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Behavior of $IrCl_3$ as a Homogeneous Catalyst on the Oxidation of *N*-Acetylglucosamine in Acid Medium and Uncatalyzed Reaction in Alkaline Medium with Bromamine-B: Exploration of Kinetic, Mechanistic and Catalytic Chemistry

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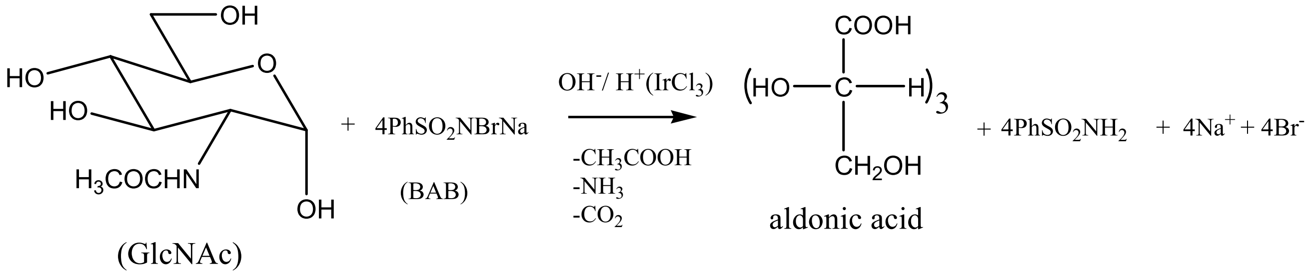
Abstract

The experimental rate laws for the oxidation of *N*-acetylglucosamine with bromamine- B are: – d[BAB]/dt = $k^{/}$ $[BAB]^1$ $[GlcNAc]^{0.69}$ $[HClO_4]^{-0.76}$ $[IrCl_3]^{0.48}$ $[BSA]^{-0.33}$ in acid medium and –d[BAB]/dt = $k^{/}$ $[BAB]^1$ $[GlcNAc]^1$ $[NaOH]^{0.79}$ in alkaline medium. The $IrCl_3$ catalyzed reaction is thirteen fold faster than uncatalyzed reaction. Appropriate mechanisms and rate laws were deduced.

Graphical Abstract

The reaction of *N*-acetylglucosamine with Bromamine-B in acid and alkaline medium is



Keywords $IrCl_3$ catalysis · *N*-Acetylglucosamine · Bromamine-B · Acid and alkaline media · Kinetics-mechanism

1 Introduction

N-Acetylglucosamine (GlcNAc) is chemically known as 2-(acetylamino)-2-deoxy-D-glucose, which is a monosaccharide derivative of glucose [1]. This is a monomeric unit of chitin being the second most abundant natural polymer, next to cellulose. Chitin is a polymer present in exoskeleton of insects and crustaceans. GlcNAc is also used as a dietary supplement similar to the usage of glucosamine. From the literature survey, it is evident that a lot of attention has been paid on the determination of this substrate, however negligible attention has been drawn on the oxidation of GlcNAc from the standpoint of its kinetic and mechanistic chemistry [2–5]. Additionally, the impact of platinum group metal ions in the catalytic transformation of this substrate has not yet been investigated. In biochemical reactions, kinetic as well as catalytic knowledge is very important to optimize a particular redox system. Hence, current research knowledge would be very beneficial to the kineticists who are working on the oxidative-mechanistic chemistry of this substrate in biological systems.

Organic *N*-haloamines have attracted much attention in the past few years owing to their diverse behavior to act as

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halonium cations, hypohalites and *N*-anions [6]. They can perform both as electrophiles and as nucleophiles depending on the reaction conditions. These compounds contain positive halogen ions and are well known mild oxidants. As a result, they react with a wide range of functional groups affecting an array of molecular transformations. Sodium *N*-chloro-*p*-toluenesulfonamide or chloramine-T (CAT) and sodium *N*-chloro-benzenesulfonamide or chloramine-B (CAB) are the prominent members of this group of compounds. These reagents have been employed as oxidizing/chlorinating agents in the kinetic and mechanistic studies for oxidation of different functional groups [7–9]. The bromine analogues of CAT and CAB are bromamine-T ($C_6H_4SO_2NBrNa{\cdot}3H_2O$ or BAT) and bromamine-B ($C_6H_5SO_2NBrNa$ $1.5H_2O$ or BAB). These compounds can be easily prepared by the bromination of CAT and CAB and were found to be superior oxidizing agents than the chloro compounds. Existing literature reveals that relatively less attention [10, 11] was paid towards the kinetics and mechanism of oxidation of organic substrates involving BAT and BAB as oxidizing agents. Our preliminary kinetic runs began with the examination of oxidation of GLcNAc with both CAT and CAB in acid and alkaline media under different experimental conditions. Both the reactions were too sluggish to be measured kinetically. Then we thought of using BAT and BAB as oxidants in both acid and alkaline media and found that the reactions to be feasible. However, the reaction was found to be more brisk with BAB in comparison with BAT, under similar experimental conditions. Hence, we have opted BAB as an oxidant for the oxidation of GlcNAc in both acid and alkaline media. However, the oxidation reaction is still sluggish to be measured kinetically in acid medium and hence it requires some catalyst.

Catalysis by platinum group metal ions plays a vital role in understanding the mechanistic chemistry of a particular redox system. The mechanistic chemistry of these catalytic reactions are quite complex due to the formation of different intermediate complexes, free radicals and different oxidation states of these catalysts. They are of immense practical importance as they deal with control of chemical processes leading to the better understanding of reactions involving such metal complexes and to reveal mechanistic details of a particular redox reaction through kinetic study. Amongst all platinum group metal ions, ruthenium trichloride ($RuCl_3$) and osmium tetroxide (OsO_4) have been extensively used as homogeneous catalysts for a number of redox reactions [12–14]. By contrast, little attention has been paid towards iridium trichloride ($IrCl_3$) catalyst in comparison with other platinum group metal ions. GlcNAc–BAB redox reactions were found to be sluggish in acid medium. Alternatively, we found that $IrCl_3$ catalyst even at trace concentrations (ca. 5.0×10^{-5} mol dm^{-3}) can potentially catalyze the GlcNAc–BAB reaction and oxidation underwent at a kinetically measurable speed by enhancing the reaction rate by 13-fold faster in comparison with uncatalyzed reaction. For these reasons, $IrCl_3$ was chosen as a catalyst in acid medium.

In view of these varied observations, the title investigations were undertaken. In this paper, for the first time, we have taken up a systematic kinetic study of the oxidation of GlcNAc–BAB in acid medium catalyzed by $IrCl_3$ and uncatalyzed reaction in alkaline medium to probe the mechanistic and catalytic chemistry of this redox system in both media. Efforts were made to arrive at the related rate laws and to judge the relative reactivity of the reaction in acid and alkaline media.

2 Experimental and Methods

2.1 Materials

Bromamine-B was obtained by the method of Ahmed and Mahadevappa [15]. The purity of BAB was verified iodometrically via its halogen content. An aqueous solution of BAB was prepared afresh, standardized by iodometric method and preserved in brown bottles to prevent its photochemical deterioration. Analytical grade GlcNAc was purchased from SRL and was used without further purification. Aqueous solution of GlcNAc was freshly prepared whenever required. A solution of $IrCl_3$ (s.d.fine) in 0.1 mol dm^{-3} HCl was employed as catalyst in acid medium. Allowance was made for the amount of HCl present in the catalyst solution while preparing solutions for kinetic runs. All other chemicals used were of analytical grade. Double distilled water was used throughout the work.

