1}$)
2.00	1.00	2.50	5.50
2.50	1.00	2.50	5.94
3.34	1.00	2.50	6.38
5.00	1.00	2.50	7.46
6.67	1.00	2.50	8.54
10.00	1.00	2.50	10.24
2.00	1.00	2.50	5.50
2.00	1.25	2.50	5.58
2.00	1.66	2.50	5.46
2.00	2.00	2.50	5.52
2.00	2.50	2.50	5.60
2.00	5.00	2.50	5.44
2.00	1.00	1.11	5.48
2.00	1.00	1.34	5.42
2.00	1.00	1.67	5.40
2.00	1.00	2.00	5.44
2.00	1.00	2.50	5.50
2.00	1.00	3.34	5.56

The reaction was studied at different temperatures and the rate constants measured at $30, 35, 40$ and 45°C led to compute energy of activation (E_a), enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and free energy of activation (ΔG^\ddagger). Arrhenius factor (A) was calculated using specific rate constant (k_r) at 35°C (Table 3).

Table 3 Effect of temperature and values of activation parameter for the oxidation of 1, 2-propanediol by NBS in the presence of Ir(III) chloride as catalyst in alkaline medium at 35⁰C

Temperature (K)	$k_{\text{obs}} \times 10^4 \text{ s}^{-1}$
303	7.16
308	11.0
313	15.16
318	23.12
Parameters	Values
$k_r (\text{mol}^{-2} \text{ dm}^6)$	41.04
Log A	11.68
$E_a (\text{kcal mol}^{-1})$	14.20
$\Delta H^\ddagger (\text{kcal mol}^{-1})$	13.58
$\Delta S^\ddagger (\text{e.u.})$	-7.16
$\Delta G^\ddagger (\text{kcal mol}^{-1})$	15.80

Solution conditions: $[\text{NBS}] = 10.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$,
 $[\text{DMD}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Ir(III)}] = 13.40 \times 10^{-6} \text{ mol dm}^{-3}$,
 $[\text{KCl}] = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Hg(OAc)}_2] = 2.50 \times 10^{-3} \text{ mol dm}^{-3}$

Test for free radical

The addition of the reaction mixture to aqueous acrylamide monomer solution in dark did not initiate polymerization, indicating the absence of formation of free radical species in the reaction sequence. The control experiments were also performed under the same reaction conditions.

Discussion

Role of mercuric acetate in 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 sets parallel oxidation of the substrate and thus creates complications in NBS oxidation. In order to prevent parallel Br_2 oxidation of the substrate, mercuric acetate²² has been used as bromide ions scavenger. Hg (II) traps free bromide ions to form the complex $[\text{HgBr}_4]^{2-}$ and thus formation of complex, $[\text{HgBr}_4]^{2-}$ ensures pure NBS oxidation of DMD. Earlier, it is also reported that Hg(II) acts as an oxidant²³ as well as co-catalyst²⁴. Therefore, it needs to ascertain the role of Hg(OAc)_2 as oxidant and co-catalyst in the present investigation also in addition to its role as Br^- ions scavenger. In preliminary experiments, it has been observed that in the absence of NBS at constant concentrations of all other reagents viz. DMD, Hg(OAc)_2 , NaOH, Ir(III) and KCl the reaction did not proceed at all, indicating non-involvement of Hg(OAc)_2 as oxidant. Further, in another experiments with NBS used as oxidant and at constant concentration of all other reagents including Ir(III) rate of the reaction was found to remain almost unchanged with increase in $[\text{Hg(OAc)}_2]$, negating thus role of mercuric acetate in the reaction as co-catalyst. These observations indicate that Hg(II) is involved in the present reaction only as Br^- ion scavenger.

