Short Communication

Rapid iodination kinetics of alkyl derivatives of aniline by iodine monochloride using competition technique: a quantitative assessment of substrate nucleophilicity

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Abstract

Rapid iodination kinetics of aniline and its alkyl derivatives in aqueous medium by iodine monochloride have been studied by the competition technique. The specific reaction rates of iodination of these substrates are evaluated as 300, 920, 1777 and 2200 $M^{-1}s^{-1}$, at 26.0°C, for aniline, N-ethyl aniline, N-methyl aniline and N,N-dimethyl aniline, respectively. These values quantitatively assess the relative nucleophilicity of these alkyl derivatives in aqueous medium. The competition technique has been used to evaluate the specific rates of the fast reactions studied herein.

Keywords: Iodination, Substitution, Aniline derivatives, Competition technique.

Introduction

Among halogenations of aromatic substrates using aqueous molecular halogens, bromination is the fastest followed by chlorination, iodination being the slowest[1]. Iodine monochloride is a polar molecule unlike molecular iodine hence iodination rates by ICl are markedly greater than those by I_2. Rapid iodination kinetics of aniline and its alkyl derivatives using aqueous iodine monochloride are presently investigated to provide a quantitative scaffold to assess the relative nucleophilicity and thereby the reactivity of these aromatic substrates. The four electrophilic substitution reactions investigated are rapid and necessitate a special technique for their study[2]. The method adopted is based on a competition between the aromatic substrate and KI to react with ICl. The displacement of iodine from aqueous iodide by iodine monochloride has been reported to be 7900 M^{-1} s^{-1} at 26.0°C[3]. When a very small concentration of iodine monochloride is added to an aqueous mixture of large concentrations of potassium iodide and an aromatic substrate, typically aniline, there is a competition between KI and aniline to react with ICl. The two competing reactions that occur simultaneously in the competition are,

(1) Substitution of H in aniline by iodine from ICl
Aniline + ICl → 4-iodoaniline + I_2 ....Reaction 1 (Under study) and

(2) Displacement of iodine from KI by ICl ……….. Reaction 2 (Reference reaction)
KI + ICl → KCl + I_2

The known specific reaction rate of Reaction 2 is used to evaluate that of Reaction 1. The products of Reaction 1 are ascertained by stoichiometry and from NMR studies. Aniline or its derivatives do not react with either KI or iodine at any significant rate under the competition conditions. Hence KI and aniline are the sole reagents that compete with each other to react with ICl. The amount of iodine liberated in the competition is equivalent to v cm^3 of sodium thiosulphate in the iodometric titration carried out after the competition. The amount of I_2 liberated in the absence of competition in Reaction 2 alone, is equivalent to V cm^3 .The competition ratio [V-v] **/** v, is a measure of the relative rates of the two competing Reactions 1 and 2.Upon establishing the order of Reaction 1, its specific reaction rate was evaluated, having known that for Reaction 2. In order to ascertain the order of the reaction under study, the competition was carried out with different concentrations of KI and aniline. Order determines the dependence of the reaction rate on reactant concentrations hence variation in the competitor concentrations elucidates the reaction order[3].

Materials and methods

Chemicals: AR grade samples of aniline derivatives, potassium iodide and iodine monochloride were used to prepare the stock solutions in conductivity water. ICl solution was standardized by iodometric titration with sodium thiosulphate.

Determination of the specific reaction rate: The titre value v cm^3 of sodium thiosulphate in the iodometric titration at the end of the competition, corresponds to the amount of ICl reacted in Reaction 2 while (V-v) cm^3 corresponds to that consumed in Reaction 1 in the competition. The ratio v/(V-v) is the

competition ratio. When the competition ratio [V-v] **/** v is unity, the error in it is minimum[4]. This critical value was arrived at, by repeated trials with different values of competitor concentrations. The relative rapidity of the two competing reactions depends on the relative reactivity of KI and aniline towards ICl. The concentrations of both the competitors are large and almost constant compared to that of iodine monochloride in the competition. Under these conditions,

$$\frac{k_1[\text{aniline}] x \times [\text{ICl}] y}{k_2 [\text{KI}] x [\text{ICl}]} = \frac{[V-v]}{v}$$

