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CHEMICAL KINETICS
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Kinetics and Mechanism of Acid Catalyzed Oxidation of Phenol and Substituted Phenols by Isoquinolinium Bromochromate[1]

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Abstract—Oxidation of phenols by isoquinolinium bromochromate (IQBC) in aqueous acetic acid leads to the formation of corresponding quinones. The reaction is first order with respect to both phenol and IQBC and catalysed by hydrogen ion. The rate of oxidation decreases with increase in dielectric constant of solvent indicating ion–dipole interaction. The rate of oxidation decreases with increase in concentration of KCl, this may be due to the formation of less reactive species by interaction of Cl^- and protonated IQBC. The specific rates of oxidizing phenol reaction correlate with substituents constants affording negative reaction constants. 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 320 K.

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INTRODUCTION

Halochromates have been used as mild and selective oxidizing reagent in synthetic organic chemistry. Varieties 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 reaction of Cr (VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with diverse substrates [1]. 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 [2], quinolinium chlorochromate [3], 2,2'-bipyridinium chlorochromate [4], pyridinium fluorochromate [5], quinolinium fluorochromate [6], quinolinium bromochromate [7], quinolinium dichromate [8], pyridinium fluorochromate [9], imadazolium fluorochromate [10] have been used to study the kinetics and mechanism of oxidation of various organic compounds.

However most of these reagents that have been developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, hygroscopic, low selectivity, long reaction time and need for large volume of reagent. To overcome these disadvantages we synthesized new reagent isoquinolinium bromochromate (IQBC) which is mild, efficient, stable and works as both oxidizing as well as brominating reagent.

Literature survey reveals that no report is available on the kinetics of oxidation of phenols by isoquinolinium bromochromate (IQBC), hence, here we have study in detail kinetics and mechanism of oxidation of phenols by isoquinolinium bromochromate.

EXPERIMENTAL

All the chemicals and reagents were of analytical grade. The phenols used have the following substituents m-CH_3, –H, m-Cl, p-Cl, p-OH, p-NO_2. The solid phenols were used as received while the liquids were distilled under vacuum before use. All the solutions used in the study were made by using distilled acetic acid and doubly distilled water. Isoquinolinium bromochromate was prepared as follows. Chromium trioxide (10 g : 0.1 mol) was dissolved in water (15 ml) and cooled to 0°C. To this solution hydrobromic acid (17 ml : 48%) was added slowly with vigorous stirring then isoquinoline (13 ml, 0.1 mol) was added drop wise during 10 min. The reaction mixture was cooled for 2–3 h and filtered. The resulting yellow orange needles were dried and crystallized from aqueous ethyl alcohol. The purity of the reagent was checked by iodometric method and its' structure was confirmed by both infrared spectroscopic and elemental analysis. Infrared spectrum (KBr) gave bands at 945, 868, 767, and 621 cm^{-1} characteristics of dichromate ion [11].

$$\text{M.P.} = 105\text{–}106°\text{C},$$

$$\text{M.F.} = [C_9H_7N^+HCrO_3^-Br(\text{iso})].$$

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[1] The article is published in the original.

Table 1. Dependence of rate constant ($k \times 10^4$ s^{-1}) on [Substrate]: [IQBC] = 0.001 M, [H_2SO_4] = 1 M, T = 308 K, solvent = 50% acetic acid (v/v)

[Substrate], M	m-CH_3	-H	m-Cl	p-Cl	p-OH	p-NO_2
0.01	14.09 ± 0.10	11.87 ± 0.13	8.72 ± 0.09	6.32 ± 0.00	5.01 ± 0.21	3.12 ± 0.00
0.02	23.19 ± 0.15	21.74 ± 0.21	15.44 ± 0.11	11.01 ± 0.17	7.98 ± 0.00	4.32 ± 0.03
0.03	35.84 ± 0.08	32.61 ± 0.00	21.04 ± 0.17	15.09 ± 0.14	11.17 ± 0.11	5.44 ± 0.27
0.04	49.32 ± 0.07	43.39 ± 0.09	27.98 ± 0.24	19.28 ± 0.30	14.08 ± 0.02	7.58 ± 0.19