Reactive catalytic species of Ir(III) chloride in alkaline medium:

It has been earlier reported in NBS^{25} and NBA^{26} (N-bromoacetamide) oxidation of reducing sugars in the presence of acidic solution of Ir(III) chloride that Ir(III) chloride exists in the following equilibrium, showing thus negative effect of $[\text{Cl}^-]$ when $[\text{IrCl}_6]^{3-}$ is assumed as catalytic species.



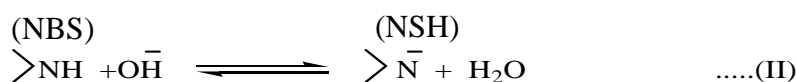
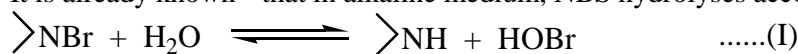
It has also been reported²⁷ that in 0.1M [HCl], Ir(III) chloride remains as $[\text{IrCl}_3(\text{H}_2\text{O})_3]$ at room temperature and 70°C while in 8.0M [HCl], it remains as $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ and $[\text{IrCl}_6]^{3-}$ respectively. This shows the predominant species of Ir(III) chloride²⁸ between 0.1M 8.0M [HCl] are $[\text{IrCl}_3(\text{H}_2\text{O})_3]$, $[\text{IrCl}_4(\text{H}_2\text{O})_2]^{-1}$ and $[\text{IrCl}_5(\text{H}_2\text{O})_3]^{2-}$. In the present investigation, since study has been made in alkaline solution, therefore, it is proposed that starting species of Ir(III) chloride in alkaline media is $[\text{IrCl}_2(\text{H}_2\text{O})_3\text{OH}]$ as is evident from the following equilibrium^{29,30}.



Thus in alkaline medium $[\text{IrCl}_2(\text{H}_2\text{O})_3\text{OH}]$ species is the starting species of Ir(III) chloride.

Identification of oxidizing species of NBS in alkaline solution

It is already known³⁰ that in alkaline medium, NBS hydrolyses according to the following equilibria

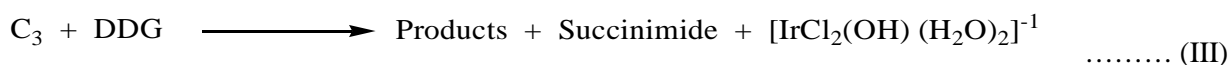
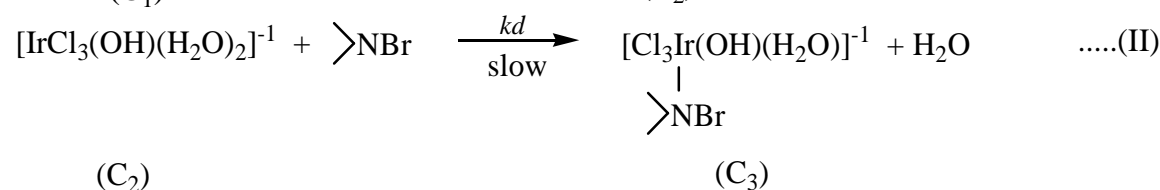
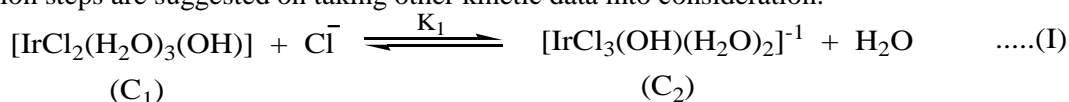


Thus either NBS, HOBr or >N^- may be involved in the oxidation process. In view of zero effect of $[\text{OH}^-]$ on the rate, the species >N^- is not likely to occur. Zero effect of NHS (succinimide) on the rate also negates the role of HOBr as oxidising species. Therefore the only choice left is to assume NBS as such to be oxidising species. Also when NBS is taken as oxidising species the rate law derived on its basis explains all the observed kinetic results.

