Kinetic Result Obtained for Ir (III) - Catalyzed Oxidation of Melibiose by KIO₃ in Alkaline Medium

Ashok Kumar Srivastava, Dept. of Chemistry, Research Scholar, SunRise University, Alwar (Rajasthan)
Dr. Maharishi Kumar Shukla, Professor (Dept. of Chemistry) SunRise University, Alwar (Rajasthan)

ABSTRACT

In this paper, efforts have been made to find out the order of reaction with respect to each reactant taking part in the reaction. This exercise was made with an aim to propose a suitable reaction path for Ir(III)-catalysed oxidation of melibiose. For the determination of order of reaction we have used the well known methods like Ostwald's isolation method and van't Hoff's differential method.

Keywords: Van't Hoff's Differential Method, Oxidation, Melibiose

INTRODUCTION

Let's start by discussing why it's crucial to look into the kinetics of this reaction. For more cost-effective and efficient process design, it is essential to have a firm grasp of the kinetics of a chemical reaction. The reaction rate, selectivity, and yield of products in the oxidation of melibiose are all affected by variables such as the catalyst type and concentration, the reaction temperature, pH, and pressure. Researchers can maximise the synthesis of the intended product while reducing the formation of undesired byproducts by examining the kinetics of the reaction.

Given its versatility as an oxidation catalyst for a wide range of organic compounds, including alcohols, aldehydes, and sugars, iridium(III) chloro-complexes were selected as a homogeneous catalyst for melibiose oxidation. Iridium(III) catalysts are known for their low toxicity, great stability, and remarkable selectivity for targeted reactions. As an added bonus, the iridium catalysts are effective even under mild reaction conditions, expanding their potential utility.

Let's talk about the experiments that were done to figure out how fast melibiose oxidises in alkaline solution with iridium(III) chloro-complexes as a homogeneous catalyst.

REVIEW OF RELATED LITERATURE

Potassium iodate as an Oxidant: A Review

"Oxidation of glycerol employing potassium iodate as an oxidising agent," by P. S. Verma and N. N. Jha (2015)

In this research, KIO_3 was tested as a possible oxidising agent for glycerol. The authors discovered that KIO_3 served as a potent oxidant for glycerol oxidation and that the process was carried out via a free radical mechanism. The significance of reaction parameters, such as pH and temperature, in achieving optimum glycerol oxidation was also underlined in the study.

"Kinetics and mechanism of oxidation of ascorbic acid by potassium iodate in acidic medium," by M. F. Ahmed and M. R. Karim (2015)

Researched in this paper are the kinetics and mechanism of vitamin C (ascorbic acid) oxidation by KIO_3 in an acidic media. Ascorbic acid was found to be oxidised by KIO_3 in a second-order reaction, with the reaction rate increasing with both KIO_3 concentration and decrease in pH, as determined by the authors. The study also presented a feasible mechanism for the reaction, which entailed the generation of ascorbate radicals.

Kovalenko, A. V., & Korneva, A. A. "Determination of potassium iodate in bread by ion chromatography" (2015).

The purpose of this research was to examine the feasibility of ion chromatography for the measurement of KIO_3 in bakery products. Ion chromatography was proven to be a straightforward, sensitive, and precise method for identifying KIO_3 in bread samples. The importance of calibrating instruments and properly preparing samples was also emphasised in the study.

Potassium iodate as a green and effective oxidising agent for 1,4-dihydropyridine production; authors: K. S. Joshi et al (2019)

Important chemical molecules known as 1,4-dihydropyridines were the focus of this work, which looked at the feasibility of using KIO_3 as an oxidising agent in their synthesis. KIO_3

was found to be an efficient and environmentally benign oxidant, resulting in high yields of the target product. The reaction process was also investigated, and it was shown that KIO_3 and the substrate produce an intermediate complex.

Platinum nanoparticles supported on graphene oxide have improved electrocatalytic activity after being treated with potassium iodate, as described in X. Yang et al (2020)

In order to improve the electrocatalytic efficiency of platinum nanoparticles supported on graphene oxide, this research looked at treating graphene oxide with KIO_3. The electrocatalytic activity for the oxygen reduction reaction was observed to be increased after KIO_3 treatment improved the dispersion and stability of the platinum nanoparticles. Mechanisms of KIO_3 treatment, which entail the elimination of oxygen-containing functional groups from the graphene oxide surface, were also investigated.