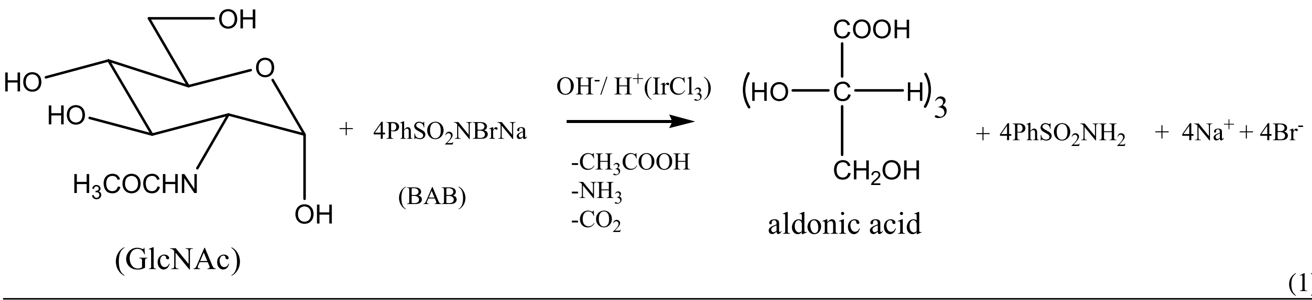
2.2 Kinetic Procedure

All the kinetic experiments were performed under pseudo-first-order conditions by taking a known excess of $[GlcNAc]_0$ over $[BAB]_0$. Raagaa Ultra Cold Chamber with digital temperature control (Chennai, India) was used to control the temperature with an accuracy of 0.1 °C. The kinetic procedure followed to study the progress of the reaction was according to a literature procedure [16]. For each kinetic run, requisite amount of solutions of GlcNAc, $NaOH/HClO_4$, $IrCl_3$ (in acid medium) and water (to maintain the total volume constant for all runs) were taken in glass stoppered Pyrex boiling tubes which are coated black from outside. The reaction mixture was kept in thermostat at 303 K for about 30 min to attain thermal equilibrium. A measured amount of BAB solution, which was also thermostated at the same temperature, was rapidly added with stirring to the mixture in the tube. The course of the reaction was monitored by the iodometric determination of unreacted BAB in 5 ml aliquots of the reaction mixture withdrawn at different intervals of time. The pseudo-first-order rate constants (k′ s^{-1}) were calculated from linear plot of log [BAB] versus time. Kinetic runs were repeated twice and had $<5\%$ standard deviation. All regression coefficients (R^2) calculations were performed with the f_x-100z scientific calculator.

3 Results

3.1 Reaction Stoichiometry

Reaction mixtures containing various compositions of BAB to GlcNAc in the presence of 8.0×10^{-3} mol dm^{-3} NaOH/$HClO_4$ (also 5.0×10^{-5} mol dm^{-3} $IrCl_3$ in acid medium) were equilibrated at 303 K for 24 h. Iodometric titrations of unreacted BAB showed that one mole of GlcNAc consumed four moles of BAB in both the media. Accordingly, the following stoichiometric equation was formulated:



(1)

3.2 Product Characterization

The GlcNAc–BAB reaction was allowed to progress for 24 h at 303 K under stirred conditions in the presence of NaOH/$HClO_4$ (also $IrCl_3$ in acid medium) separately. After completion of the reaction (monitored by TLC), the organic products were subjected to spot tests and chromatographic analysis (TLC technique). Aldonic acid was identified as the oxidation product of GlcNac and was confirmed by GC-MS analysis. The mass spectrum showed a molecular ion peak at 166 (M+1) amu, confirming aldonic acid (Fig. 1). Acetic acid was identified by spot test [16]. Ammonia was detected by Nessler's reagent test according to the method of Vogel [17]. The evolving carbon dioxide was detected by conventional lime water test. It was also noted that there was no further oxidation of aldonic acid under the present kinetic conditions. Benzensulfonamide (BSA), the reduced product of BAB, was extracted with ethyl acetate and identified [18] by thin layer chromatography using petroleum ether: chloroform: 1-butanol (2:2:1 v/v) as the solvent system and iodine as the spray reagent ($R_f=0.88$) The determined R_f value agrees with the value reported in the literature [18].

3.3 Kinetic Data

At comparable experimental conditions, the kinetics of oxidation of GlcNAc by BAB was investigated at several initial concentrations of reactants in acid medium catalyzed by $IrCl_3$ and uncatalyzed reaction in alkaline medium at 303 K.

3.3.1 Effect of Varying Concentrations of GlcNAc and BAB on the Rate of Reaction

Under pseudo-first-order conditions of $[GlcNAc]_0 \gg [BAB]_0$, at constant $[GlcNAc]_0$, [NaOH]/[$HClO_4$], (also $IrCl_3$ in acid medium) and temperature, plots log [BAB] versus time were linear ($R^2>0.9918$), indicating a first-order dependence of rate on $[BAB]_0$ in both the media. The pseudo-first-order rate constants (k′, s^{-1}) calculated are independent of $[BAB]_0$, confirming the first-order dependence of rate on $[BAB]_0$ (Tables 1, 2). Values of k′ increased with increase in $[GlcNAc]_0$ (Tables 1, 2) in both media. A plot of log k′ versus log $[GlcNAc]_0$ was linear ($R^2=0.9989$) with a unit slope, suggesting a first-order dependence of rate on $[GlcNAc]_0$ in alkaline medium. Whereas the order of reaction with respect to $[GlcNAc]_0$ in acid medium is fractional (Table 1). Furthermore, a plot of k′ versus $[GlcNAc]_0$ were linear in both cases ($R^2>0.9905$). Such a plot is passing through the origin in alkaline medium and with a y-intercept in acid medium, clearly confirms the order of the reaction is first-order in alkaline medium and fractional-order in acid medium.

3.3.2 Effect of Varying Concentrations of Media and $IrCl_3$ on the Rate of Reaction

It is seen from the data in Tables 1 and 2 that values of k′ decreases with increase in [$HClO_4$] and increases with increase in [NaOH]. Further, log–log plots of k′ and [$HClO_4$]/[NaOH] were linear ($R^2>0.9946$) with slopes of -0.76 and 0.79 in $HClO_4$ and NaOH medium respectively, suggesting a negative-fractional-order dependence of rate on [$HClO_4$] and fractional-order with respect to [NaOH]. However, the rate increased with an increase in $IrCl_3$ in acid medium (Table 1). The slope of log k′ versus log [$IrCl_3$]

