

Rapid Kinetics of Chlorination of Regioisomers of Nitrophenol by Molecular Chlorine in Aqueous Medium Using Rotating Platinum Electrode (RPE)

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Abstract: The rapid kinetics of chlorination of isomers of nitrophenol in aqueous solution by molecular chlorine in KNO_3 as supporting electrolyte has been studied using the rotating platinum electrode (RPE). The specific reaction rate (k), energy of activation (E_a), free energy change of activation (ΔG^*), enthalpy change of activation (ΔH^*), entropy change of activation (ΔS^*) were evaluated. The reaction was found to be rapid and of the second order. The rapidity of the reaction necessitated the use of a special technique RPE. The diffusion current of unreacted chlorine in the reaction was measured. Thus, the present work provides the quantitative verification of the reactivity of the electrophile in the reaction.

Keywords: Rapid Chlorination, Rotating Platinum Electrode, Kinetics

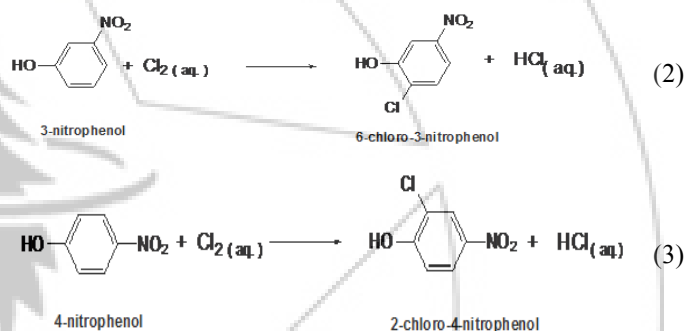
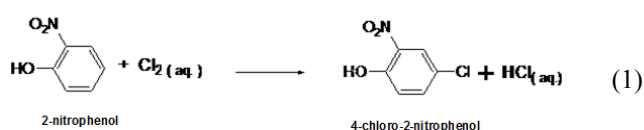
1. Introduction

The dropping mercury electrode (DME)^[1] cannot be used at markedly positive potential (say, above about 0.4 Vs SCE) because of the oxidation of the mercury. By replacing DME by an inert platinum electrode, it was hoped to extend the range of polarographic work. The attainment of the steady diffusion current was slow with a stationary platinum electrode, but the difficulty has been overcome by rotating platinum electrode at constant speed. In order to obtain a linear relation between current and concentration of reagent added, the speed of stirring must be kept constant during the titration.

The RPE^[2-5] although used less commonly than the dropping mercury electrode in voltammetric measurements, has yet proved to be a convenient device for the study of several rapid reactions in aqueous solutions. Some rapid halogenations, for instances, have been studied by Rao, Mali and Dangat^[6,7] using the RPE. Since such halogenation reactions were often of the second order, their half-lives can be extended by diluting the solutions and the reaction can be carried out using the RPE which can estimate very low concentration of halogens.

The reactions presently studied were the kinetics of chlorination of 2-nitrophenol, 3-nitrophenol and 4-nitrophenol using KNO_3 as a supporting electrolyte with different fold of chloride ion in aqueous medium.

The reactions under study can be represented as:



The major product of the reactions (1), (2) and (3) were 4-chloro-2-nitrophenol, 6-chloro-3-nitrophenol and 2-chloro-4-nitrophenol. Other isomers in each reaction formed in traces^[8]. Among the reactants and products in the reaction, only the chlorine was electroreducible at the RPE, hence the kinetics of the reaction has been studied by measuring the diffusion current due to chlorine at various intervals of time from the start of the reaction. In the present study the kinetic measurements of the 3-nitrophenol has been carried out at five different temperatures to find the energy of activation for the reaction and hence the thermodynamic parameters such as free energy change of activation (ΔG^*), enthalpy change of activation (ΔH^*) and entropy change of activation (ΔS^*).

2. Experimental

2.1 Chemicals

AR grade samples of 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, potassium nitrate, potassium chloride, sodium thiosulphate, potassium iodide, starch were used to prepare the stock solutions in conductivity water. Chlorine water was prepared from bleaching powder and concentrated hydrochloric acid. It was bubbled through conductivity water to free it from hydrochloric acid and its exact strength has been determined by iodometric titration.

2.2 Electrodes

The cathode was a platinum electrode fused to a glass tube rotated at 600 rpm with the aid of an ac motor. The anode was a saturated calomel electrode.

2.3 The Rotating Platinum Electrode (RPE)

The rotating platinum electrode constructed from a standard 'mercury seal'. About 5mm of platinum wire protrudes from the wall of length of 6mm inverted t-shaped glass tubing. A pulley and the pair of ball bearing were mounted on the glass tube, having the total length of 32 cm. The ball bearings were fixed rigidly to a stand and the pulley was connected to a synchronous motor. The radius of the pulley was so adjusted that the electrode rotates at the speed of 600 rpm. The electrical connection was made to the electrode by a stout amalgamated copper wire passing through the tubing to the mercury covering the sealed-in platinum wire. The inverted T-shape of the electrode facilitates the stirring action.