Mechanism of Ir(III) chloride catalysed oxidation of dimethyl digol by alkaline

N-bromosuccinimide

On the basis of N-bromosuccinimide (NBS) a such as reactive oxidative species in alkaline medium and the species $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_2]^{-1}$ as the real catalytic species of Ir(III) chloride in alkaline medium, the following reaction steps are suggested on taking other kinetic data into consideration.



The rate of the reaction may be written in terms of rate of loss of concentration of NBS as eqn (1).

$$-\frac{d[\text{NBS}]}{dt} = k_d[\text{C}_2][\text{NBS}] \quad \text{.....(1)}$$

From step (I) we have

$$K_1 = \frac{[\text{C}_2][\text{H}_2\text{O}]}{[\text{C}_1][\text{Cl}^-]}$$

$$\text{or } [\text{C}_2][\text{H}_2\text{O}] = K_1[\text{C}_1][\text{Cl}^-]$$

or

$$[C_1] = \frac{[C_2][OH]}{K_1[Cl^-]} \quad \dots (2)$$

The total concentration of Ir(III) as $[Ir(III)]_T$ can be written as eqn (3) on the basis of step (I)

$$[Ir(III)]_T = [C_1][C_2] \quad \dots (3)$$

On substituting the value of $[C_1]$ from eqn (2) in eqn (3) we have, on further solving for $[C_2]$, eqn (4)

$$\begin{aligned} [Ir(III)]_T &= \frac{[C_2][H_2O]}{K_1[Cl^-]} + [C_2] \\ &= [C_2] \left(\frac{[H_2O]}{K_1[Cl^-]} + 1 \right) \\ &= [C_2] \left(\frac{1}{K'_1[Cl^-]} + 1 \right) \\ &= [C_2] \left(\frac{1 + K'_1[Cl^-]}{K'_1[Cl^-]} \right) \end{aligned}$$

or

$$[C_2] = \frac{K'_1[Ir(III)]_T[Cl^-]}{1 + K'_1[Cl^-]} \quad \dots (4)$$

Where $K'_1 = K_1/[H_2O]$

Further on considering eqn (1) and (4) we have finally eqn (5)

$$-\frac{d[NBS]}{dt} = \frac{k_d K'_1 [Ir(III)]_T [NBS] [Cl^-]}{1 + K'_1 [Cl^-]} \quad \dots (5)$$

The rate law (5) fully explains all the observed kinetic data. Absence of [DMG] in rate law (5) evidently indicates zero-order dependence of the reaction on [DMG]. Absence of $[OH^-]$ in rate law (5) also proves that the reaction is independent of $[OH^-]$. Positive effect of added $[Cl^-]$ is evident from rate law (5). Absence of $[Hg(OAc)_2]$ in rate law (5) also suggests that mercuric acetate in the reaction is involved in the reaction only as Br^- ion scavenger and it does not play any role either as catalyst or as co-oxidant in the reaction. Negligible effect of variation of ionic strength of the medium is also evident from slow and rate determining step (II) which involves dipole-ion interaction.

Conclusions

On the basis of our study on Ir(III) catalysed oxidation of DMD by alkaline NBS the following conclusions are drawn:

1. The title reaction shows first-order kinetics with respect to N-bromosuccinimide.
2. Zero-order kinetics with respect to dimethyl digol has been observed.
3. In case of iridium (III) chloride used as catalyst first-order kinetics was observed.
4. Zero effect of $[OH^-]$ variation on reaction rate was observed.
5. A negligible effect of mercuric acetate was observed.
6. Positive effect of added KCl on rate of the reaction was observed.
7. Negligible effect of ionic strength of medium was observed.
8. Negligible effect of added succinicimide [NHS] was observed
9. Marked effect of rise in temperature was observed.

Shipra Tripathi, Sandeep Kumar Mishra and Bharat Singh

Acknowledgement: Authors wish to thank University Grants Commission, Government of India, New Delhi for the financial assistance.

