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Kinetics and Mechanism of Oxidation of Iodide by Quinolinium Dichromate and its Application for in situ Iodination of Aromatic Compounds

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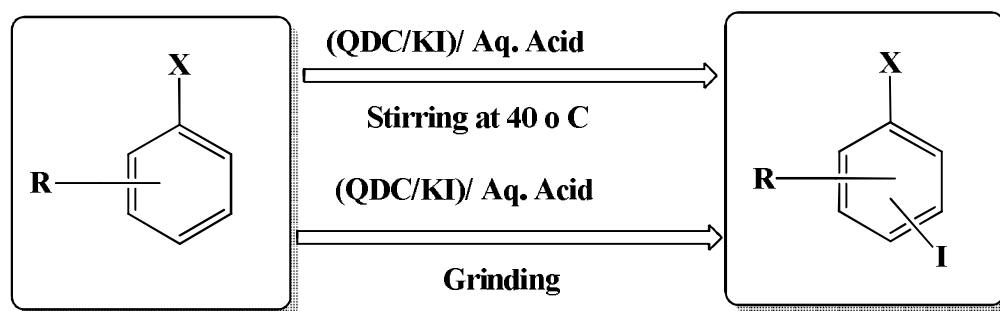
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Abstract: A kinetic study of oxidation of iodide (I^-) by quinolinium dichromate (QDC) revealed first order dependence on $[QDC]$ as well as on $[I^-]$. On the basis of salt and acid effect studies, a most plausible mechanism, comprising the participation of cationic QDC species and I^- in rate limiting step to liberate (I_2) has been proposed. When aromatic compounds are added to the reaction mixture containing $[QDC]$ and $[I^-]$ aryl iodides were formed as characterized by spectroscopic methods. Reactions in mortar-pestle grinding conditions under solvent-free conditions accelerated quite significantly compared to solution phase reactions.

Keywords: Kinetics and Mechanism; Oxidation of Iodide; quinolinium dichromate; aryl iodides; mortar-pestle reaction; rate enhancement; iodination of aromatic compounds

I. INTRODUCTION

Hexavalent chromium Cr(VI), is an easily available reagent as chromium trioxide (CrO_3), and sodium or potassium dichromate ($Na_2Cr_2O_7$ or $K_2Cr_2O_7$) salt, which are highly soluble in water, while its reduced form is an insoluble hydroxide ($Cr(OH)_3$) in water. However, Cr(VI) is reported to be highly toxic, while Cr(III) is an essential nutrient and is used as a dietary supplement [1-3]. In the presence of suitable biomolecules reduction of Cr(VI) occurs, leading to the formation of Cr(III), through intermediate species like Cr(V) and Cr(IV). Besides, a perusal of literature reveals that selectivity of classical Cr(VI) reagent could be increased by complexing it with heterocyclic bases like pyridine (py), 2,2'-bipyridyl (Bipy), quinoline (Q). The work of Collins et al[4], and Corey's research group [5,6] made a land mark in this direction. Review article published by Sabitha Patel and Mishra provided excellent bibliography on these reagents [7]. In continuation of our ongoing work on quinolinium bound reagents [8], we have taken up kinetics of oxidation of simple inorganic compound such as I^- by quinolinium dichromate (QDC) with a view to explore its redox behavior in various acid media. Further, we also want to explore the synthesis of aryl derivatives, through iodination of aromatic compounds using *insitu* generated (I_2) species. It is believed that aryl iodides find their use as precursors for the preparation several industrially and pharmaceutically important compounds.



Scheme-1: QDC-KI iodination of Phenols and Aromatic amines

II. EXPERIMENTAL DETAILS

QDC [$(C_6H_7NH^+)_2Cr_2O_7^{2-}$] has been prepared according to literature methods [8,9]. Infrared Spectrum (KBr) of the recrystallized sample exhibited the characteristic bands of dichromate ion [9] viz., 930, 875, 765 and 730 cm^{-1} . The other chemicals used were of either Annular BDH or Merck samples. Laboratory distilled water was further distilled over alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$ in a sequence. In order to check the content of QDC a spectrophotometric method was developed. A centimolar stock solution of QDC was prepared by dissolving required amount of the compound in triply distilled water, which was further diluted to millimolar and less than millimolar depending on the necessity.

A. Kinetic Method for QDC-I Reaction

Progress of the reaction was followed by estimating the $[I_2]$ liberated at regular time intervals iodometrically. Aliquots of the reaction mixture were quenched in ice cold water and titrated against standard thiosulphate at starch and point. A centimolar acidified QDC (with dilute HCl) was added to 10% KI solution and liberated I_2 was titrated against standard thiosulphate according literature procedures. On the basis of this observation synthetic protocols were developed for the preparation aryl iodides in solution phase as well as under solvent-free grinding method.