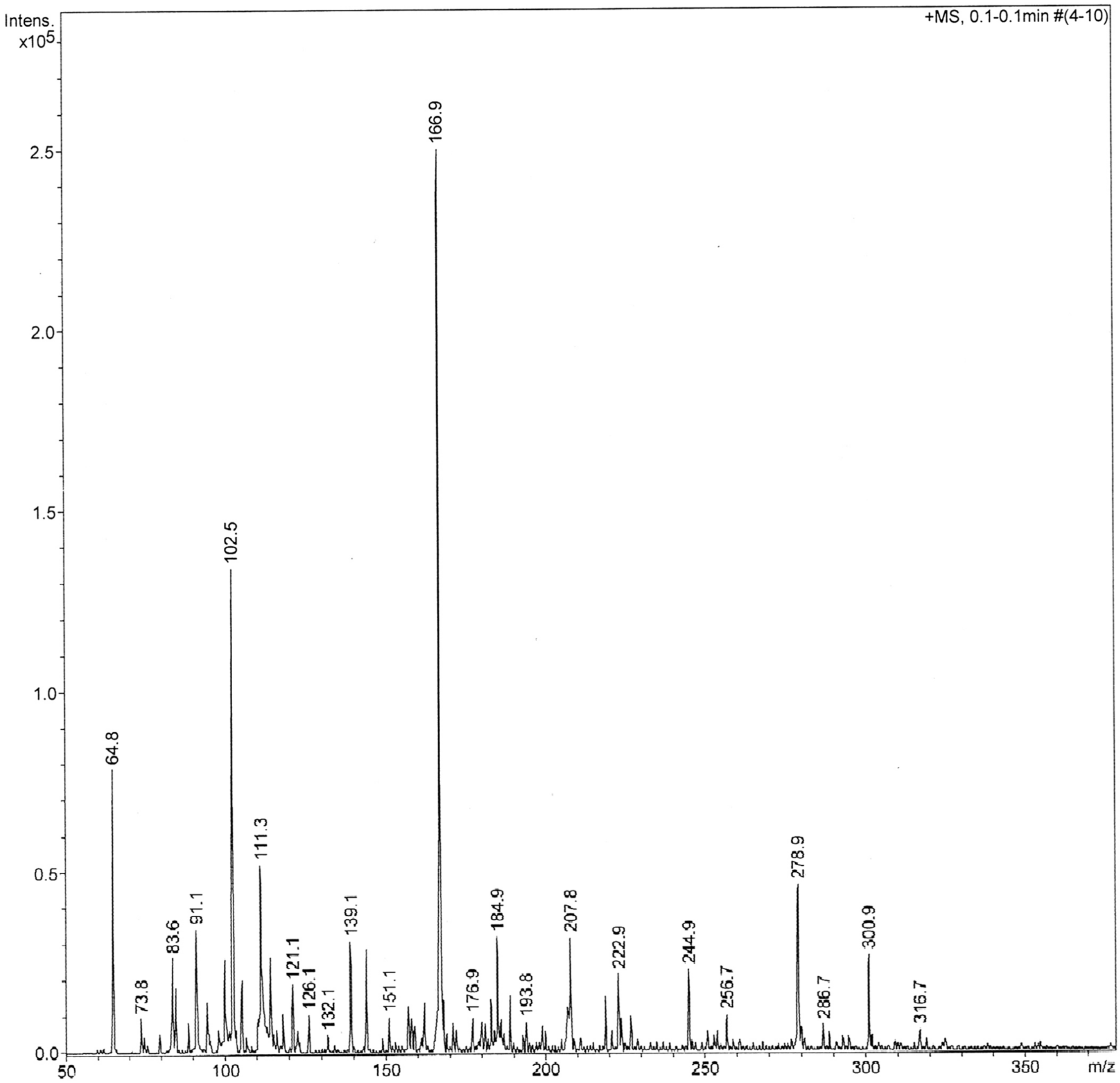


Fig. 1 Mass spectrum of aldonic acid with molecular ion peak at 166 (M+1) amu

($R^2 = 0.9881$) was found to be 0.48, establishing a fractional-order dependence of rate on [$IrCl_3$].

3.3.3 Effect of Varying Dielectric Constant of the Media on the Rate of Reaction

Rate studies were made in H_2O–MeOH mixtures at different compositions (0–20% v/v) in order to study the effect of dielectric constant (D) of the solvent medium, with all other experimental conditions being held constant. The rate was found to decrease with increase in MeOH content (Table 3) in both the media. Further, plots of log k′ versus 1/D were linear ($R^2 > 0.9951$, Fig. 2) with negative slopes. The dielectric constant values of MeOH–H_2O mixtures reported in the literature [19] were employed. Blank experiments showed that oxidation of MeOH with BAB under the present experimental conditions are negligible.

3.3.4 Effect of Varying Concentration of BSA and Ionic Strength of Media on the Rate of Reaction

Addition of benzenesulfonamide (BSA) in the range of 0.3×10^{-4} to 5.0×10^{-4} mol dm^{-3} to the reaction mixture retarded the rate in acid medium, whereas negligible effect was noticed in alkaline medium (Table 4). This indicates that BSA is involved in the pre-equilibrium step in acid medium but the same does not in alkaline medium. Further, a plot of log k′ versus log [BSA] was linear ($R^2 = 0.9945$, Fig. 3) with a negative slope (-0.33), confirming a negative-fractional-order dependence of rate on [BSA] in acid medium. The influence of ionic strength (I) of the medium on the reaction

Table 1 Effect of varying BAB, GlcNAc, $HClO_4$ and $IrCl_3$ concentrations on the reaction rate at 303 K

10^4 $[BAB]_0$ (mol dm^{-3})	10^3 $[GlcNAc]_0$ (mol dm^{-3})	10^3 $[HClO_4]$ (mol dm^{-3})	10^5 $[IrCl_3]$ (mol dm^{-3})	10^4 k′ (s^{-1})
0.3	2.0	8.0	5.0	5.42
0.5	2.0	8.0	5.0	5.38
1.0	2.0	8.0	5.0	5.44
2.0	2.0	8.0	5.0	5.46
3.0	2.0	8.0	5.0	5.41
1.0	0.5	8.0	5.0	3.39 (1.84)
1.0	1.0	8.0	5.0	4.41 (2.56)
1.0	2.0	8.0	5.0	5.44 (3.26)
1.0	4.0	8.0	5.0	7.05 (4.16)
1.0	8.0	8.0	5.0	8.66 (4.60)
1.0	2.0	2.0	5.0	15.5
1.0	2.0	4.0	5.0	10.1
1.0	2.0	8.0	5.0	5.44
1.0	2.0	12.0	5.0	4.09
1.0	2.0	16.0	5.0	3.22
1.0	2.0	8.0	1.0	2.75
1.0	2.0	8.0	3.0	4.38
1.0	2.0	8.0	5.0	5.44
1.0	2.0	8.0	7.0	6.91
1.0	2.0	8.0	9.0	7.95

Values in parenthesis refer to rate constants obtained for varying GlcNAc concentrations at constant $[PhSO_2NH_2]=5.0\times10^{-4}$ mol dm^{-3}

Table 2 Effect of varying BAB, GlcNAc and NaOH concentrations on the reaction rate at 303 K

10^4 $[BAB]_0$ (mol dm^{-3})	10^3 $[GlcNAc]_0$ (mol dm^{-3})	10^3 [NaOH] (mol dm^{-3})	10^4 k′ (s^{-1})
0.3	2.0	8.0	4.40
0.5	2.0	8.0	4.31
1.0	2.0	8.0	4.36
2.0	2.0	8.0	4.29
3.0	2.0	8.0	4.30
1.0	0.5	8.0	1.19
1.0	1.0	8.0	2.22
1.0	2.0	8.0	4.36
1.0	4.0	8.0	8.77
1.0	8.0	8.0	17.2
1.0	2.0	2.0	1.42
1.0	2.0	4.0	2.43
1.0	2.0	8.0	4.36
1.0	2.0	12.0	5.30
1.0	2.0	16.0	7.16

Experimental conditions: I = 0.1 mol dm^{-3}

Table 3 Effect of varying the dielectric constant of the medium on the reaction rate at 303 K

% MeOH (v/v)	D	10^4 k′ (s^{-1})	
		Acid ($IrCl_3$ catalyzed)	Alkaline
0	76.73	5.44	4.36
5	74.50	4.89	4.10
10	72.37	4.56	3.89
20	67.48	3.45	3.50

Experimental conditions: $[BAB]_0=1.0\times10^{-4}$ mol dm^{-3}; $[GlcNAc]_0=2.0\times10^{-3}$ mol dm^{-3}; $[NaOH/HClO_4]=8.0\times10^{-3}$ mol dm^{-3}; $[IrCl_3]=5.0\times10^{-5}$ mol dm^{-3} (in acid medium); I = 0.1 mol dm^{-3}(in alkaline medium); T = 303 K

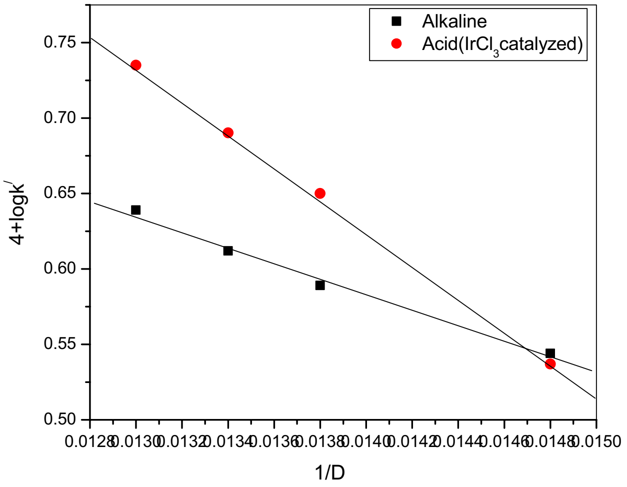


Fig. 2 Plots of log k′ versus 1/D

Table 4 Effect of varying the benzenesulfonamide concentrations on the reaction rate at 303 K