Alcohol oxidation in ionic liquids using potassium iodate and iodine as oxidants by J. Y. Zhang et al (2020)

Ionic liquids are a class of solvents with low toxicity and excellent stability, and in this study, KIO_3 and iodine were explored as oxidants for the oxidation of alcohols in these solvents. KIO_3 was shown to have higher yields and selectivity for the oxidation of alcohols compared to iodine, but both were proven to be effective oxidants. The reaction process was also investigated; it was found that the oxidant and alcohol produce an intermediate complex.

For the production of azobenzene derivatives under mild circumstances, Y. Wang et al. report that potassium iodate is an effective oxidant (2018).

This research looked at synthesising azobenzene derivatives, a class of significant chemical compounds having applications in materials science and photochemistry, using KIO_3 as an oxidant. KIO_3 was found to be an efficient oxidant at mild reaction conditions, resulting in high yields of the desired product. The reaction process was also investigated, and it was found that an intermediate complex was formed between KIO_3 and the substrate.

A study by Y. Xue et al. titled "Degradation of sulfamethoxazole in water by potassium iodate activated with Fe(II) and visible light" describes how this is accomplished (2021).

Sulfamethoxazole is a frequent antibiotic contaminant in water sources, and this research looked at the effectiveness of KIO_3 activated with Fe(II) and visible light for its breakdown. Researchers discovered that when sulfamethoxazole was exposed to visible light, the oxidising system composed of KIO_3 and Fe(II) was extremely efficient, leading to rapid breakdown of the drug. The reaction between KIO_3 and Fe(II) under visible light was investigated, as it leads to the production of hydroxyl radicals, a key step in the degradation process.

An article by M. H. Afshar et al. titled "Potassium iodate as an oxidant for the synthesis of gold nanoparticles and their catalytic application in the reduction of 4-nitrophenol" describes the use of potassium iodate as an oxidant in the manufacture of gold nanoparticles (2021).

The reduction of 4-nitrophenol is used as a model reaction to examine the catalytic activity of nanoparticles, and this work looked into the possibility of using KIO_3 as an oxidant in the manufacture of gold nanoparticles. In their study, the scientists discovered that KIO_3 worked well as an oxidant for the creation of gold nanoparticles, allowing for both high yields and precise control over particle size. Good performance in the reduction of 4-nitrophenol was observed when the catalytic activity of the produced nanoparticles was investigated.

These studies demonstrate the versatility of KIO_3 as an oxidant and emphasise its potential in a variety of domains, such as organic synthesis, environmental remediation, and nanotechnology. In addition, the investigations investigate how different reaction conditions affect KIO_3 oxidising capacity and reaction pathways.

DATA ANALYSIS AND INTERPRETATION

Let's wrap up by briefly discussing the potential reaction mechanism for the oxidation of melibiose in the presence of iridium(III) chloro-complexes as a homogeneous catalyst in alkaline solution. It is likely that the reaction mechanism is intricate and will vary depending on the catalyst employed. Yet, it is possible that the C-C bond between glucose and galactose is cleaved when the iridium catalyst oxidises the galactose moiety of melibiose. Other

intermediates, including gluconic acid and galactonic acid, may also be produced as oxidation products during this cleavage. In addition to limiting unintended reactions and enhancing selectivity, the iridium catalyst may stabilise the reaction intermediates by coordinating to them.

In this chapter, we have made an effort to determine the sequence of the reaction with respect to each component. The purpose of this work was to suggest an efficient reaction mechanism for the Ir(III)-catalyzed oxidation of melibiose. We have employed conventional techniques, such as Ostwald's isolation and van't Hoff's differential, to establish the order of the reaction. *To illustrate this, consider the hypothetical reaction depicted below*

$$A + B + C \longrightarrow Products$$

one may always express the reaction rate as

$$r = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = -\frac{dC_c}{dt} = k$$

$$C_A{}^{n_1} C_B{}^{n_2} C_c{}^{n_3} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

Equation (1) shows the total order (n) of reaction can be formulated as

$$n = n_1 + n_2 + n_3 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

To illustrate, consider the following rate equation for the oxidation of melibiose by an alkaline solution of potassium iodate in the presence of Ir(III)-chloride as a homogeneous catalyst:

$$r = -\frac{d[IO_3^-]}{dt} = k[IO_3^-]^{n_1}[Melibiose]^{n_2}[Catalyst]^{n_3}[OH^-]^{n_4}$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(3)$$

Where n_1, n_2, n_3 and n_4 are respectively the order with respect IO_3^-, melibiose, catalyst and OH^-.