B. General Procedure for the QDC/KI Triggered Iodination of Aromatic Compounds in Acid Media

QDC (2 mmol) was added to a well stirred solution of KI (4.0 mmol) and substrate (2.0 mmol) in small amount of $KHSO_4$ (1.0 mmol) and the reaction mixture was stirred at (30 to 40°C) temperature range. Progress of the reaction was monitored by thin layer chromatography (TLC). After completion of reaction, as indicated by TLC, the reaction mixture is quenched with 2% sodium thiosulphate solution, and the organic layer was separated by the addition of ethyl acetate, dried over Na_2SO_4 and evaporated under vacuum. Product thus obtained is, further, purified with column chromatography using Ethyl acetate: hexane (2:8) as eluent to get pure product. The products were purified by column chromatography over silica gel, and characterized by IR, 1H NMR and Mass spectroscopic methods and the in accordance with with standard literature reports [10], and also in good agreement as well as the data reported from our laboratory[11].

C. General Procedure for QDC/KI Triggered Iodination of Aromatic Compounds under Solvent free Conditions

QDC (2 mmol), KI (4 mol), substrate (2 mmol p-Nitro amine), and small amount of $KHSO_4$ (1 mmol), were taken in a mortar and ground with a pestle. After completion of reaction as indicated by TLC, a similar work-up procedure is adopted for the separation of product as detailed in the preceding section. Reaction times and yields of the products in solution phase and solvent-free conditions have been compiled in table-1.

Table- 1: Iodination of Aromatic Amines and Phenols using QDC-KI

Entry	Substrate	Product	Solution Phase		Solvent-free Grinding	
			R.T (h)	Yield (%)	R.T (min)	Yield (%)
1.	Aniline	4-iodoaniline	1.0	65	20	62
2.	p-toluidine	2-iodo-4-methylaniline	1.5	76	20	60
3.	p-chloro Aniline	2-iodo-4-chloroaniline	2.5	68	20	65
4.	p-nitroaniline	2-iodo-4-nitro aniline	2.0	75	40	68
5.	Phenol	4-iodophenol	1.5	70	30	62
6.	p-cresol	2-iodo-4-methylphenol	1.0	67	30	50
7.	o-cresol	4-iodo-2-methylphenol	1.5	62	25	60
8.	p-Chloro phenol	2,6-diiodo-4-Chlorophenol	3.0	77	20	66
9.	p-nitro phenol	2,6-diiodo-4-nitrophenol	2.5	70	25	60
10.	p-methyl phenol	2,6-diiodo-4-methylphenol	3.0	69	25	58
11.	β -naphthol	1-iodo-2-naphthol	2.0	82	25	54
12.	p-methyl phenol	2,6di-iodo-4-methyl phenol	1.0	67	25	65
13.	p-nitro phenol	2,6di-iodo 4-nitro phenol	1.5	65	20	55

III. RESULTS AND DISCUSSIONS

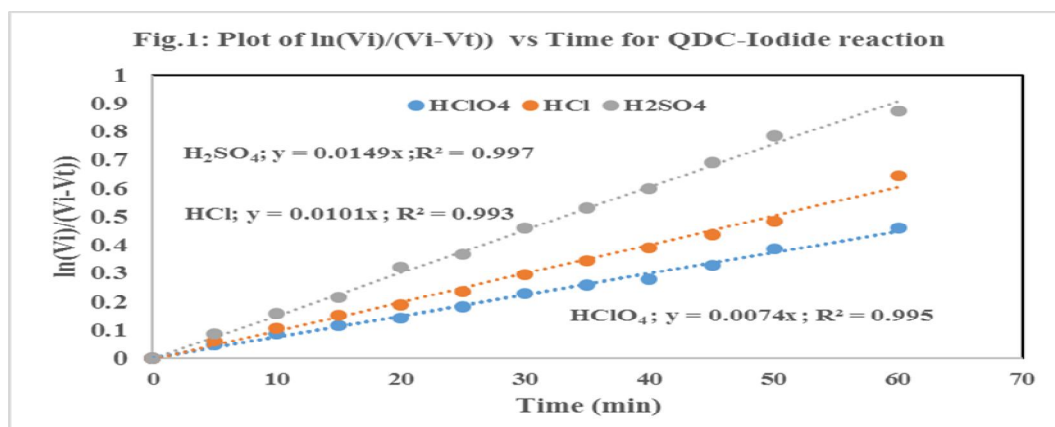
A wide range of phenols and aromatic amines were used as substrates for QDC/KI triggered iodination of aromatic compounds. Phenols afforded iodophenols while aromatic amines corresponding iodo anilines (Scheme -1), in good yields (Table- 1). Thus, the direct iodination of a wide range of aromatic compounds, which are substituted with electron-donating groups such as Me, MeO, OH, or NO₂ groups was achieved efficiently with high regioselectivity under mild conditions. Enthused by the green chemistry principles of Paul Anastas and others [12,13], we have tried to further improve the synthesis of aryl iodides. Solvent-free organic synthesis using grind-stone (mortar-pestle) method is one of the safest methods[14,15] owing to its simplicity in the experimental technique. It doesn't require sophisticated equipment. Mortar and pestle are available in any under graduate or pre-university institutions, Therefore, we have developed solvent-free synthetic protocol using mortar-pestle grinding technique for the introduction of an iodo group to various activated and deactivated aromatic compounds such as phenols. In this method aromatic compound is mixed with QDC and KI with small amount of KHSO₄ in a mortar and ground with a pestle for few minutes, which afforded corresponding mono iodo derivatives in good yields. Similarly, when aromatic amines were used as substrates the reactions afforded corresponding iodo anilines and iodo phenols respectively.