10^4 [BSA] (mol dm^{-3})	10^4 k′ (s^{-1})	
	Acid ($IrCl_3$ catalyzed)	Alkaline
0.3	7.02	4.33
0.5	6.39	4.28
1.0	5.44	4.36
3.0	3.98	4.44
5.0	3.22	4.41

Experimental conditions: $[BAB]_0=1.0\times10^{-4}$ mol dm^{-3}; $[GlcNAc]_0=2.0\times10^{-3}$ mol dm^{-3}; $[NaOH/HClO_4]=8.0\times10^{-3}$ mol dm^{-3}; $[IrCl_3]=5.0\times10^{-5}$ mol dm^{-3} (in acid medium); I = 0.1 mol dm^{-3}(in alkaline medium); T = 303 K

rate was carried out in the range of 0.05–0.3 mol dm^{-3} using $NaClO_4$ solution, with other experimental conditions kept constant. We have noticed salient results in this regard (Table 5). The ionic strength showed negligible influence on the reaction rate in acid medium, whereas in alkaline medium the rate of reaction increases with increase in ionic strength. A plot of log k′ versus $I^{1/2}$ was linear ($R^2=0.9994$)

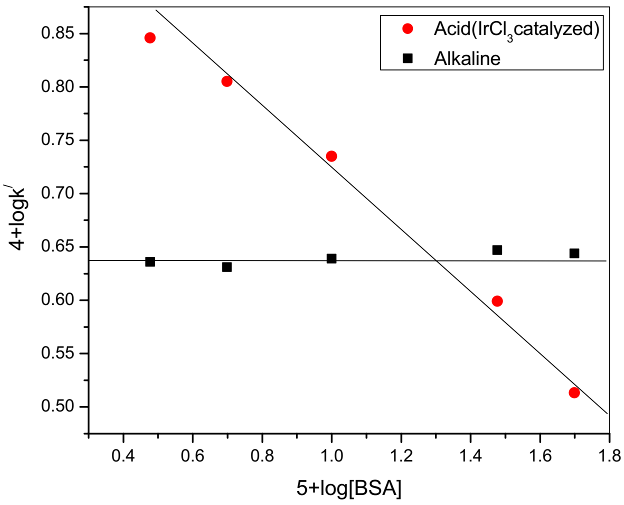


Fig. 3 Plots of log k′ versus log [BSA]

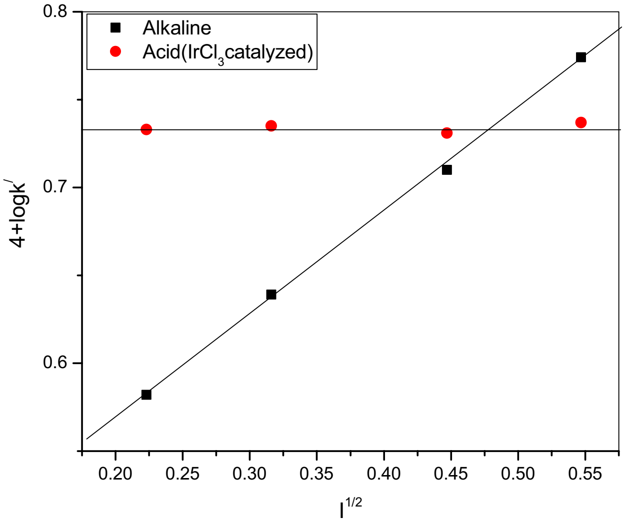


Fig. 4 Plots of log k′ versus $I^{1/2}$

Table 5 Effect of varying ionic strength of the medium on the reaction rate at 303 K

$[NaClO_4]$ (mol dm^{-3})	10^4 k′ (s^{-1})	
	Acid ($IrCl_3$ catalyzed)	Alkaline
0.05	5.41	3.82
0.1	5.44	4.36
0.2	5.39	5.14
0.3	5.46	5.95

Experimental conditions: $[BAB]_0 = 1.0 \times 10^{-4}$ mol dm^{-3}; $[GlcNAc]_0 = 2.0 \times 10^{-3}$ mol dm^{-3}; [NaOH]/$[HClO_4] = 8.0 \times 10^{-3}$ mol dm^{-3}; $[IrCl_3] = 5.0 \times 10^{-5}$ mol dm^{-3} (in acid medium); I = 0.1 mol dm^{-3} (in alkaline medium); T = 303 K

with positive slope in alkaline medium (Fig. 4). For this reason, the ionic strength of the reaction system was maintained at constant concentration of 0.1 mol dm^{-3} for kinetic runs in alkaline medium in order to swamp the reaction.

3.3.5 Effect of Varying Concentration of Halide ions and on the Rate of Reaction

The effects of Cl^- or Br^- were studied by adding 2.0×10^{-2} mol dm^{-3} NaCl or NaBr solution to the reaction mixture. There was no significant effect of these halide ions on the rate of the reaction, suggesting that no interhalogen was formed in the reaction.

3.3.6 Effect of Varying Temperature on the Rate of Reaction

The effect of temperature on the rate of the reaction was studied in the temperature range of 293–313 K, keeping other experimental conditions constant. From the linear Arrhenius plots of log k′ versus 1/T ($R^2 > 0.9988$), activation parameters for the overall reaction were computed for acid and alkaline media. All these results are summarized in Table 6.

3.3.7 Test for Free Radicals

No induced polymerization was observed when acrylamide was added to the reaction mixture ruling out a free radical mechanism.

4 Discussion

4.1 Reactive Species of BAB

As organic *N*-haloamines have similar chemical properties, it is expected that similar equilibria exists in solutions of these compounds [20]. Bromamine-B acts as an oxidizing agent in both acidic and alkaline media. In general BAB undergoes a two-electron change in its reactions. The oxidation potential of BAB/sulfonamide couple is pH dependent and decreases with increase in the pH of the medium [20]. Bromamine-B like its chlorine analogues CAT and CAB behaves as a strong electrolyte in aqueous solutions [21–23] forming different species as shown in Eqs. (2–8):

$$PhSO_2NBrNa \rightleftharpoons PhSO_2BNBr^- + Na^+ \quad (2)$$

$$PhSO_2NBr^- + H^+ \rightleftharpoons PhSO_2NHBr \quad (3)$$

Table 6 Effect of varying temperature on the rate of reaction and activation parameters for the oxidation of GlcNAc with BAB in acid and alkaline media

Temperature (K)	10^4 k′ (s^{-1})			Kc
	Alkaline	Acid		
		$IrCl_3$ Catalyzed	Uncatalyzed	
293	2.13	2.83	0.22	0.03
298	3.23	4.22	0.32	0.04
303	4.36	5.44	0.43	0.06
308	6.61	8.52	0.66	0.09
313	8.95	11.5	0.83	0.12
E_a (kJ mol^{-1})	51.7	44.6	60.5	55.7
$\Delta H^{\neq}$ (kJ mol^{-1})	49.2 (±0.01)	42.1 (±0.02)	57.9 (±0.02)	53.2
$\Delta G^{\neq}$ (kJ mol^{-1})	93.7 (±0.23)	93.0 (±0.24)	99.6 (±0.29)	81.3
$\Delta S^{\neq}$ (JK^{1} mol^{1})	− 146 (±0.05)	− 168 (±0.18)	− 137 (±0.22)	− 92.7

