Kinetics and Mechanism of Oxidation of Aniline and Substituted Anilines by Isoquinolinium Bromochromate in Aqueous Acetic Acid

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Oxidation of anilines by isoquinolinium bromochromate (IQBC) in aqueous acetic acid leads to the formation of corresponding azobenzenes. The reaction is first order with respect to both aniline and IQBC and is catalyzed by hydrogen ion. The rate of oxidation decreases with increasing dielectric constant of solvent, indicating the presence of an ion-dipole interaction. The rate of oxidation decreases with increase in concentration of KCl, possibly due to the formation of less reactive species by interaction of Cl⁻ and protonated IQBC. The specific rate of oxidizing species anilines reaction correlates with substituents constant affording a negative reaction constant. Hammett plot is found to be valid and the correlation between enthalpies and free energies of activation is reasonably linear with an isokinetic temperature of 401 K.

INTRODUCTION

Halochromates have been used as mild and selective oxidizing reagent in synthetic organic chemistry. A variety of compounds containing chromium(VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group. The kinetics and mechanism of oxidation of Cr(VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with diverse substrates. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be of interest.

A number of new chromium containing compounds like pyridinum bromochromate [1], quinolinium chlorochromate [2], 2,2'-bipyridinium chlorochromate [3], pyridinium fluorochromate [4], quinolinium fluorochromate [5], quinolinium bromochromate [6], quinolinium dichromate [7], pyridinium fluorochromate [8], imadazolium fluorochromate

[9] have been used to study the kinetics and mechanism of oxidation of various organic compounds.

However, most of the reagents developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, hygroscopicity, low selectivity, long reaction time and need for large excess of reagent. To overcome these disadvantages, we have synthesized isoquinolinium bromochromate (IQBC) as a new mild, efficient and stable reagent which is able to work as both an oxidizing agent and a brominating reagent.

Literature survey reveals that no report is available on the kinetics of oxidation of amines by isoquinolinium bromochromate (IQBC); hence, we have considered it worthwhile to study the kinetics and mechanism of oxidation of anilines by IQBC.

EXPERIMENTAL

Reagents

All the chemicals and reagents were of analytical grade.

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The aniline derivatives used were *m*-CH₃, -H, *p*-Br, *m*-NO₂, *p*-NO₂, and *p*-Cl substitued anilines. The solid anilines were used as received, and the liquid ones were used after vacuum distillation. All the solutions used in the study were made by using distilled acetic acid and doubly distilled water.

Isoquinolinium bromochromate was prepared by the following method: Chromium trioxide (10 g, 0.1 mol) was dissolved in water (15 ml) and cooled to 0 ºC. To this solution was added hydrobromic acid (17 ml, 48%) slowly with vigorous stirring; then, isoquinoline (13 ml, 0.1 mol) was added dropwise during 10 min. The reaction mixture was cooled for 2-3 h and filtered. The resulting yellow orange needles were dried and recrystallised. The purity of reagent was checked by iodometric method and structure was confirmed by spectral and elemental analysis. Infrared spectrum (KBr) gave bands at 945, 868, 767 and 621 cm⁻¹ characteristics of dichromate ion. The reagent had a melting point of 105-106 ºC and a molecular formula of $C_9H_7N^+HCrO_3^-Br$ (iso).

Kinetics Measurements

The reactions were carried out under pseudo first order conditions by keeping an excess of substrate over IQBC. The progress of reaction was followed by monitoring the decrease in concentration of IQBC iodometrically for 80% of the reactions. The rate constants were determined by a least square method from the linear plots of log[IQBC] *vs*. time. Replicate runs showed that the rate constants were reproducible to within ±3%.

Stoichometry and Product Analysis

The stoichometry of the reaction was determined by carrying out several sets of experiments with varying amounts of IQBC largely in excess over aniline. The estimation of unreacted IQBC showed that 1 mol of aniline reacts with 1 mol of IQBC. The oxidative products were analyzed using preparative TLC on silica gel, which yields azobenzene (M.P. = 66 ºC, Lit. 68 ºC and UV Abs. (EtOH) at λ ₘₐₓ 320 nm.