Table 2. Dependence of rate constant ($k \times 10^4$, s^{-1}) on [IQBC]: [Substrate] = 0.03 M, [H_2SO_4] = 1 M, T = 308 K, solvent = 50% acetic acid (v/v)

[IQBC], M	m-CH_3	-H	m-Cl	p-Cl	p-OH	p-NO_2
0.001	35.84 ± 0.21	32.61 ± 0.00	21.04 ± 0.12	15.11 ± 0.00	11.17 ± 0.18	5.44 ± 0.00
0.002	34.19 ± 0.18	32.92 ± 0.26	21.10 ± 0.14	15.49 ± 0.21	11.12 ± 0.02	4.94 ± 0.16
0.003	35.84 ± 0.08	32.61 ± 0.00	21.04 ± 0.17	15.09 ± 0.14	11.17 ± 0.11	5.44 ± 0.21
0.004	35.91 ± 0.18	33.14 ± 0.07	21.42 ± 0.13	15.98 ± 0.12	11.92 ± 0.19	5.09 ± 0.03

Kinetic 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 the concentration of IQBC iodometrically for 80% of the reactions. The rate constants were determined by least square method, from the linear plots of log [IQBC] versus time. Replicate runs showed that the rate constants were reproducible to within ±3%.

Stoichiometry and Product Analysis

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amount of [IQBC] largely in excess over [phenols]. The estimation of unreacted IQBC showed that 1 mol of phenol reacts with 1 mol of IQBC. The oxidative products were analyzed using preparative TLC on silica gel, which yields the following product: 1,4-benzoquinone M.P. =112–114°C (Lit 114–116°C), UV (Et OH)–λ_{max} = 360 nm. IR–ν_{max}, cm^{-1}: 3010, 1650, 1317, 1070, 1460, 900 (KBr); ^{1}H NMR ($CDCl_3$)–6.7(s, 4H)

RESULTS AND DISCUSSION

The results of oxidation of phenols by IQBC are presented in Tables 1–6.

Effect of Variation of [Substrate]

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

Effect of Variation of [IQBC]

At constant [substrate] and [H_2SO_4], the increase in [IQBC] did not affect the rate of reaction. The first order plots of log [IQBC] versus time were 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 rate on isoquinolinium bromochromate in all cases (Table 2).

Effect of Variation of [H$^+$]

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 plot of logk_{obs} versus log[H^+] are also straight lines with unit slope in each case, indicating a first order dependence on [H^+] (Table 3).

Effect of Ionic Strength

The rate of reaction decreases with increase in concentration of KCl, this is may be due to the formation of less reactive species of oxidant [12] by interaction between Cl^- ion and protonated IQBC (Table 4).

Effect of Solvent Composition

At fixed ionic strength and [H^+], the rate of oxidation of phenols with isoquinolinium bromochromate increases with decrease in polarity of solvent. In other words decrease in rate with increase in dielectric constant is observed, this is due to polar character of transition state as compared to the reactant [13]. The plot of logk_{obs} versus $1/D$ (dielectric constant) is linear with positive slope indicating ion–dipole type of reaction (Table 5).

Table 3. Dependence of rate constant ($k \times 10^4$, s^{-1}) on [H_2SO_4]: [Substrate] = 0.03 M, [IQBC] =0.001 M, $T = 308$ K, solvent = 50% acetic acid (v/v)

[H_2SO_4], M	*m*-CH_3	–H	*m*-Cl	*p*-Cl	*p*-OH	*p*-NO_2
0.5	18.92 ± 0.19	17.32 ± 0.14	11.94 ± 0.21	8.54 ± 0.00	6.52 ± 0.17	2.72 ± 0.10
0.75	27.38 ± 0.14	24.95 ± 0.13	16.94 ± 0.00	11.82 ± 0.13	8.84 ± 0.13	4.48 ± 0.21
1	35.84 ± 0.03	32.61 ± 0.00	21.04 ± 0.17	15.09 ± 0.14	11.17 ± 0.11	5.44 ± 0.27
1.25	40.04 ± 0.00	40.61 ± 0.11	25.59 ± 0.21	18.29 ± 0.20	13.48 ± 0.14	6.80 ± 0.14