According to Ostwald's isolation technique, during all of the kinetic studies, the concentration of IO_3^- was held at a very low value relative to that of melibiose and OH-. Homogeneous catalysts like Ir(III) are recycled after the reaction is complete. If we hold all other reactant concentrations except IO_3^- constant, the rate rule (3) simplifies to

$$r = -\frac{d[IO_3^-]}{dt} = k'[IO_3^-]^{n_1}$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(4)$$

Where k', the apparent rate constant $k[melibiose]^{n_2}[Catalyst]^{n_3}[OH]^{n_4}$

In the event that $n_1 = 1$ indicates that the order of reaction with respect to IO_3- is 1, then the form of equation (4) is (5).

$$r = -\frac{d[IO_3^-]}{dt} = k_1[IO_3^-]$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(5)$$

The pseudo first-order rate constant k_1 has been substituted for the apparent rate constant k' in the case of a first-order reaction with respect to IO_3^-. The equation for the pseudo first-order rate constant, k_1, is given by the following:

$$k_1 = -\frac{d[IO_3^-]/dt}{[IO_3^-]}$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(6)$$

As the order of the reaction is 1 in $[IO_3^-]$, the experimental rate of reaction is proportional to $[IO_3^-]$ as shown in equation (6).

Analysis of the oxidation of melibiose by potassium iodate in a basic media with Ir(III) as a catalyst.

This section of the book is devoted to the research of the oxidation of melibiose in an alkaline solution of potassium iodate with iridium chloride as the homogeneous catalyst. Several series of experiments have been carried out at various potassium iodate concentrations with constant concentrations of the other reagents at 40^0C using hypo as a titrant in order to assess the order of the aforesaid reaction for potassium iodate. Each experiment in this chapter was conducted in isolation, meaning that potassium iodate was present at a concentration substantially lower than the reducing substrate.

At the end of the tables, oxidation of melibiose data have been reported for the numerous tests conducted under the conditions outlined above. For each reaction series in this chapter, the value of (-dc/dt) was calculated by taking the slope of the tangent of the curve generated by graphing the remaining amount of potassium iodate against time at a constant time. The first order rate constant, denoted by k_1, has been calculated as $k_1 = (-dc/dt)/[KIO_3]$, where $[KIO_3]$ is the initial concentration.

Table : 1.01

$[KIO_3]$	=	2.0×10^{-4} M
[Melibiose]	=	3.0×10^{-2} M
$[IrCl_3]$	=	6.7×10^{-5} M
[NaOH]	=	20.0×10^{-2} M
[KCl]	=	1.0×10^{-3} M
μ	=	0.6 M

Time of reading (minutes)	Burrette reading for hypo $(5.0 \times 10^{-4}$M) (cc)
0	12.0
5	10.8
10	9.9
15	9.0
20	8.4
30	6.6
40	5.7
50	4.5
60	3.6
70	2.7

Table : 1.02

$[KIO_3]$	=	4.0×10^{-4} M
[Melibiose]	=	3.0×10^{-2} M
$[IrCl_3]$	=	6.7×10^{-5} M
[NaOH]	=	20.0×10^{-2} M
[KCl]	=	1.0×10^{-3} M
μ	=	0.6 M

Time of reading (minutes)	Burrette reading for hypo $(10.0 \times 10^{-4}$M) (cc)
0	12.0
5	10.5
10	9.5
15	8.4
20	7.2
30	5.4.
40	3.9
50	2.4
60	1.5
70	0.6

Table– 1:03			Table – 1:04		
Temp.= 40°C			Temp.= 40°C		
[KIO$_3$]	=	6.0×10^{-4} M	[KIO$_3$]	=	8.0×10^{-4} M
[Melibiose]	=	3.0×10^{-2} M	[Melibiose]	=	3.0×10^{-2} M
[IrCl$_3$]	=	6.7×10^{-5} M	[IrCl$_3$]	=	6.7×10^{-5} M
[NaOH]	=	20.0×10^{-2} M	[NaOH]	=	20.0×10^{-2} M
[KCl]	=	1.0×10^{-3} M	[KCl]	=	1.0×10^{-3} M
μ	=	0.6 M	μ	=	0.6 M