Experimental condition: $[BAB]_0 = 1.0 \times 10^{-4}$ mol dm^{-3}; $[GlcNAc]_0 = 2.0 \times 10^{-3}$ mol dm^{-3}; [NaOH]/$[HClO_4] = 8.0 \times 10^{-3}$ mol dm^{-3}; $[IrCl_3] = 5.0 \times 10^{-5}$ mol dm^{-3} (in acid medium); I = 0.1 mol dm^{-3} (in alkaline medium)

$$2\ PhSO_2NHBr \rightleftharpoons PhSO_2NH_2 + PhSO_2NBr_2 \tag{4}$$

$$PhSO_2NBr_2 + H_2O \rightleftharpoons PhSO_2NHBr + HOBr \tag{5}$$

$$PhSO_2NHBr + H_2O \rightleftharpoons PhSO_2NH_2 + HOBr \tag{6}$$

$$HOBr \rightleftharpoons H^+ + OBr^- \tag{7}$$

$$HOBr + H^+ \rightleftharpoons H_2O^+Br \tag{8}$$

In acidified solution of BAB, the probable oxidizing species are $PhSO_2NHBr$, $PhSO_2NBr_2$, HOBr and possibly H_2O^+Br. If $PhSO_2NBr_2$ was to be the reactive species, then the rate law predicts the second-order dependence on $[BAB]_0$ (Eq. 4) which is not true, since the first-order with respect to $[BAB]_0$ is noticed in the present case. This clearly rules out the possibility of $PhSO_2NBr_2$ being reactive species. Further, protonation of monochloramine-B has been reported [24] as:

$$PhSO_2NHBr + H^+ \rightleftharpoons PhSO_2N^+H_2Br \tag{9}$$

Because organic *N*-haloamines have similar chemical properties, the same equilibrium can be expected for BAB also. In the present investigations, the inverse-fractional-order dependence of rate on $[H^+]$ suggests that the reverse of reaction (9) is quite favorable. Furthermore, the rate retarded by the added BSA suggests that Eq. (6) plays a dominant role and HOBr is the most active oxidizing species in the present investigations.

4.2 Study of Complex Formation of $IrCl_3$ and Reactive Species

It is known that $IrCl_3$ in hydrochloric acid gives $IrCl_6{}^{3-}$ species [25]. It has also been reported that iridium (III) and iridium (I) ions are the stable species of iridium [26]. Further, the aqueous solution of $IrCl_6{}^{3-}$ gives $[IrCl_5(H_2O)]^{2-}$, $[IrCl_4(H_2O)_2]^-$ and $[IrCl_3(H_2O)_3]$ species [27–29] as shown below:

$$IrCl_3.xH_2O\ +\ 3HCl\ \rightarrow\ \left[IrCl_6\right]^{3-}\ +\ xH_2O\ +\ 3H^+ \tag{10}$$

$$\left[IrCl_6\right]^{3-}\ +\ H_2O \rightleftharpoons\ \left[IrCl_5\left(H_2O\right)\right]^{2-}\ +\ Cl^- \tag{11}$$

In the present study, addition of Cl^- in the form of NaCl at fixed $[H^+]$ had no effect on the rate, suggesting that equilibrium (11) does not play any role in the reaction. Hence, the complex ion $[IrCl_5(H_2O)]^{2-}$ is assumed to be the active catalyst species that interacts with the oxidant species HOBr to form a complex intermediate.

Evidence for the complex formation between oxidant, substrate and catalyst is acquired from the UV–Visible spectra of BAB, GlcNAc, $IrCl_3$, and their mixture. Absorption maxima appear at 218 nm for BAB, 444 nm for $IrCl_3$ in aqueous acidic medium, and 418 nm for (BAB + $IrCl_3$) mixture. A hypsochromic shift of 26 nm from 444 to 418 nm of $IrCl_3$ suggests that the complexation occurs between BAB and $IrCl_3$. Further, the spectra show an absorption maxima for GlcNAc at 214 nm and for ($IrCl_3$ + BAB + GlcNAc) mixture at 437 nm. A bathochromic shift of 19 nm supports the formation of complex between oxidant, catalyst and substrate in acid medium (Fig. 5).

4.3 Reaction Scheme and Rate Law in Acid Medium

In view of the above facts and considering all the experimental data, the following mechanism (Scheme 1) may be formulated for $IrCl_3$ catalyzed oxidation of GlcNAc by BAB in acid medium.

Scheme 2 depicts electron flow for the oxidation of GlcNAc by BAB in acid medium catalyzed by $IrCl_3$ along with structures of intermediate complexes. In the fast equilibrium step (step (i)), $PhSO_2N^+H_2Br$ undergoes deprotonation to give $PhSO_2NHBr$. In the next step (step (ii)), $PhSO_2NHBr$

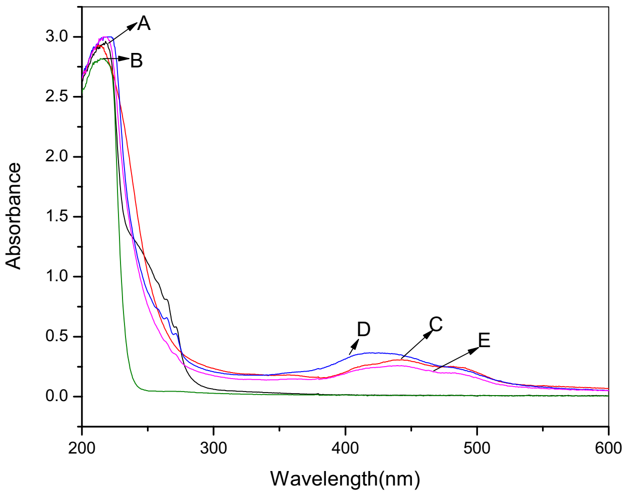


Fig. 5 UV–Visible spectra of (*a*) BAB, (*b*) GlcNAc, (*c*) $IrCl_3$, (*d*) Mixture of (BAB + $IrCl_3$), (*e*) Mixture of (BAB + $IrCl_3$ + GlcNAc)

undergoes hydrolysis to form HOBr, which is the active oxidizing species, along with the elimination of $PhSO_2NH_2$. In the next fast equilibrium step (step (iii)), HOBr co-ordinates to catalytic species and forms an intermediate complex-I. Further, in the step (iv), this intermediate complex-I reacts with substrate to give an another intermediate complex-II. In the slow and rds step (step (v)), complex-II disproportionates to form an another intermediate complex-III. Finally, the complex-III reacts with three more moles of oxidant followed by several fast steps, leading to the formation of the ultimate product, aldonic acid.

If $[BAB]_t$ is the total effective concentration of oxidant, then

$$[BAB]_t = \left[PhSO_2N^+H_2Br\right] + \left[PhSO_2NHBr\right] + [HOBr] + \left[\text{Complex-I}\right] + \left[\text{Complex-II}\right] \tag{12}$$

From steps (i), (ii), (iii) and (iv) of the Scheme 1, we obtain

$$[PhSO_2NHBr] = \frac{[PhSO_2NH_2][\text{Complex-II}]}{K_2K_3K_4[IrCl_3][GlcNAc][H_2O]} \tag{13}$$

$$[PhSO_2N^+H_2Br] = \frac{[PhSO_2NH_2][\text{Complex-II}][H^+]}{K_1K_2K_3K_4[GlcNAc][IrCl_3][H_2O]} \tag{14}$$

$$[HOBr] = \frac{[\text{Complex-II}]}{K_3K_4[IrCl_3][GlcNAc]} \tag{15}$$

$$[\text{Complex-I}] = \frac{[\text{Complex-II}]}{K_4[GlcNAc]} \tag{16}$$

By substituting for $[PhSO_2NHBr]$, $[PhSO_2N^+HBr]$, [HOBr] and [Complex-I] from Eqs. (13–16) into Eq. (12) and solving for [Complex-II], we obtain,

$$[\text{Complex-II}] = \left\{ \frac{K_1K_2K_3K_4[BAB]_t[GlcNAc][IrCl_3][H_2O]}{[PhSO_2NH_2][H^+] + K_1[PhSO_2NH_2] + K_1K_2[H_2O] + K_1K_2K_3[IrCl_3][H_2O] + K_1K_2K_3K_4[GlcNAc][IrCl_3][H_2O]} \right\} \tag{17}$$