A. Kinetics and Mechanism of Oxidation of I⁻

- 1) The kinetic study was taken up under the conditions [QDC] << [I⁻], plots of $\ln(V_{\infty}/(V_{\infty}-V_t))$ vs time were linear passing through origin indicating first order kinetics in [QDC] in aqueous acid media containing either HClO₄, HCl or H₂SO₄, as shown in fig.1. According to the basic principles of kinetics slope of such plots are equal to pseudo first order rate constant (k').

Fig-1: Order with respect to [QDC] in various acid media

10^3 [QDC] = 1.0 mol/ dm³; [Acid] = 0.04 mol/ dm³; [I⁻] = 0.1 mol dm⁻³, Temp. = 300 K



- 2) Under the conditions [QDC] << [I⁻], increase in [I⁻] increased (k') values proportionately showing with first power raised to [I⁻] which suggested that order in [I⁻] is also one at constant acidity in all the acid media (Tables 2).

Table -2 : Order with respect to [I⁻] in various acid media

10^3 [QDC] = 1.0 mol dm⁻³, [Acid] = 0.04 mol dm⁻³, Temp. 305 K

[H ⁺] mol dm ⁻³	10 ² k' (min ⁻¹)		
	H ₂ SO ₄	HCl	HClO ₄
0.02	0.786	0.500	0.365
0.04	1.570	0.010	0.745
0.08	3.160	2.100	1.520
0.16	6.280	4.300	2.400
0.20	7.860	5.050	3.720

- 3) The added (salt) (viz., LiClO_4 , NaClO_4 , KNO_3 , $[(\text{NH}_2)_2\text{SO}_4]$ and NaOAc) did not affect the rate to any considerable extent. Although the rate of oxidation was not altered by any of the added salt, the reactions were found to increase with an increase in [Acid]. It is also noticed that rate of oxidation also depended on the nature of mineral acid and depicted an increasing order $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HClO}_4$ (Table-3).

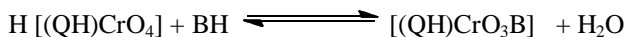
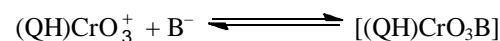
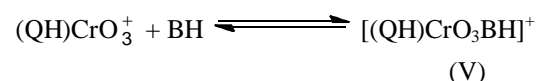
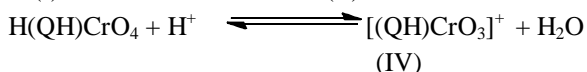
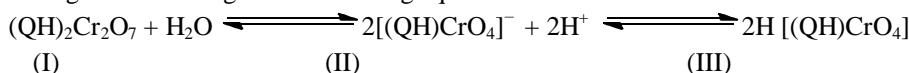
Table.3 : Variation of acid of QDC- I^- reaction
 $10^3[\text{QDC}] = 1.0 \text{ mol dm}^{-3}$, $[\text{I}^-] = 0.1 \text{ mol dm}^{-3}$, Temp. 305 K

[I] (mol/dm ³)	10 ³ k' (min ⁻¹)		
	(C) H ₂ SO ₄	(B) HCl	(A) HClO ₄
0.02	0.310	0.204	0.151
0.05	0.790	0.510	0.376
0.10	1.570	1.010	0.748
0.15	2.380	1.520	1.130
0.20	3.20	2.03	1.52

This observation revealed that primary effect caused in rate determining step might be negated by the secondary salt effect arising from the protolitic equilibrium due to the dissociation of Brosted acids HClO_4 , HCl or H_2SO_4 . Further, this observation may indicate the slow step could be either ion-dipole or dipole-dipole type reaction [14].