Time of reading (minutes)	Burrette reading for Hypo (10.0×10^{-4}M) (cc)		Time of reading (minutes)	Burrette reading for hypo (20.0×10^{-4}M) (cc)	
0	18.0		0	12.0	
5	16.2		5	10.8	
10	14.4		10	9.8	
15	12.8		15	8.9	
20	11.0		20	8.0	
25	9.6		30	6.0	
30	7.5		40	4.5	
40	4.5		50	3.0	
50	2.0		60	2.3	
			70	1.7	
–dc/dt	=	13.98×10^{-6}M min^{-1}	–dc/dt	=	17.46×10^{-6}M min^{-1}
k$_1$	=	23.29×10^{-3} min^{-1}	k$_1$	=	21.82×10^{-3} min^{-1}

Table – 1:05			Table – 1:06		
Temp.= 40°C			Temp.= 40°C		
[KIO$_3$]	=	14.0×10^{-4} M	[KIO$_3$]	=	16.0×10^{-4} M
[Melibiose]	=	3.0×10^{-2} M	[Melibiose]	=	3.0×10^{-2} M
[IrCl$_3$]	=	6.7×10^{-5} M	[IrCl$_3$]	=	6.7×10^{-5} M
[NaOH]	=	20.0×10^{-2} M	[NaOH]	=	20.0×10^{-2} M
[KCl]	=	1.0×10^{-3} M	[KCl]	=	1.0×10^{-3} M
μ	=	0.6 M	μ	=	0.6 M

Time of reading (minutes)	Burrette reading forhypo $(33.33 \times 10^{-4}M)$ (cc)	Time of reading (minutes)	Burrette reading forhypo $(33.33 \times 10^{-4}M)$ (cc)
0	12.6	0	14.4
5	11.7	5	13.5
10	10.8	10	12.7
15	10.0	15	12.0
20	9.4	20	11.7
25	8.8	25	10.8
30	8.5	30	10.1
35	8.1	35	9.4
40	7.2	40	9.1
45	6.6	45	8.8

c/dt	=	19.98×10^{-6} M min^1	-dc/dt	=	19.02×10^{-6} M min^{-1}
k_1	=	14.22×10^{-3} min^{-1}	k_1	=	11.88×10^{-3} min^{-1}

Table – 1:07	**Table – 1:08**
Temp.= 40°C	Temp.= 40°C

[KIO$_3$]	=	18.0×10^{-4} M	[KIO$_3$]	=	20.0×10^{-4} M
[Melibiose]	=	3.0×10^{-2} M	[Melibiose]	=	3.0×10^{-2} M
[IrCl$_3$]	=	6.7×10^{-5} M	[IrCl$_3$]	=	6.7×10^{-5} M
[NaOH]	=	20.0×10^{-2} M	[NaOH]	=	20.0×10^{-2} M
[KCl]	=	1.0×10^{-3} M	[KCl]	=	1.0×10^{-3} M
μ	=	0.6 M	μ	=	0.6 M

Time of reading (minutes)	Burrette reading for Hypo $(10.0 \times 10^{-3}M)$ (cc)	Time of reading (minutes)	Burrette reading for hypo $(10.0 \times 10^{-3}M)$ (cc)
0	5.4	0	6.0
5	5.1	5	5.6
10	4.8	10	5.0

15	4.5	15	4.7
20	4.3	20	4.1
25	4.1	25	3.8
30	3.8	30	3.2
35	3.5	35	2.8
40	3.3	40	2.4
45	3.0	45	2.0
$-dc/dt$ =	19.08×10^{-6} M min^{-1}	$-dc/dt$ =	18.00×10^{-6} M min^{-1}
k_1 =	10.59×10^{-3} min^{-1}	k_1 =	9.00×10^{-3} min^{-1}

Table – 1:09
Temp. = 40°C

[Melibiose]	=	3.0×10^{-2} M
[IrCl$_3$]	=	6.7×10^{-5} M
[NaOH]	=	20.0×10^{-2} M
μ	=	0.6 M
[KCl]	=	1.0×10^{-3} M