Effect of Temperature

The oxidation of the phenols were carried out at different temperature between the range of 293 to 323 K at constant concentrations of substrate and the oxidant. The rate constants are given in Table 6. The plots of $\log k_{obs}$ versus $1/T$ are 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 [14]. The nearly constant ΔG value indicates that similar mechanism is operative for the oxidation of phenols (Table 7). The values of $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ are calculated by using following formulae

$$\text{(a) } \Delta H^{\#} = E_a - RT,$$

$$\text{(b) } \Delta S^{\#} = 19.16(\log k - 10.576 - \log T + E_a/19.16T),$$

$$\text{(c) } \Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}.$$

Energy–Entropy Relationship

The entropy of activation and heat of reaction are correlated by the equation

$$\Delta H^{\#} = \Delta H^0 + \beta\Delta S^{\#}, \qquad (1)$$

where β is the isokinetic temperature, the isokinetic temperature for the reactions between phenols and IQBC in aqueous acetic acid is which is greater than experimental temperature. The values of entropy of activation also suggest that the reaction is entropy as well as enthalpy controlled. The values of free energies of activation ($\Delta G^{\neq}$) of the reaction were found to be nearly the same. These trends also suggest that identical reaction mechanism is being followed in these reactions [15]. The linear relationship in Exner plot [16, 17] at $3 + \log k_{303\,K}$ and $3 + \log k_{308\,K}$ observed in present study also supports the conclusion drawn from isokinetic temperature. The isokinetic temperature is the temperature at which all the compounds of series react equally fast. Also, at the isokinetic temperature the variation of substituent has no influence on the free energy of activation. Based on above experimental observations a probable mechanism of oxidation of phenol by isoquinolinium bromochromate is in the scheme below:

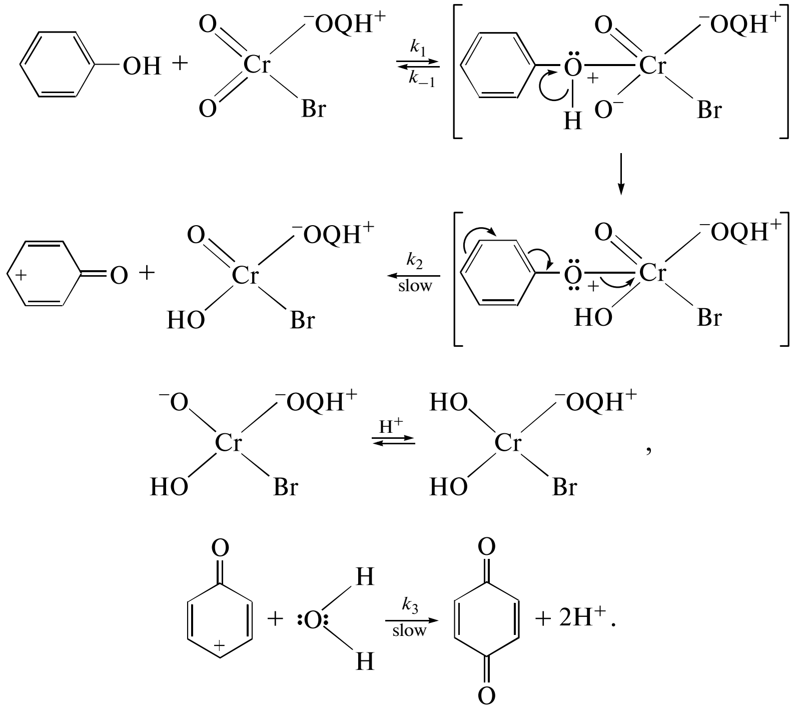

Table 4. Dependence of rate constant ($k \times 10^4$, s^{-1}) on [KCl]: [Substrate] = 0.03 M, [H_2SO_4] = 1 M, [IQBC] = 0.001 M, $T = 308$ K, solvent = 50% acetic acid (v/v)

