

Studies on Kinetics of Oxidation of Some Benzaldehydes by Isoquinolinium Bromochromate in Aqueous Acetic Acid

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ABSTRACT: Kinetics of oxidation of benzaldehydes by isoquinolinium bromochromate (IQBC) has been studied in aqueous acetic acid medium. The oxidation of benzaldehydes leads to the formation of corresponding carboxylic acids. The reaction is first order with respect to both benzaldehydes and IQBC and is catalyzed by hydrogen ion. Various thermodynamic parameters were calculated and discussed along with validity of isokinetic relationship. The rate of oxidation increases in a medium of low dielectric constant. The effect of substituent on rate of oxidation of benzaldehyde also studied

Key Words: Kinetics, oxidation, benzaldehydes, isoquinolinium bromochromate, isokinetic relationship

1. Introduction:

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 efficient and stable reagent which is able to work as both an 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, quinolinium chlorochromate¹, quinolinium fluorochromate², quinolinium bromochromate³, quinolinium dichromate⁴ 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. overcome these disadvantages, we have synthesized isoquinolinium bromochromate (IQBC) as a new mild, oxidizing agent and a brominating reagent.

Literature survey reveals that quinolinium dichromate⁵, imidazolium fluorochromate⁶ were used for the study of kinetics of oxidation of benzaldehydes but no report is available on the kinetics of oxidation of benzaldehydes by isoquinolinium. (IQBC); hence, we have considered it worthwhile to study the kinetics and mechanism of oxidation of benzaldehydes by IQBC.

2. Experimental section

2.1 Preparation of reagent IQBC

Chromium trioxide (10 g, 0.1 mol) was dissolved in water (15 ml) and cooled to 0 °C. 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. Melting point of 105 °C, Molecular formula of $C_9H_7N^+HCrO_3^- Br$ (iso).

The effect of various parameter on the rate of chemical reaction studied are as follows

2.2 Kinetics measurement

The reactions were carried out under pseudo first order conditions by keeping an excess of substrate over IQBC. The reactions were followed by monitoring the decrease in concentration of IQBC iodometrically for 80% of reaction. The rate constant were determined by least square method, from linear plots of $\log[IQBC]$ versus time. Replicate runs show that the rate constant were reproducible.

3. RESULT AND DISCUSSION

3.1 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. The plot of $\log k_{obs}$ vs. $\log[\text{substrate}]$ for different initial concentrations of substrate found to be linear with unit slope, indicating the first order dependence of reaction rate on substrate.

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

Substrate (M)	$k \times 10^3 \text{ s}^{-1}$				
	<i>o</i> -Cl	-H	<i>m</i> -OCH ₃	<i>m</i> -NO ₂	<i>p</i> -Cl
0.01	2.68	3.14	5.41	12.52	16.54
0.02	5.40	6.30	10.21	23.98	31.27
0.03	8.15	9.45	16.33	35.97	48.50
0.04	10.20	12.56	19.87	47.98	64.21

3.2 Effect of Variation of IQBC Concentration

At constant concentrations of substrate and H_2SO_4 , the increase in concentration of IQBC did not affect the rate of reaction. 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.

Table 2. Dependence of Rate Constant on [IQBC] Conditions: [substrate] = 0.01 M, [H₂SO₄] = 1 M, Temp. = 308 K, Solvent = 50% (v/v) Acetic Acid

[IQBC] (M)	$k \times 10^3 \text{ s}^{-1}$				
	<i>o</i> -Cl	-H	<i>m</i> -OCH ₃	<i>m</i> -NO ₂	<i>p</i> -Cl

0.001	2.68	3.14	5.41	12.52	16.54
0.002	2.55	3.11	5.63	12.28	16.22
0.003	2.49	2.98	5.34	12.65	16.80
0.004	2.68	3.09	5.28	12.11	16.36

3.3 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 H₂SO₄ concentration, the plot of log*k*_{obs} vs. log[H⁺] are also straight line with unit slope, indicating a first order dependence on [H⁺].

Table 3. Dependence of Rate Constant on [H⁺] Conditions: [substrate] = 0.01 M, [IQBC] = 0.001 M, Temp. = 308 K, Solvent = 50% (v/v) Acetic Acid

[H ₂ SO ₄] (M)	<i>k</i> x 10 ³ s ⁻¹				
	<i>o</i> -Cl	-H	<i>m</i> -OCH ₃	<i>m</i> -NO ₂	<i>p</i> -Cl
0.25	0.67	0.77	1.18	3.10	4.28
0.50	1.34	1.55	2.40	6.21	8.45
0.75	2.11	2.41	3.65	9.32	12.63
1	2.68	3.14	5.41	12.52	16.54

3.4 Effect of Solvent Composition

At fixed ionic strength and [H⁺], the rate of oxidation of benzaldehydes 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 reactant. The plot of log*k*_{obs} vs. 1/D (dielectric constant) is linear with positive slope indicating ion-dipole type of reaction.

Table 4. Dependence of Rate Constant on solvent composition: [substrate] = 0.01 M, [H₂SO₄] = 1 M, [IQBC] = 0.001 M, Temp. = 308 K, Solvent = 50% (v/v) Acetic Acid

% of acetic acid -water(V/V)	1/D	<i>k</i> x 10 ³ s ⁻¹				
		<i>o</i> -Cl	-H	<i>m</i> -OCH ₃	<i>m</i> -NO ₂	<i>p</i> -Cl
30 %	0.01798	1.36	1.72	3.21	8.01	11.48
40%	0.02238	1.92	2.32	4.16	10.02	13.78
50%	0.02604	2.68	3.14	5.41	12.52	16.54
60%	0.03170	3.75	4.21	6.75	15.65	19.84

3.5 Effect of temperature:

The study of oxidation of different benzaldehydes has been subjected to different temperature range 293 K to 323 K by keeping the concentration of substrate and reagent constant. The rate constants are given in Table . The plots of $\log k_{\text{obs}}$ vs. $1/T$ found to be linear. The activation parameters are presented in Table 5. 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 benzaldehydes .

Table 5. Dependence of Rate Constant on solvent composition: [substrate] = 0.01 M, [H₂SO₄] = 1 M, [IQBC] = 0.001 M, Temp. = 308 K, Solvent = 50% (v/v) Acetic Acid

Sr no	Temperature → Substrate↓	$k \times 10^3 \text{ s}^{-1}$				
		293	303	308	313	323
1	<i>o</i> -Cl	1.17	1.78	2.68	4.02	6.12
2	-H	1.61	2.24	3.14	4.36	6.14
3	<i>m</i> -OCH ₃	3.22	4.16	5.41	7.08	11.65
4	<i>m</i> -NO ₂	8.69	10.43	12.52	15.04	18.04
5	<i>p</i> -Cl	13.66	15.03	16.54	18.19	20.01

3.6 Energy-entropy Relationship

The entropy of activation and heat of reaction are correlated by: $\Delta H^\ddagger = \Delta H^\circ + \beta \Delta S^\ddagger$ where β is the isokinetic temperature. The isokinetic temperature for the reactions between anilines and IQBC in aqueous acetic acid is 398 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 more or less similar. These trends also support the identical reaction mechanism being followed in these reactions⁷. The linear relationship in Exner plot^{8,9} at $3 + \log k_{303\text{K}}$ and $3 + \log k_{308\text{K}}$ 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 1.22.

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