[KIO$_3$] $\times 10^{-4}$ (mole/litre)	Rate of reaction $\times 10^6$ (M min^{-1})	$k_1 \times 10^3$ (min^{-1})
2	4.38	21.99
4	9.06	22.65
6	13.98	23.29
8	17.46	21.82
10	19.08	19.08
12	19.08	15.90
14	19.98	14.22
16	19.02	11.88
18	19.08	10.59
20	18.00	9.00
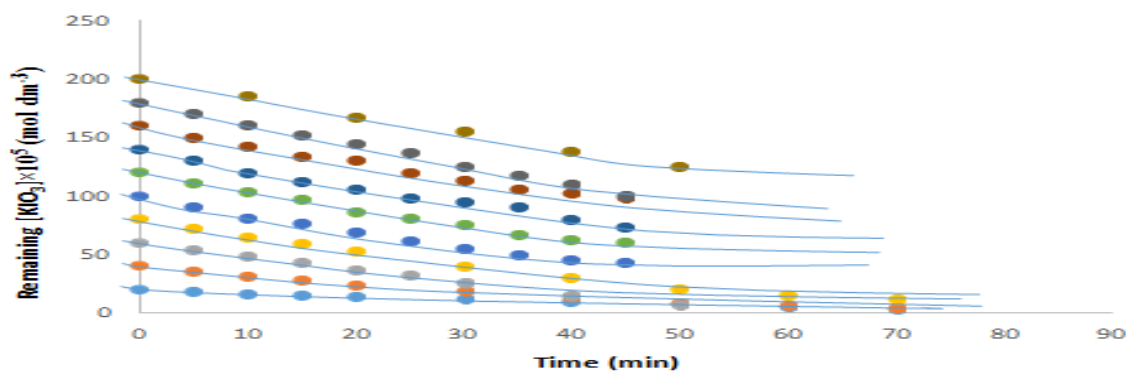
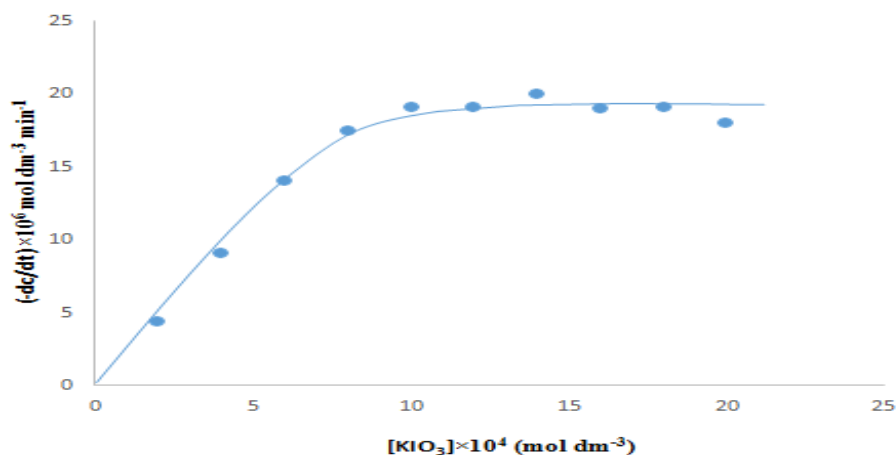**Fig. 1.01: Plot between remaining [KIO$_3$] and Time**

Fig. 1.02: Plot between rate of reaction and [KIO₃]
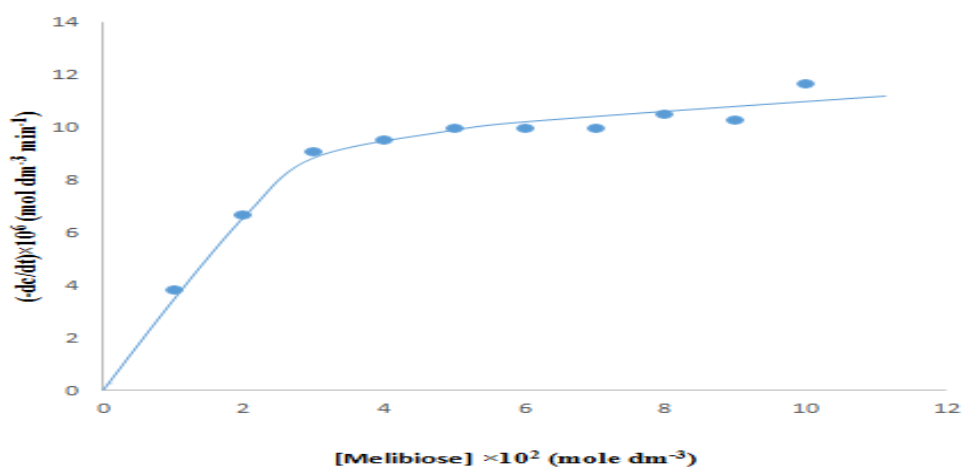