References

- Stankovic L & Vastko J, *Chem. Zvesti*, 14 (1960) 434.
- Rao V S, Sethuram B & Rao T N, *Intl. J. Chem. Kinet.* 11(1979) 165.
- Mathur N K & Narang C K, *The determination of organic compounds with N-bromosuccinimide*, Academic press, New York (1975).
- Radhakrishnamurthi P S & Sarangi L D, *Indian J. Chem.*, 20 A (1981) 30.
- Mukharjee J & Banerji K K, *J. Org. Chem.*, 46 (1981) 2323.
- Venkatasubramanian N & Thiagarajan V, *Can. J. Chem.*, 47 (1969) 694.
- Kistayya Surekha, Reddy M & Sushama K, *Indian J. Chem.*, 25 A (1986) 905.
- Sharma J P, Singh R N P, Singh A K & Singh Bharat, *Tetrahedron*, 42 (1986) 2739 and references therein.
- Singh A K, Srivastava R, Srivastava S, Srivastava J, Rahmani S & Singh Bharat, *J. Mol. Catal. A: Chemical*, 310 (2009) 64 and references therein.
- Gowda B T & Bhatt J I, *Indian J. Chem.*, 28A (1989) 43.
- Kamble D L, Huger G H & Nandibewoor S T, *Indian J. Chem.*, 35 A (1996) 144.
- Kamble D L, Chougale R B & Nandibewoor S T, *Indian J. Chem.*, 35 A (1996) 865.
- Singh B, Singh V K, Singh A K & Singh M B, *J. Ind. Chem. Soc.*, LX III (1986) 1049 and references therein.
- Singh A K, Gupta T, Singh V K, Kesarwani D & Singh Bharat, *Oxid. Commun.* 23 (3) (2000) 416.
- Singh A K, Chpora D, Rahmani S & Singh Bharat, *Carbohydr. Res.*, 314 (1998) 157.
- Saxena R, Shukla A & Upadhyay S K, *Trans. Met. Chem.*, 19 (1994) 91.
- Tripathi R, Kambo N & Upadhyay S K, *Trans. Met. Chem.*, 29 (2004) 861.
- Singh A K, Singh R, Srivastava J, Rahmani S & Srivastava S., *J. Organomet. Chem.*, 692 (2007) 4270.
- Srivastava S, Srivastava S, Singh S Parul, & Jaiswal A, *Bull. Catal. Soc. India*, 6 (2007) 140.
- Singh A K, Rahmani S, Singh V K, Gupta V, Kesarwani D & Singh Bharat, *Indian J. Chem.*, 40 A (2000) 519.
- Singh A K, Rahmani S, Singh V, Gupta V & Singh Bharat, *Oxid. Commun.*, 23 (1) (2000) 55.
- Singh A K, Singh V, Rahmani S, Singh Ajaya K & Singh Bharat, *J. Mol. Catal. A: Chem.*, 197 (2003) 91 and references therein.
- Feigl F, *Spot tests in Organic Analysis*, 7th ed, Elsevier, New York, (1975) p 454.
- Feigl F, *Spot tests in Organic Analysis*, Elsevier, New York, (1960) p 368.
- D.L. Kamble, R.B. Chougale and S.T. Nandibewoor, *Indian J. Chem.*, 35A, 865 (1996).
- Singh B, Tripathi S and Mishra S K, *Intl. J. Pure & Appl. Chem.*, 9 (1-2), 71 (2014).
- du Preez J.G.H., C. Viviers, T. Louw, E. Hosten and H. Jonck, *Solv. Extr. Ion Exch.*, 22, 175 (2004).
- A.K. Singh, S. Srivastava, J. Srivastava, and R. Singh, *Carbohydr. Res.* 342, 1078 (2007).
- Singh A K, Srivastava S, Srivastava J & Singh R, *Carbohydr. Res.*, 342(2007) 1078.
- Singh B, Tripathi S & Mishra S K, *Intl. J. Pure & Appl. Chem*, 8 (2013) 113.