B. Reactive Species

Quinolinium dichromate (QDC) resembles the structure of $\text{K}_2\text{Cr}_2\text{O}_7$, it exists as several unprotonated and protonated forms analogous to those of $\text{K}_2\text{Cr}_2\text{O}_7$ [1, 2]. In aqueous acid solutions, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is known to exist as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , H_2CrO_4 , $[\text{HCrO}_3]^+$ and $[\text{HCrO}_3\text{B}]$ (where $\text{B} = \text{HSO}_4^-$, ClO_4^- and Cl^- , etc.). Analogous species with quinoline moiety have been given according to the following equilibria:

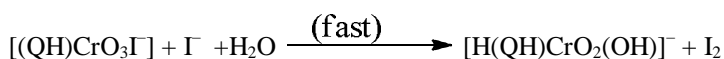
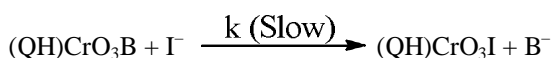
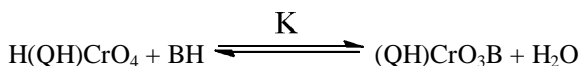


(where Q = Quinoline, $(\text{QH})^+$ = Quinolinium cation; $\text{B} = \text{HSO}_4^-$, Cl^- , ClO_4^- ;

$\text{BH} = \text{H}_2\text{SO}_4$, HCl , HOAc , HClO_4 , etc)

On the basis of observed kinetic features viz., first order in [QDC], $[\text{I}^-]$ and [acidity] (i.e., H_2SO_4 , HCl , HClO_4) protonation of oxidizing species prior to biomolecular rate determining step could be proposed. Since the magnitudes of k'-values are found to differ in different acid media (with an increasing order: $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HClO}_4$; Table 2.4) it is reasonable to assume formation of $[(\text{QH})\text{CrO}_3\text{B}]$ which in turn reacts with I^- in the slow step to give first stage oxidation product as shown in Scheme-2.

Scheme-2



For the above mechanism, the rate law comes out as,

$$\frac{-d[\text{QDC}]}{dt} = k[\text{I}^-][(\text{QH})\text{CrO}_3\text{B}]$$

But $[(\text{QH})\text{CrO}_3\text{B}] = \text{K}[\text{H}(\text{QH})\text{CrO}_4][\text{BH}]$

Thus, the rate equation could be written as,

$$\frac{-d[\text{QDC}]}{dt} = kK[\text{QDC}][\text{BH}][\text{I}^-]$$

(where $[\text{QDC}] = [\text{H}(\text{GH})\text{CrO}_4]$).

At constant acidity (BH) and ionic strength, the above equation is reduced to

$$-\frac{d[\text{QDC}]/dt}{[\text{QDC}]} = k' = k''[\text{I}^-] \quad (\text{where } k'' = kK).$$

The k'' -values were evaluated at various temperatures and activation parameters were calculated, which increased with an increase in temperature showing the applicability of Arrhenius theory of activation energy (E_a). Enthalpy of activation (ΔH^\ddagger) is computed from the relationship [16],

$$\Delta H^\ddagger = E_a - RT$$

Free energy of activation is computed using Eyring's equation [16,17],

$$\Delta G^\ddagger = RT \ln (RT/Nhk')$$

Enthalpy of activation is obtained from one of the form of Gibbs-Helmholtz equation [16-18],

$$\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger) / T$$

Table-4 : Second order rate constants and activation parameters of QDC- I^- reactions

Parameter	Medium		
	H_2SO_4	HCl	HClO_4
k'' ($\text{dm}^3/\text{mol.s}$)	0.164	0.141	0.126
ΔH^\ddagger (kJ/mol)	74.6	56.9	57.9
ΔG^\ddagger (kJ/mol)	78.0	78.4	77.6
ΔS^\ddagger (J/K mol)	-11.4	-63.2	-57.5

Negative magnitude of activation entropy values show a rigid transition state due to solvation.

IV. CONCLUSIONS

Kinetics of oxidation of iodide (I^-) by quinolinium dichromate (QDC) obeyed first order dependence on [QDC] as well as on $[\text{I}^-]$. On the basis of salt and acid effect studies, a most plausible mechanism, with the participation of $[(\text{QH})\text{CrO}_3\text{B}]$ species and I^- in the slow step has been proposed. When aromatic compounds are added to the reaction mixture containing [QDC] and $[\text{I}^-]$ aryl iodides were formed as characterized by spectroscopic methods. Reactions in mortar-pestle grinding conditions under solvent-free conditions accelerated quite significantly compared to solution phase reactions.

V. ACKNOWLEDGMENTS

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A. Statement for Conflict Interest

Authors declare that they do not have any conflict of interest.

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