[KCl], M	*m*-CH_3	–H	*m*-Cl	*p*-Cl
0.02	26.08 ± 0.00	24.99 ± 0.00	17.08 ± 0.07	12.09 ± 0.00
0.01	28.97 ± 0.04	27.28 ± 0.08	18.28 ± 0.21	13.65 ± 0.14
0.005	32.21 ± 0.18	29.81 ± 0.09	19.59 ± 0.00	14.34 ± 0.00
0	35.84 ± 0.08	32.61 ± 0.00	21.04 ± 0.17	15.09 ± 0.14

Table 5. Dependence of rate constant ($k \times 10^4$, s^{-1}) on solvent composition (acetic acid (*c*)-water) [Substrate] = 0.03 M, [H_2SO_4] = 1 M, [IQBC] = 0.001 M, $T = 308$ K, solvent = 50%

c, %	$1/D$	*m*-CH_3	–H	*m*-Cl	*p*-Cl
30	0.01798	28.69 ± 0.10	24.68 ± 0.21	19.60 ± 0.16	13.12 ± 0.08
40	0.02238	31.90 ± 0.18	26.95 ± 0.20	20.69 ± 0.19	14.34 ± 0.19
50	0.02604	35.49 ± 0.00	29.12 ± 0.18	21.04 ± 0.00	15.09 ± 0.12
60	0.03170	39.50 ± 0.14	34.09 ± 0.19	22.14 ± 0.21	16.81 ± 0.00

Table 6. Rate constants ($k \times 10^4$, s^{-1}) of oxidation of phenols by isoquinolinium bromochromate in aqueous acetic acid at different temperatures, [Phenols] = 0.03 M, [H_2SO_4] = 1 M, [IQBC] = 0.001 M

Sr. no.	Substrate	293 K	303 K	308 K	313 K	323 K
1	*m*-Creasol	28.86 ± 0.01	33.33 ± 0.14	35.84 ± 0.08	38.54 ± 0.00	44.62 ± 0.00
2	Phenol	26.83 ± 0.08	29.56 ± 0.19	32.61 ± 0.00	35.97 ± 0.03	42.87 ± 0.11
3	*m*-Chlorophenol	14.51 ± 0.00	18.55 ± 0.14	21.04 ± 0.17	23.89 ± 0.10	30.94 ± 0.10
4	*p*-Chlorophenol	8.84 ± 0.09	12.84 ± 0.09	15.09 ± 0.14	17.61 ± 0.11	24.47 ± 0.00
5	*p*-Hydroxyphenol	6.58 ± 0.07	9.27 ± 0.12	11.17 ± 0.11	13.55 ± 0.13	20.33 ± 0.01
6	*p*-Nitrophenol	2.49 ± 0.00	4.60 ± 0.14	5.44 ± 0.27	6.33 ± 0.08	9.55 ± 0.0

Table 7. Activation parameters at [Phenols] = 0.03 M, [IQBC] = 0.001 M, [H_2SO_4] = 1 M, $T = 308$ K

Name of Substrate	$k \times 10^4$, s^{-1}	E_a, kJ mol^{-1}	$\Delta H^{\#}$, kJ mol^{-1}	$-\Delta S^{\#}$, J mol^{-1} K^{-1}	$\Delta G^{\#}$, kJ mol^{-1}
m-Creasol	35.84	14.40	11.84	250.73	88.84
Phenol	32.61	18.34	15.78	238.10	89.11
m-Chlorophenol	21.04	25.89	23.33	216.85	90.11
p-Chlorophenol	15.01	31.63	29.07	199.63	90.55
p-Hydroxyphenol	11.17	39.40	36.84	178.19	91.72
p-Nitrophenol	5.44	43.42	40.86	170.72	93.44

A linear free energy relationship is attempted by casting the data in Hammett equation. The value of slope of Hammett plot known as the reaction constant (ρ) is found to be 0.61. 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 [18]. The order of reactivities with substituents is *m*-CH_3 > –H > *m*-Cl > *p*-Cl > *p*-OH > *p*-NO_2 based on above experimental observations.

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