When x and y are both taken as 1, over a variation of the concentration range of aniline, the specific reaction rates values k_1 obtained for the iodination of aniline were found to be constant suggesting an overall order of 2 for the reaction. This was found to be the case in all the four reactions studied herein.The reactions of aniline and N-alkyl derivatives of aniline using ICl as iodinating reagent are as follows,
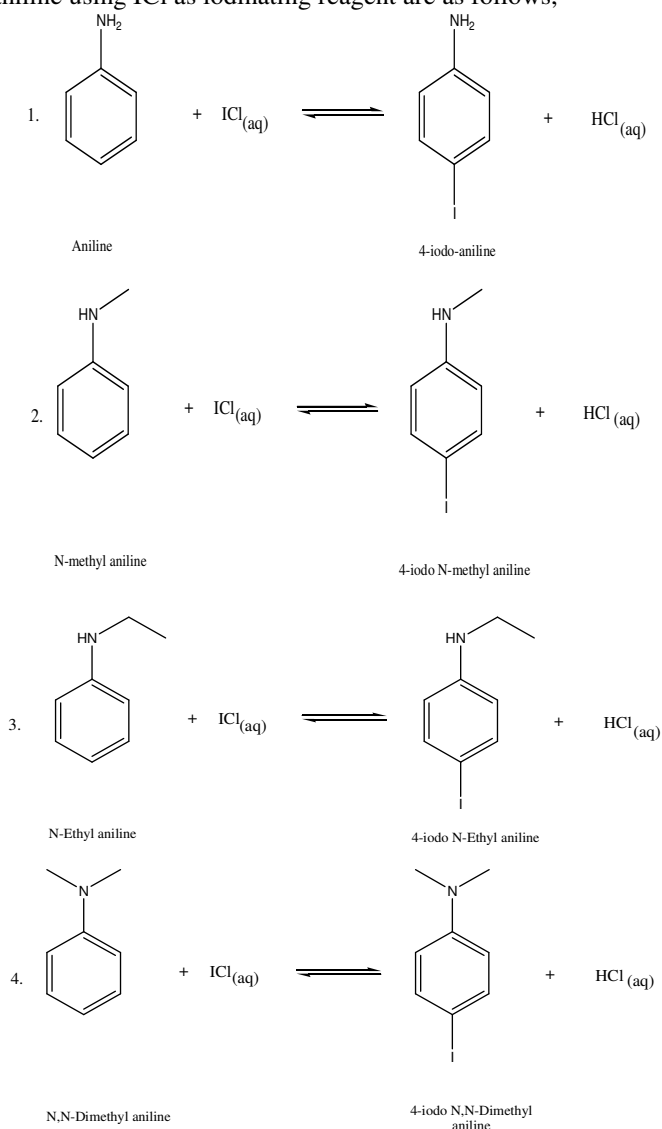

1. Aniline + $ICl_{(aq)}$ ⇌ 4-iodo-aniline + $HCl_{(aq)}$

2. N-methyl aniline + $ICl_{(aq)}$ ⇌ 4-iodo N-methyl aniline + $HCl_{(aq)}$

3. N-Ethyl aniline + $ICl_{(aq)}$ ⇌ 4-iodo N-Ethyl aniline + $HCl_{(aq)}$

4. N,N-Dimethyl aniline + $ICl_{(aq)}$ ⇌ 4-iodo N,N-Dimethyl aniline + $HCl_{(aq)}$

Table-1: Iodination of aniline: concentrations of reactants in 100 cm^3 reaction mixture.