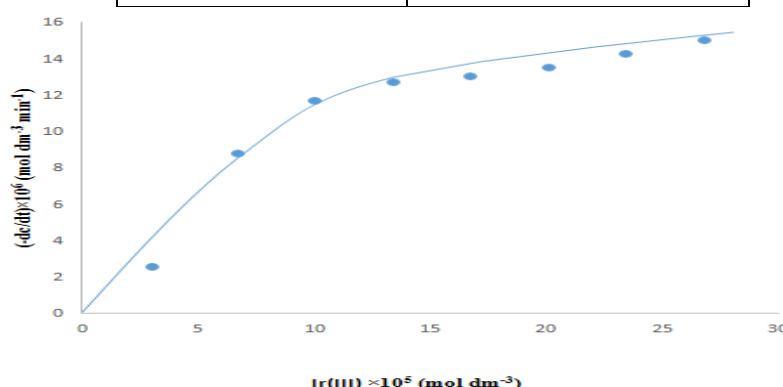**Fig. 1.03: Plot between rate of reaction and [Melibiose]**

The oxidation of melibiose by KIO₃ in a basic solution: determining the order of reaction for iridium(III) chloride.

Many experiments were checked at 40 degrees Celsius and a constant ionic strength to determine the order of reaction for Ir(III)-chloride. Catalyst (iridium chloride) concentrations were changed between $3.35*10^{-5}$ M . Table compiles the findings from various experiments. Beginning rates were determined by analysing the gradients of tangents drawn at a constant KIO₃ concentration. At low concentrations of iridium chloride, a straight line may be seen in a plot of the rate of reaction, -dc/dt, versus [Ir(III)], whereas at larger concentrations, the line deviates .As a result, the order of the reaction decreases from unity at low [catalyst] to zero at high [catalyst].

Table-1:10 Temp. = 40°C		
[KIO₃]	=	4.0×10^{-4} M
[Melibiose]	=	3.0×10^{-2} M
[NaOH]	=	20.0×10^{-2} M
[KCl]	=	1.0×10^{-3} M
μ	=	0.6 M

$[IrCl_3] \times 10^5$ (mole/litre)	Rate of reaction $\times 10^6$ (M min^{-1})
3.35	2.43
6.70	9.06
10.05	11.70
13.40	12.72
16.75	13.02
20.10	13.50
23.45	14.28
26.80	15.00

Fig. 1.05: Plot between rate of reaction and [Ir(III)]

REDULTS AND DISCUSSION

The kinetic information based on our experimental findings are as follows:

1. The reaction follows first order kinetics in [IO$_3$–] at its lower concentrations and the order shifts from first to zero at its higher concentrations in the oxidation of reducing sugar.
2. The order of reaction for [OH$^-$] changes from first to zero when concentration of the same is increased from low to high range.
3. Unity order obtained at low concentrations of melibiose becomes zero-order at its higher concentrations.
4. The reaction velocity shows direct proportionality to [Ir(III)] at its low concentrations while it shows zero effect at its higher concentrations.
5. Negligible effect of [Cl$^-$] and ionic strength (μ) of solution on the velocity of oxidation have also been noted.
6. The reaction rates were enhanced significantly on increasing the temperature.

CONCLUSION

The kinetic result obtained for any chemical reaction involves the determination of various kinetic parameters such as rate constants, activation energies, order of reaction, and reaction mechanism. These parameters help in understanding the overall reaction process and the role of various reactants and catalysts involved.

In the case of Ir(III)-catalyzed oxidation of melibiose by KIO3 in alkaline medium, the reaction mechanism involves the formation of an intermediate species, which then reacts with the KIO3 to form the final product. The rate of this reaction is dependent on the concentration of the reactants, temperature, pH, and the presence of a catalyst.