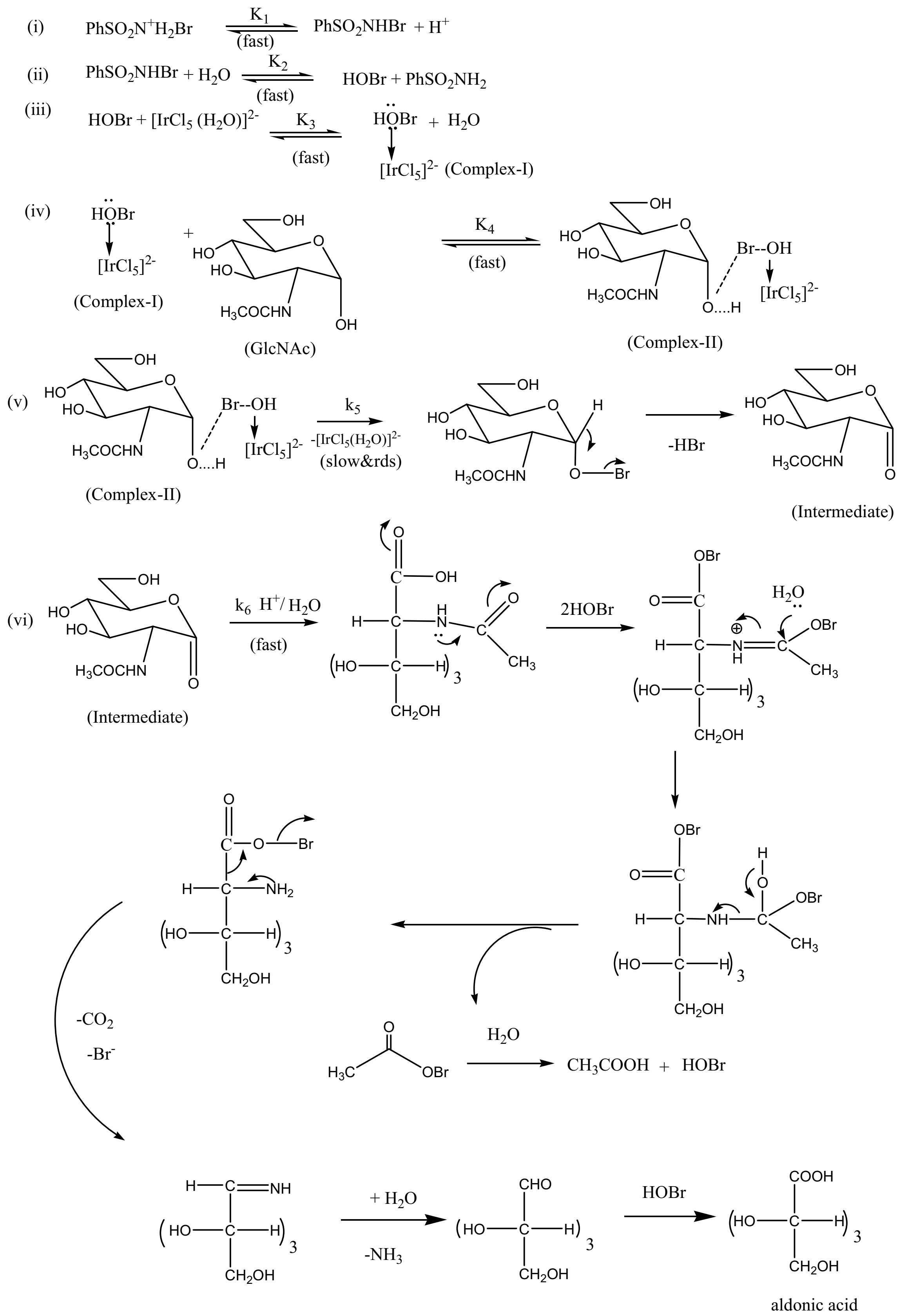
From the slow and rds (step (v)) of Scheme 1,

$$\text{Rate} = k_5\left[\text{Complex} - \text{II}\right] \tag{18}$$

By substituting for [Complex-II] from Eq. (17) into Eq. (18), the following rate law is obtained:

$$\begin{array}{lll}
PhSO_2N^+H_2Br \xrightleftharpoons{K_1} PhSO_2NHBr + H^+ & & \text{fast (i)} \\
PhSO_2NHBr + H_2O \xrightleftharpoons{K_2} PhSO_2NH_2 + HOBr & & \text{fast (ii)} \\
HOBr + IrCl_3 \xrightleftharpoons{K_3} \text{Complex-I} & & \text{fast (iii)} \\
\text{Complex-I} + GlcNAc \xrightleftharpoons{K_4} \text{Complex-II} & & \text{fast (iv)} \\
\text{Complex-II} \xrightarrow{k_5} \text{Complex-III} & & \text{slow \& rds (v)} \\
\text{Complex-III} + 3\ HOBr \xrightarrow{k_6} \text{Products} & & \text{fast (vi)}
\end{array}$$

Scheme 1 A general reaction scheme for $IrCl_3$-catalyzed oxidation of GlcNAc by BAB in acid medium



Scheme 2 A descriptive mechanistic interpretation for the $IrCl_3$ catalyzed oxidation of GlcNAc by BAB in acid medium

$$\text{Rate} = \frac{K_1K_2K_3K_4k_5[BAB]_t[GlcNAc][IrCl_3][H_2O]}{[PhSO_2NH_2][H^+] + K_1[PhSO_2NH_2] + K_1K_2[H_2O] + K_1K_2K_3[IrCl_3][H_2O] + K_1K_2K_3K_4[GlcNAc][IrCl_3][H_2O]} \tag{19}$$

Rate law (19) is in complete agreement with the observed kinetic data wherein a first-order dependence of rate on $[BAB]_t$ fractional-order on both [GlcNAc] and $[IrCl_3]$ and negative fractional-order each on $[H^+]$ and $[PhSO_2NH_2]$ was observed.

Since rate = k′ $[BAB]_t$, then Eq. (19) becomes

$$k' = \frac{K_1K_2K_3K_4k_5[GlcNAc][IrCl_3][H_2O]}{[PhSO_2NH_2][H^+] + K_1[PhSO_2NH_2] + K_1K_2[H_2O] + K_1K_2K_3[IrCl_3][H_2O] + K_1K_2K_3K_4[GlcNAc][IrCl_3][H_2O]} \tag{20}$$

Inversion and transformation of the above equation yields,

$$\frac{1}{k'} = \left\{ \frac{[PhSO_2NH_2][H^+]}{K_1K_2K_3K_4k_5[GlcNAc][IrCl_3][H_2O]} + \frac{[PhSO_2NH_2]}{K_2K_3K_4k_5[IrCl_3][GlcNAc][H_2O]} + \frac{1}{K_3K_4k_5[GlcNAc][IrCl_3]} + \frac{1}{K_4k_5[GlcNAc]} \right\} + \frac{1}{k_5} \tag{21}$$

$$\frac{1}{k'} = \frac{1}{[GlcNAc]} \left\{ \frac{[PhSO_2NH_2][H^+]}{K_1K_2K_3K_4k_5[IrCl_3][H_2O]} + \frac{[PhSO_2NH_2]}{K_2K_3K_4k_5[IrCl_3][H_2O]} + \frac{1}{K_3K_4k_5[IrCl_3]} + \frac{1}{K_4k_5} \right\} + \frac{1}{k_5} \tag{22}$$

According to Eq. (22), a plot of 1/k′ versus 1/[GlcNAc] should be linear with an intercept equal to $1/k_5$. The applicability of Eq. (22) is clearly shown that 1/k′ versus 1/[GlcNAc] plot is linear ($R^2 = 0.9960$) with an intercept for the standard run at constant [BAB], $[HClO_4]$, $[IrCl_3]$, $[PhSO_2NH_2]$ and temperature as shown in Table 1. The value of the decomposition constant k_5 was found to be $4.34 \times 10^{-4}\ s^{-1}$.