RESULTS AND DISCUSSION

Effect of Variation of Substrate Concentration

At constant concentrations of IQBC and H_2SO_4, the increase in amount of substrate enhances the reaction rate (Table 1). The plot of logk_{obs} *vs*. log[substrate] for different initial concentrations of substrate found to be linear with unit slope, indicating the first order dependence of reaction rate on substrate.

Effect of Variation of IQBC Concentration

At constant concentrations of substrate and H_2SO_4, the increase in concentratio of IQBC did not affect the rate of reaction (Table 2). The first order plots of log[IQBC] *vs*. time found to be linear. The pseudo first order rate constants computed from the plots remained unaffected by the change in [IQBC], establishing the first order dependence of the reaction rate on isoquinolinium bromochromate in all cases.

Effect of Variation of H⁺ Concentration

The reaction is catalyzed by hydrogen ion; the acid catalysis may well be attributed to the protonated ion of IQBC to give a stronger oxidant and electrophile. The rate of reaction increases with increase in H_2SO_4 concentration, the plot of logk_{obs} *vs*. log[H⁺] are also straight line with unit slope, indicating a first order dependence on [H⁺] (Table 3).

Table 1. Dependence of Rate Constant on [Substrate] Conditions: [IQBC] = 0.001 M, [H₂SO₄] = 2 N, Temp. = 308 K, Solvent = 50% (v/v) Acetic Acid

[Substarate] (M)	$k \times 10^3$ (s⁻¹)					
	m-CH₃	-H	*p*-Br	*m*-NO₂	*p*-NO₂	*p*-Cl
0.01	12.09 ± 0.10	9.87 ± 0.13	6.72 ± 0.09	4.32 ± 0.00	3.01 ± 0.21	1.12 ± 0.00
0.02	21.19 ± 0.15	19.74 ± 0.21	13.44 ± 0.11	9.01 ± 0.17	5.98 ± 0.00	2.32 ± 0.03
0.03	33.84 ± 0.08	30.61 ± 0.00	19.04 ± 0.17	13.09 ± 0.14	9.17 ± 0.11	3.44 ± 0.27
0.04	47.32 ± 0.07	41.39 ± 0.09	25.98 ± 0.24	17.28 ± 0.30	12.08 ± 0.02	4.58 ± 0.19

Table 2. Dependence of Rate Constant on [IQBC]. Conditions: [Substrate] = 0.03 M, [H_2SO_4] = 2 N, Temp. = 308 K, Solvent = 50% Acetic Acid (V/V)

[IQBC] (M)	$k \times 10^3$ (s^{-1})					
	m-CH$_3$	-H	p-Br	m-NO$_2$	p-NO$_2$	p-Cl
0.001	33.84 ± 0.21	30.61 ± 0.00	19.04 ± 0.12	13.11 ± 0.00	9.17 ± 0.18	3.44 ± 0.00
0.002	32.19 ± 0.18	30.92 ± 0.26	19.10 ± 0.14	13.49 ± 0.21	9.12 ± 0.02	2.94 ± 0.16
0.003	33.48 ± 0.08	30.09 ± 0.00	19.04 ± 0.17	13.01 ± 0.14	9.41 ± 0.11	3.44 ± 0.21
0.004	33.91 ± 0.18	31.14 ± 0.07	19.42 ± 0.13	12.98 ± 0.12	8.92 ± 0.19	3.09 ± 0.03

Table 3. Dependence of Rate Constant on [H_2SO_4]. Conditions: [Substrate] = 0.03 M, [IQBC] = 0.001 M, Temp. = 308 K, Solvent = 50% Acetic Acid (V/V)

[H_2SO_4] (N)	$k \times 10^3$ (s^{-1})					
	m-CH$_3$	-H	p-Br	m-NO$_2$	p-NO$_2$	p-Cl
1.0	16.92 ± 0.19	15.32 ± 0.14	9.94 ± 0.21	6.54 ± 0.00	4.52 ± 0.17	1.72 ± 0.10
1.5	25.38 ± 0.14	22.95 ± 0.13	14.94 ± 0.00	9.82 ± 0.13	6.84 ± 0.13	2.48 ± 0.21
2 .0	33.84 ± 0.03	30.61 ± 0.00	19.04 ± 0.17	13.11 ± 0.14	9.47 ± 0.11	3.43 ± 0.27
2.5	38.04 ± 0.00	38.61 ± 0.11	23.59 ± 0.21	16.29 ± 0.20	11.48 ± 0.14	4.80 ± 0.14