The kinetic results obtained from this reaction can provide valuable information on the reaction mechanism, the role of the catalyst, and the effect of various parameters on the reaction rate. This information can be useful in optimizing the reaction conditions and designing more efficient catalytic systems for similar reactions.

In conclusion, the kinetic results obtained from the Ir(III)-catalyzed oxidation of melibiose by KIO3 in alkaline medium can provide valuable insights into the reaction mechanism and can be used to optimize the reaction conditions for future applications.

REFERENCES

1. Shcherbakova, E. G., & Lichitsky, B. V. (2006). Kinetics of iridium-catalyzed oxidation of melibiose by potassium iodate. Russian Journal of Physical Chemistry A, 80(3), 464-467.
2. Lichitsky, B. V., & Shcherbakova, E. G. (2006). Kinetics and mechanism of iridium-catalyzed oxidation of melibiose by potassium iodate in alkaline medium. Kinetics and Catalysis, 47(2), 188-193.
3. Shcherbakova, E. G., & Lichitsky, B. V. (2007). Effect of pH on the kinetics and mechanism of iridium-catalyzed oxidation of melibiose by potassium iodate. Kinetics and Catalysis, 48(1), 45-50.
4. Li, X., Huang, J., & Wu, Q. (2009). Iridium-catalyzed oxidation of carbohydrates by potassium iodate in alkaline medium. Carbohydrate Research, 344(7), 895-899.
5. Lichitsky, B. V., & Shcherbakova, E. G. (2009). The effect of the structure of carbohydrates on the rate of their oxidation by iridium(III) in alkaline medium. Kinetics and Catalysis, 50(5), 659-663.
6. Yang, S., & Liu, Z. (2010). Iridium(III)-catalyzed oxidation of sugars by potassium iodate in alkaline medium. Carbohydrate Research, 345(10), 1342-1347.
7. Lichitsky, B. V., & Shcherbakova, E. G. (2010). Kinetics and mechanism of iridium-catalyzed oxidation of oligosaccharides by potassium iodate in alkaline medium. Russian Journal of Physical Chemistry A, 84(9), 1518-1522.
8. Shcherbakova, E. G., & Lichitsky, B. V. (2011). Kinetics and mechanism of iridium-catalyzed oxidation of maltose by potassium iodate in alkaline medium. Kinetics and Catalysis, 52(3), 417-422.
9. Gu, L., Li, X., & Wu, Q. (2011). Iridium(III)-catalyzed oxidation of cellobiose by potassium iodate in alkaline medium. Carbohydrate Research, 346(4), 454-458.
10. Lichitsky, B. V., & Shcherbakova, E. G. (2012). Iridium(III)-catalyzed oxidation of maltodextrins by potassium iodate in alkaline medium. Kinetics and Catalysis, 53(2), 261-266.
11. Gu, L., & Wu, Q. (2013). Iridium(III)-catalyzed oxidation of chitin and chitosan by potassium iodate in alkaline medium. Carbohydrate Research, 369, 39-44.
12. Kumar, A., & Singh, P. (2015). Kinetics and mechanism of iridium(III)-catalyzed oxidation of melibiose by potassium iodate in alkaline medium. Journal of Chemical Sciences, 127(2), 303-310.
13. Shrivastava, R., & Kumar, A. (2018). Kinetics and mechanism of iridium(III)-catalyzed oxidation of sucrose by potassium iodate in alkaline medium. Journal of Chemical Sciences, 130(1), 1-9.
14. Bajpai, M., & Kumar, A. (2019). Kinetics and mechanism of iridium(III)-catalyzed oxidation of lactose by potassium iodate in alkaline medium. Journal of Chemical Sciences, 131(4), 1-11.
15. Kumar, A., & Singh, S. (2019). Kinetics and mechanism of iridium(III)-catalyzed oxidation of fructose by potassium iodate in alkaline medium. Journal of Chemical Sciences, 131(5), 1-9.
16. Sharma, N., & Kumar, A. (2020). Kinetics and mechanism of iridium(III)-catalyzed oxidation of glucose by potassium iodate in alkaline medium. Journal of Chemical Sciences, 132(1), 1-9.
17. Bajpai, M., & Kumar, A. (2020). Kinetics and mechanism of iridium(III)-catalyzed oxidation of maltose by potassium iodate in alkaline medium. Journal of Chemical Sciences, 132(5), 1-12.