Moelwyn-Hughes [30] pointed out that the catalyzed and uncatalyzed reactions proceed simultaneously and the relationship is

$$k_1 = k_0 + K_C[\text{catalyst}]^x \tag{23}$$

Here k_1 is the observed pseudo-first-order rate constant obtained in the presence of $IrCl_3$ catalyst and k_0 is that for the uncatalyzed reaction, K_C is the catalytic constant and x is the order of the reaction with respect to $IrCl_3$ which is found to be 0.48 in the present study. The value of K_C is calculated using the equation

$$K_C = k_1 - k_0 / [IrCl_3]^{0.48} \tag{24}$$

The values of K_C have been evaluated at different temperatures (293–313 K) and K_C was found to vary with temperature. Further, a plot of log K_C versus 1/T was linear ($R^2 = 0.9988$) and the values of energy of activation and other thermodynamic parameters with respect to $IrCl_3$ catalyst were computed and recorded in Table 6.

It was thought worthwhile to compare the reactivity of GlcNAc by BAB in acid medium in the absence of $IrCl_3$ catalyst, under identical experimental conditions. Hence, the reaction was carried out at different temperatures (293–313 K) and from the Arrhenius plot of log k′ versus 1/T ($R^2 = 0.9988$), values of activation parameters for the uncatalyzed reaction in acid medium were also calculated (Table 6). It is seen from Table 6 that $IrCl_3$ catalyzed reaction rate is found to be nearly 13-fold faster than the uncatalyzed reaction. Thus, the observed rate of oxidation in the presence of $IrCl_3$ catalyst justifies the need of $IrCl_3$ catalyst for a facile oxidation of GlcNAc by BAB in acid medium. The activation parameters evaluated for the $IrCl_3$ catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction. The catalyst $IrCl_3$ forms a complex-I with the oxidizing species (HOBr), which increases the oxidizing property of the oxidant than without $IrCl_3$ catalyst. Further, the catalyst $IrCl_3$ favorably modifies the reaction path by lowering the energy of activation as shown in Table 6.

4.4 Reaction Scheme and Rate Law in Alkaline Medium

In alkaline solutions of CAB, $PhSO_2NCl_2$ does not exist [20]. Further, Bishop and Jennings [20] have shown in alkaline solutions of CAB, the possible oxidizing species are $PhSO_2NHCl$, HOCl and the anions $PhSO_2N^-Cl$ and OCl^-. Similar observations are reported for alkaline BAB solutions by Hardy and Johnston [22] and the following equilibria were also established:

$$PhSO_2N^-Br + H_2O \rightleftharpoons PhSO_2NHBr + OH^- \tag{25}$$

$$PhSO_2NHBr + H_2O \rightleftharpoons PhSO_2NH_2 + HOBr \tag{26}$$

If HOBr was to be the primary oxidizing species as indicted in Eq. (26), a first-order retardation of rate by added BSA would be expected. However, no such effect was noticed in the present study. If $PhSO_2NHBr$ is the reactive species, retardation of the rate by $[OH^-]$ is expected (Eq. 25), which is also contrary to the experimental observations. Hence, in the present investigations, the rate of reaction is accelerated by OH^- ions clearly indicating that the anion $PhSO_2N^-Br$ is the most likely oxidizing species involved in the oxidation of GlcNAc by BAB. In view of the above observations and experimental results, a reaction mechanism (Scheme 3) is formulated for oxidation of GlcNAc with BAB in alkaline medium. An anomeric carbon of GlcNAc loses a proton and gets converted to $GlcNAc^-$ in alkaline medium, which is considered as a reactive substrate species [31].

The probable mode of oxidation of GlcNAc by BAB in alkaline medium is depicted in Scheme 4. In the fast step (step (i)), GlcNAc undergoes deprotonation in alkaline medium resulting in the formation of corresponding anion ($GlcNAc^-$). In the next slow and rds (step (ii)), the anion reacts with one mole of the oxidant species ($PhSO_2N^-Br$) to form an intermediate complex-IV. In the last successive fast steps (step (iii)), intermediate complex-IV reacts with another three more moles of oxidant species yielding the final product which is the aldonic acid.

From slow and rds step (ii) of Scheme 3,

$$\text{Rate} = k_8[\text{GlcNAc}^-]\left[\text{PhSO}_2\text{N}^-\text{Br}\right] \tag{27}$$

If $[\text{GlcNAc}]_t$ is the total effective concentration of the substrate, then

$$[\text{GlcNAc}]_t = [\text{GlcNAc}^-] + [\text{GlcNAc}] \tag{28}$$

By step (i) of Scheme 3

$$[\text{GlcNAc}] = \frac{[\text{GlcNAc}^-][\text{H}_2\text{O}]}{K_7[\text{OH}^-]} \tag{29}$$

By substituting for [GlcNAc] from Eq. (29) into Eq. (28) and solving for $[\text{GlcNAc}^-]$, we obtain,

$$[\text{GlcNAc}^-] = \frac{K_7[\text{OH}^-][\text{GlcNAc}]_t}{[\text{H}_2\text{O}]+K_7[\text{OH}^-]} \tag{30}$$

By substituting for $[\text{GlcNAc}^-]$ from Eq. (30) into Eq. (27), the following rate law is obtained.

$$\text{Rate} = \frac{K_7k_8[\text{OH}^-][\text{GlcNAc}]_t[\text{PhSO}_2\text{N}^-\text{Br}]}{[\text{H}_2\text{O}]+K_7[\text{OH}^-]} \tag{31}$$

The $[\text{PhSO}_2\text{N}^-\text{Br}]$ is the concentration of the reactive species of BAB, then $[\text{PhSO}_2\text{N}^-\text{Br}]$ is [BAB], accordingly we can write Eq. (31) as Eq. (32):

$$\text{Rate} = \frac{K_7k_8[\text{OH}^-][\text{GlcNAc}]_t[\text{BAB}]}{[\text{H}_2\text{O}]+K_7[\text{OH}^-]} \tag{32}$$

Rate law (32) is in accordance with the experimental findings.

Since rate = k′ [GlcNAc]t, then

$$k' = \frac{K_7k_8[\text{BAB}][\text{OH}^-]}{[\text{H}_2\text{O}] + K_7[\text{OH}^-]} \tag{33}$$

$$1/k' = \frac{[\text{H}_2\text{O}]}{K_7k_8[\text{BAB}][\text{OH}^-]} + \frac{1}{k_8[\text{BAB}]} \tag{34}$$

Based on Eq. (34), a double reciprocal plot of 1/k′ versus $1/[\text{OH}^-]$ is a straight line ($R^2 = 0.9983$). From the intercept of such a plot, value of k_8 could be derived as 11.1 s^{-1}.

The proposed mechanisms and the derived rate laws in both the media are supported by the following experimental findings:

The ionic strength (I) effect on the reaction rate has been described according to the theory of Bronsted and Bjerrum [32], which postulates the reaction through the formation of an activated complex. According to this theory, the effect of ionic strength on the rate of a reaction involving two ions is given by the relationship:

$$\log k' = \log k_0 + 1.018Z_AZ_BI^{1/2} \tag{35}$$

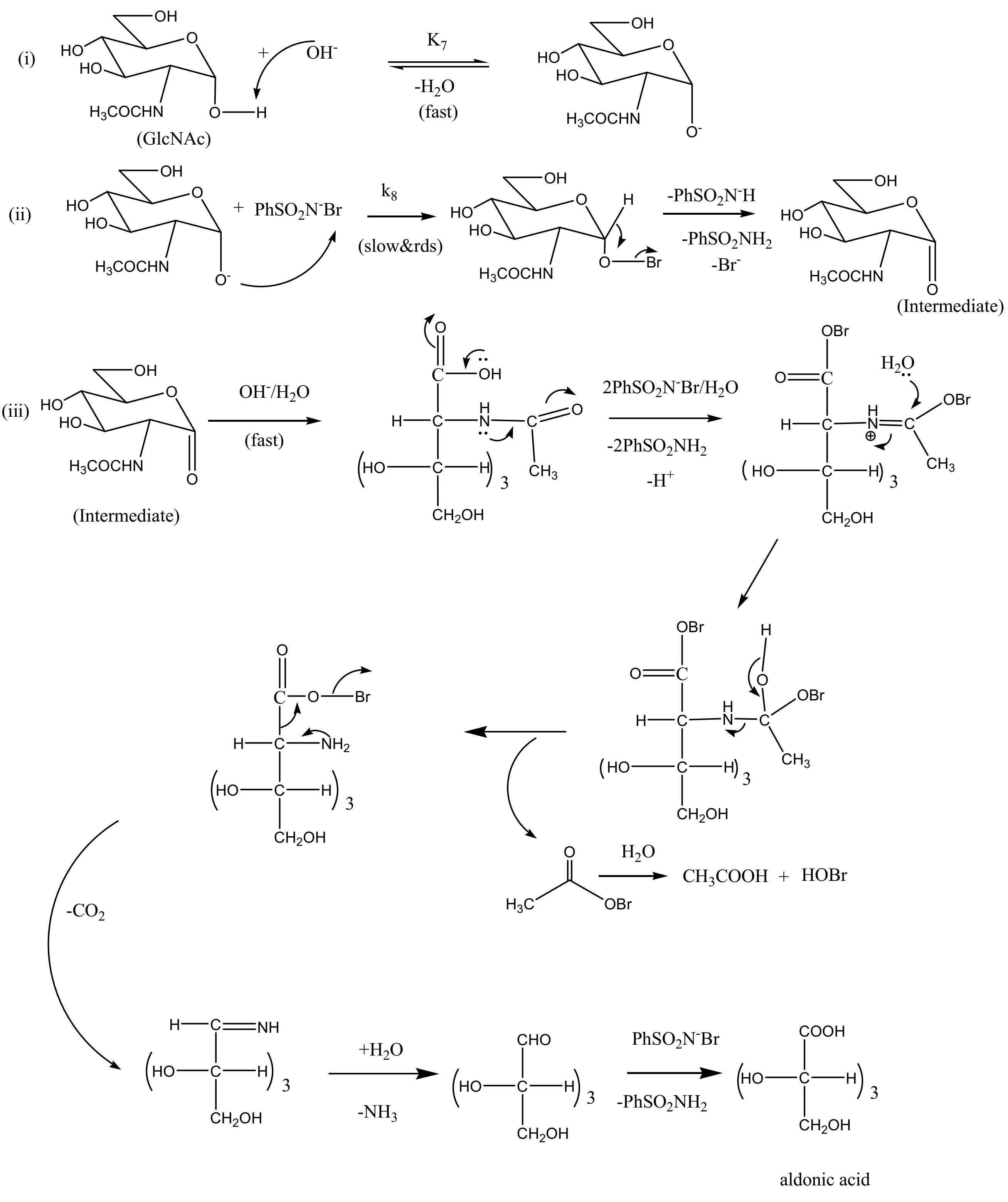
Here Z_A and Z_B are the valency of the ions A and B, and k and k_0 are the rate constants in the presence and absence of the added electrolyte, respectively. A plot of log k′ against $I^{1/2}$ should be linear with a slope of 1.018 Z_AZ_B. If Z_A and Z_B have similar signs, then the slope of such a plot is positive. Hence, the quantity Z_AZ_B is positive and consequently the rate increases with increase in the ionic strength of the

$$\text{GlcNAc} + \text{OH}^- \overset{K_7}{\rightleftharpoons} \text{GlcNAc}^- + \text{H}_2\text{O} \qquad \text{fast (i)}$$

$$\text{GlcNAc-} + \text{PhSO}_2\text{N}^-\text{Br} \xrightarrow{k_8} \text{Complex- IV} \qquad \text{slow \& rds (ii)}$$

$$\text{Complex-IV} + 3\ \text{PhSO}_2\text{N}^-\text{Br} \xrightarrow{k_9} \text{Products} \qquad \text{fast (iii)}$$

Scheme 3 A general reaction scheme for the oxidation of GlcNAc by BAB in alkaline medium



Scheme 4 A descriptive mechanistic interpretation for the oxidation of GlcNAc by BAB in alkaline medium

medium. If the ions have dissimilar charges, then slope of such a plot is negative. Hence, quantity Z_AZ_B is negative and hence the rate would decrease with an increase in ionic strength of the medium. If one of the ions is neutral, the slope of such a plot is zero. Hence the quantity of Z_AZ_B is zero and subsequently the rate of the reaction is independent of ionic strength of the medium. In the present investigations, the quantity Z_AZ_B observed is: (i) positive for the reaction carried out in alkaline medium, signifying the participation of similar charges in rds as can be seen in Scheme 4, and (ii) zero for $IrCl_3$ catalyzed reaction in acid medium indicating that one of the interacting species involved in the rds is non-ionic in nature while the other is ionic as can be seen in rds of Scheme 2. Hence, the observed ionic strength effect on the rates of the reaction in acid and alkaline media is in accordance with Bronsted and Bjerrum concept [32].

Many approaches have been put forward to explain quantitatively the effect of dielectric constant of the medium on the rates of reactions in solutions [33, 34]. For limiting case of zero angle approach between two dipoles or an ion–dipole system, Amis [33] has shown that a plot of log k′ versus 1/D gives a straight line, with a positive slope for a reaction involving a positive ion and a dipole and a negative slope for a negative ion–dipole or dipole–dipole interactions. In the present investigations, plots of log k′ versus 1/D were linear ($R^2 > 0.9951$) with negative slopes for reactions in both the media. The observation in case of $IrCl_3$ catalyzed reaction confirms the participation of a negative-ion and a dipole in the rds of Scheme 2.

The dielectric effects noted for reactions in alkaline medium cannot be explained by Amis theory, due to the presence similar charges in the rds. This observation can be explained by following equation

$$\ln k' = \ln k_0^{/} - \left(\frac{NZ_AZ_Be^2}{DRTr_\#}\right) \tag{36}$$

In this equation k_0 is the rate constant in a medium of infinite dielectric constant, Z_Ae and Z_Be are the total charges on the ions A and B, $r_\#$ is the radius of the activated complex, R, T and N have their usual meanings. This equation predicts a linear plot of log k′ versus 1/D with a negative slope if the charges on the ions are of the same sign and a positive slope if they are of opposite sign. The negative dielectric effect observed in alkaline medium clearly supports the involvement of similar charged ions in the rds of Scheme 4.

The proposed mechanisms are also supported by the moderate values of energy of activation and other thermodynamic parameters (Table 6). The positive values of $\Delta G^{\neq}$ and $\Delta H^{\neq}$ indicate that the transition state is highly solvated, while the large negative entropy of activation may be interpreted that a fraction of collisions are more stringent and form a rigid associative activated complex. Under similar experimental conditions, it is seen from Table 6 that GlcNAc–BAB oxidation reaction rate is tenfold faster in alkaline medium in compare to acid medium (in absence of $IrCl_3$ catalyst). This is confirmed by the magnitude of activation energies (Table 6).

5 Conclusion

The kinetics of the oxidation of GlcNAc by BAB in acid medium catalyzed by $IrCl_3$ and alkaline medium obeys the experimental rate laws: $-d[BAB]/dt = k^{/} [BAB]^1[GlcNAc]^{0.69}[HClO_4]^{-0.76}[IrCl_3]^{0.48} [BSA]^{-0.33}$ and $-d[BAB]/dt = k^{/} [BAB]^1[GlcNAc]^1[NaOH]^{0.79}$, respectively (here BSA is benzenesulfonamide). Aldonic acid is identified as the oxidation product of GlcNAc in both media. Activation parameters have been evaluated. $IrCl_3$ catalyzed reaction is about 13-fold faster than the uncatalyzed reaction in acid medium. Reaction of GlcNAc with BAB is tenfold faster in alkaline medium in comparison with acid medium (without $IrCl_3$ catalyst). Based on the kinetic data, suitable mechanisms and relevant rate laws have been worked out.

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