Table 5. Dependence of Rate Constant on Solvent Composition. Conditions: [Substrate] = 0.03 M, [H_2SO_4] = 2 N, [IQBC] = 0.001 M, Temp. = 308 K, Solvent = 50% Acetic Acid (V/V)

%Acetic acid-water (v/v)	1/D	$k \times 10^3$ (s^{-1})			
		m-CH$_3$	-H	p-NO$_2$	p-NO$_2$
30	0.01798	26.69 ± 0.10	22.68 ± 0.21	13.60 ± 0.16	13.26 ± 0.08
40	0.02238	29.90 ± 0.18	24.95 ± 0.20	14.69 ± 0.19	13.75 ± 0.19
50	0.02604	33.49 ± 0.00	27.12 ± 0.18	15.11 ± 0.00	14.48 ± 0.12
60	0.03170	37.50 ± 0.14	32.09 ± 0.19	17.13 ± 0.21	16.05 ± 0.00

Effect of Ionic Strength

The change in concentration of KCl affects the rate of oxidations. The rate of reaction decreases with increase in concentration of KCl, most possibly due to the formation of less reactive species [10] by interation between Cl$^-$ ion and protonated IQBC (Table 4).

Effect of Solvent Composition

At fixed ionic strength and [H$^+$], the rate of oxidation of anilines with isoquinolinium bromochromate increases with decrease in polarity (or dielectric constant) of solvent. This is due to polar character of transition state as compared to the reactant.

The plot of logk$_{obs}$ *vs*. 1/D (dielectric constant) is linear with positive slope indicating ion-dipole type of reaction [11] (Table 5).

Effect of temperature: The study of oxidation of different anilines has been subjected to different temperature range 293

Table 6. Rate Constants of Oxidation of Amines by Isoquinolinium Bromochromate in Aqueous Acetic Acid at Different Temperatures: Conditions: [Amines] = 0.03 M, [H$_2$SO$_4$] = 2 N, [IQBC] = 0.001 M

Sr. No.	Temperature (K) →	293	303	308	313	323
	Substrate			$k \times 10^3$ (s^{-1})		
1	*m*-Toluidine	26.86 $\pm$ 0.01	31.33 $\pm$ 0.14	33.84 $\pm$ 0.08	36.54 $\pm$ 0.00	42.62 $\pm$ 0.00
2	Aniline	24.83 $\pm$ 0.08	27.56 $\pm$ 0.19	30.61 $\pm$ 0.00	33.97 $\pm$ 0.03	41.87 $\pm$ 0.11
3	*p*-Bromoaniline	12.51 $\pm$ 0.00	16.55 $\pm$ 0.14	19.04 $\pm$ 0.17	21.89 $\pm$ 0.10	28.94 $\pm$ 0.10
4	*m*-Nitroaniline	7.84 $\pm$ 0.09	10.84 $\pm$ 0.09	13.01 $\pm$ 0.14	15.61 $\pm$ 0.11	22.47 $\pm$ 0.00
5	*p*-Nitroaniline	4.58 $\pm$ 0.07	7.27 $\pm$ 0.12	9.17 $\pm$ 0.11	11.55 $\pm$ 0.13	18.33 $\pm$ 0.01
6	*p*-Choloroaniline	1.49 $\pm$ 0.00	2.60 $\pm$ 0.14	3.44 $\pm$ 0.27	4.33 $\pm$ 0.08	7.55 $\pm$ 0.00

Table 7. Activation Parameters. Conditions: [Amines] = 0.1 M, [IQBC] = 0.001 M, [H$_2$SO$_4$] = 2 N, Temperature = 308 K

Sr. No.	Name of substrate	$k \times 10^3$ (s^{-1})	E$_a$ (kJ mol^{-1})	ΔH‡ (kJ mol^{-1})	-ΔS‡ (J mol^{-1} K^{-1})	ΔG‡ (kJ mol^{-1})
1	*m*-Toluidine	33.84	13.4	10.8	234.4	83.0
2	Aniline	30.61	17.3	14.8	222.6	83.3
3	*p*-Bromoaniline	19.04	24.9	22.3	197.3	83.1
4	*m*-Nitroaniline	13.01	30.6	28.1	186.4	85.5
5	*p*-Nitroaniline	9.17	38.4	35.8	164.2	86.4
6	*p*-Choloroaniline	3.44	42.1	39.6	160.4	89.0