Sr. No.	Reagent	Millimolar Strength
1	Iodine monochloride	0.1
2	Aniline	27
3	KI	1

Titre value of 1 m M $Na_2S_2O_3$ in the Competition…v = 5.05 cm^3

Titre value of 1m M $Na_2S_2O_3$ in the absence of Competition…………V = 10.0 cm^3

Competition Ratio --------- 5.05/4.95 = 1.02
Specific reaction rate k_1………300 $M^{-1} s^{-1}$

Table-2: Iodination of N-ethyl aniline: concentrations of reactants in 100 cm^3 reaction mixture

Sr. No.	Reagent	Millimolar Strength
1	Iodine monochloride	0.1
2	N-Ethyl aniline	9
3	Potassium iodide	1

Titration I - 1 m M $Na_2S_2O_3$Vs I_2 liberated in the reaction mixture in the Competition --------------- v = 5.1 cm^3

Titration II - 1 m M $Na_2S_2O_3$ Vs I_2 displaced by 0.1 mM ICl from 100 cm^3 1 m M KI - V = 10.0 cm^3

Competition Ratio ……… 5.10 **/** 4.90 = 1.04
k_1………920 $M^{-1} s^{-1}$

Table-3: Iodination of N-methyl aniline: concentrations of reactants in 100 cm^3 reaction mixture

Sr. No.	Reagent	Millimolar Strength
1	Iodine monochloride	0.1
2	N-methyl aniline	5
3	Potassium iodide	1

Titration I - 1 m M $Na_2S_2O_3$Vs I_2 liberated in the reaction mixture in the Competition -- v = 5.3 cm^3

Titration II- 1 m M $Na_2S_2O_3$ Vs I_2 displaced by 0.1 mM ICl from 100 cm^3 1 m M KI - V = 10.0 cm^3

Competition Ratio ………5.30/4.70 = 1.13
k_1…… 1775 $M^{-1}s^{-1}$

Table-4: Iodination of N-N dimethyl aniline: concentrations of reactants in 100 cm^3 reaction mixture

Sr. No.	Reagent	Millimolar Strength
1	Iodine monochloride	1
2	N,N-dimethyl aniline	3.75
3	Potassium iodide	1

Titration I - 1 m M $Na_2S_2O_3$ Vs I_2 liberated in the reaction mixture in the Competition --- v = 5.1 cm^3

Titration II- 1 m M $Na_2S_2O_3$ Vs I_2 displaced by 0.1 mM ICl from 100 cm^3 1mM KI----- V = 10.0 cm^3

Competition Ratio ……… 5.10 **/** 4.90 = 1.04
k_1………2220 $M^{-1}Ss^{-1}$

Results and discussion

The rates R_1 and R_2 of the reactions (1) and (2) are respectively,
-d [A] / dt = R_1 = k_1 $[ICl]^x$ $[A]^y$
-d [I⁻] / dt = R_2 = k_2 [ICl] [I⁻]

Where: k_1 and k_2 are the specific rates of the two competing reactions and [A] is the molar concentration of aniline. In the reaction mixture, the concentrations of the competitors are much larger than that of ICl reacting with them. Hence their concentrations are virtually unchanged during the competition. The values of x and y are both experimentally found to be one. Hence Reaction 1 may be concluded to be of the overall second order.

Table-5: Rate constants for the iodination of aniline and its alkyl derivatives by ICl.

Substrate	k_1 /M^{-1} s^{-1}
Aniline	300
N-ethyl aniline	920
N-methyl aniline	1775
N,N-dimethyl aniline	2200

Conclusion

The rate constant values arrived at in this study for the iodination of the alkyl derivatives of aniline endorse the relative reactivity of these substrates and are in accord with the steric compulsions that prevail in these reactions. The rate constants of iodination of the substrates studied are seen to follow the following order.

N-N, dimethyl aniline > N-methyl aniline >N-ethyl aniline > Aniline

Aniline has relatively the slowest rate of iodination among these substrates. The hydrogens in the amino group of aniline when replaced by electron donating alkyl groups enhances the nucleophilicity of the alkyl substituted substrates markedly. Ethyl group being bulkier than methyl, poses steric hindrance to the incoming electrophile while in N-N, dimethyl aniline the electron donating effect of the two methyl groups operate in unison to enhance the nucleophilicity of the substrate[5]. These facts are quantitatively endorsed in this study.

References

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