2.4 Calibration of diffusion current

The RPE and SCE were dipped in 50 cc of 1×10^{-1} M potassium nitrate which was the supporting electrolyte. A potential of +0.1 V versus the SCE was applied at RPE. The galvanometer light spot was adjusted to zero deflection on the scale. The potassium nitrate solution was then replaced by 1×10^{-3} M chlorine solution. The shunt was adjusted for the deflection of the galvanometer light spot to be around 40 to 50 cm. The shunt was kept constant throughout the experiment. The diffusion current values, in terms of deflection of light spot on the scale, were recorded at various concentrations of chlorine in the range of 0.4×10^{-4} M to 2.0×10^{-4} M.

The plot of deflection observed in cm versus concentration of chlorine was found to be linear as shown in figure. The calibration readings were carried out only after the solutions have attained the thermostat temperature, 28.8°C at which kinetic readings were to be observed subsequently.

Table 1: Calibration of the diffusion current

cm^3 of 1×10^{-3} M Cl_2	$[\text{Cl}_2] / 10^{-4}$ M	Galvanometer deflection / cm
2.0	0.4	13.0
4.0	0.8	21.5
6.0	1.2	30.0
8.0	1.6	38.0
1.0	2.0	46.5

Potential applied to the RPE versus SCE: 0.1V, Temperature: 28.8°C , Total volume: 50.0 cc

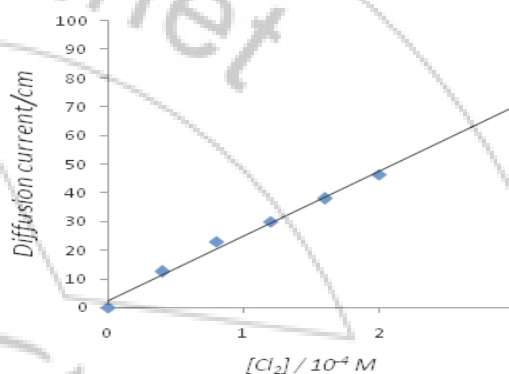


Figure 1: Calibration of diffusion current

2.5 Kinetic Measurements

Equimolar solutions of nitrophenol and chlorine containing supporting electrolyte were kept in the thermostat in separate containers. After the solutions attained the temperature of the thermostat, these were mixed in the reaction vessel in which the SCE and the RPE were dipped and stop clock was started. As the reaction proceeds, the galvanometer deflection decreased steadily. This was recorded at every 10 seconds.

The above procedure of calibration and kinetic measurement was repeated thrice for checking the reproducibility of the galvanometer measurements, and these were found to be within the limits ± 0.3 cm. From the observed deflection during the kinetic study, the concentration of the unreacted chlorine (a-x), at various instants were obtained using the calibration curve. A plot of $[\text{Cl}_2]^{-1}$ versus time t was found to be linear and hence the reaction was of the second order. From the slope of this plot, specific reaction rate k was calculated. The same procedure as given above has been used for the kinetics measurement of 3-nitrophenol and 4-nitrophenol. Also the kinetic measurements of 3-nitrophenol has been done at five different temperatures.

Table 2: Kinetics of chlorination of 2-nitrophenol by chlorine at 28.8°C in aqueous medium

T/K	T ⁻¹ /10 ⁻³ K ⁻¹	Specific reaction rate, k / M ⁻¹ s ⁻¹	log k
291.8	3.42	59.17	1.77
296.8	3.37	75.40	1.87
301.8	3.31	87.39	1.94
306.8	3.25	88.46	1.95
311.8	3.20	91.20	1.96

Initial concentration of chlorine: 2 x 10⁻⁴ M,
Initial concentration of 2-nitrophenol: 2 x 10⁻⁴ M
Temperature: 28.8°C