K to 323 K by keeping the concentration of substrate and reagent constant. The rate constants are given in Table 6. The plots of logk_{obs} *vs*. 1/T found to be linear. Activation parameters are presented in Table 6. The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant ΔG value indicates that similar mechanism is operative for the oxidation of anilines (Table 6). The values of ΔH‡, S‡ and ΔG‡ are calculated by using following equations:

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

$$\Delta S^{\ddagger} = 19.16 (\log k - 10.576 - \log T + E_a/19.16T)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

Energy-entropy Relationship

The entropy of activation and heat of reaction are correlated by:

$$\Delta H^{\ddagger} = \Delta H^o + \beta \Delta S^{\ddagger}$$

where β is the iokinetic temperature. The isokinetic temperature for the reactions between anilines and IQBC in aqueous acetic acid is 401 K, which is greater than the experimental temperature. The values of entropy of activation also suggest that the reaction is both entropy and enthalpy controlled. The values of free energies for activation of the reaction were found to be move or less similar. These trends also support the identical reaction mechanism being followed in these reactions [12]. The linear relationship in Exner plot

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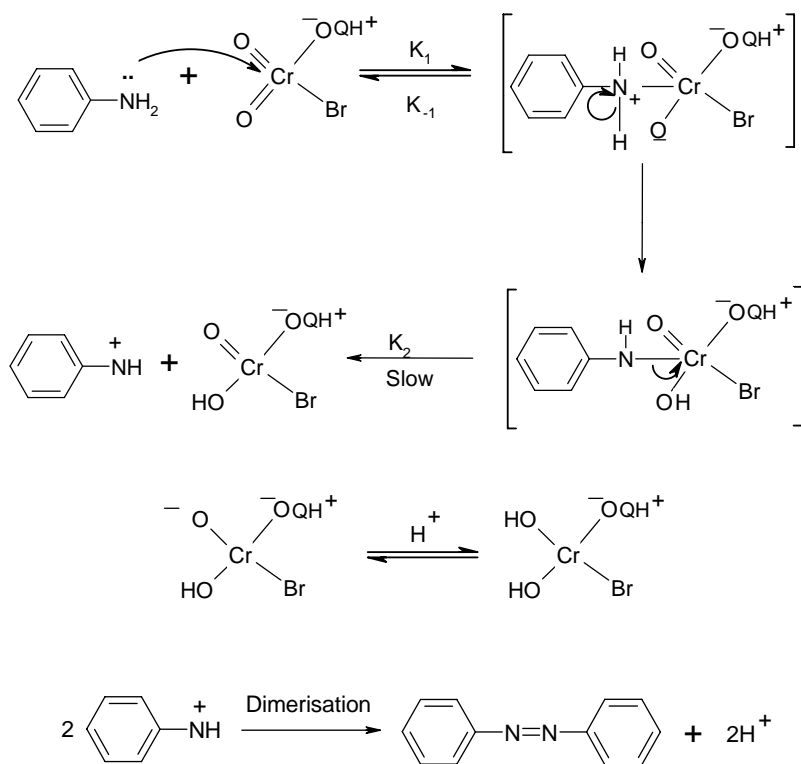
Probable Mechanism of Oxidation of Aniline by Isoquinolinium Bromochromate

[13,14] at $3 + \log k_{303K}$ and $3 + \log k_{308K}$ observed in the present study also supports the conclusion drawn from isokinetic temperature. Based on above experimental observations and probable mechanism is suggested and derived. A linear free energy relationship is attempted by casting the data in Hammett equation. The value of slope of Hammett plot is known as the reaction constant (ρ) and which is found to be -0.55. The magnitude of reaction constant (ρ) and its negative sign suggest the oxidation reaction is accelerated by electron donating groups and rate is retarded by electron withdrawing groups [15]. The order of reactivities with substituents is m-CH$_3$ > -H > p-Br > m-NO$_2$ > p-NO$_2$ > p-Cl based on above experimental observations and a probable mechanism (Scheme 1) is suggested.

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