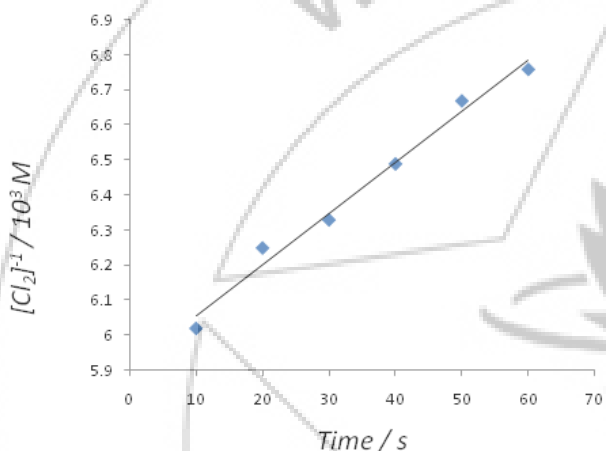


Figure 2: Kinetics of chlorination of 2-nitrophenol in KNO₃

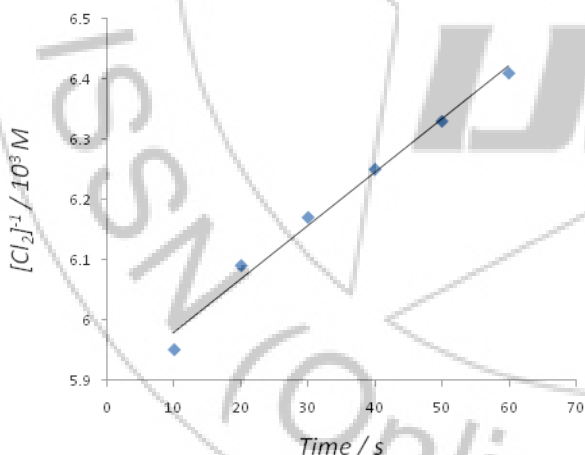


Figure 3: Kinetics of chlorination of 3-nitrophenol in KNO₃

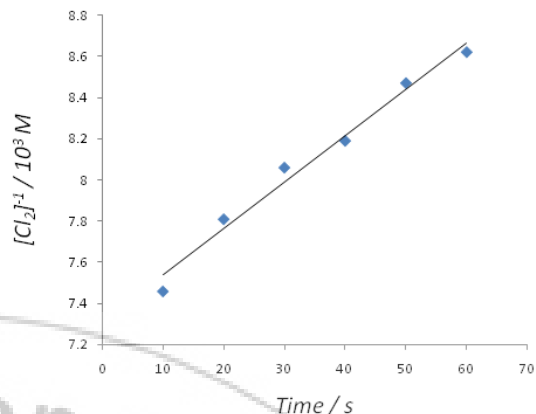


Figure 4: Kinetics of chlorination of 4-nitrophenol in KNO₃

Table 3: The variation of specific reaction rates of chlorination of m-nitrophenol in aqueous medium with temperature

T/K	T ⁻¹ /10 ⁻³ K ⁻¹	Specific reaction rate, k / M ⁻¹ s ⁻¹	log k
291.8	3.42	59.17	1.77
296.8	3.37	75.40	1.87
301.8	3.31	87.39	1.94
306.8	3.25	88.46	1.95
311.8	3.20	91.20	1.96

The specific reaction rate, k, is obtained from the slope of the plot of [Cl₂]⁻¹ Vs time at each temperature.

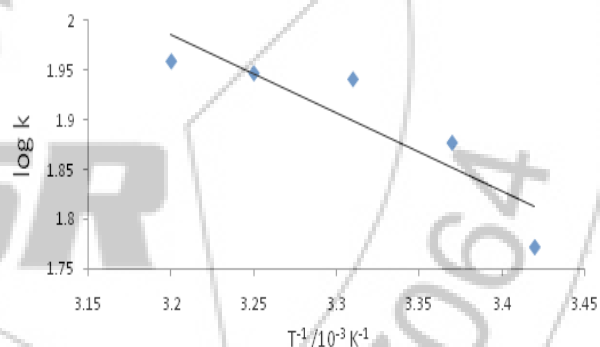


Figure 5: A graph of log k versus reciprocal of absolute temperatures: Arrhenius plot

3. Results and Discussion

The specific reaction rate determination has been carried out at 28.8°C. The kinetic measurements have an error of not more than ± 2% in view of the reproducibility of the diffusion current.

In case of 2-nitrophenol, the specific reaction rate was 16.67 M⁻¹ s⁻¹. In case of 3-nitrophenol, the specific reaction rate was 10.40 M⁻¹ s⁻¹. In case of 4-nitrophenol, the specific reaction rate was 14.17 M⁻¹ s⁻¹. The kinetic measurements of 3-nitrophenol has also been carried out at five different temperatures to determine the energy of activation (E_a) and thermodynamic parameters such as free energy change of activation(ΔG^{*}), enthalpy change of activation(ΔH^{*}) and entropy change of activation(ΔS^{*}) as given below:

Table 4: Thermodynamic parameters for the chlorination of 3-nitrophenol in aqueous medium at 28.8°C

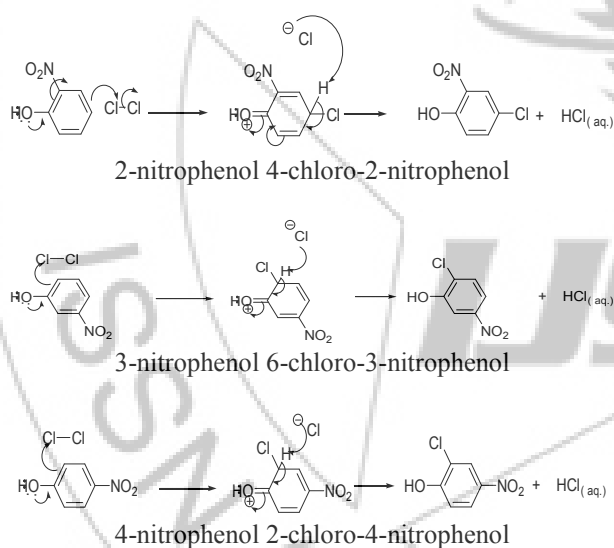
Obs. No.	Thermodynamic parameters	Values
1	Energy of activation (Ea)	13.402 kJ mol ⁻¹
2	Free Energy of activation (ΔG*)	62.96 kJ/mol
3	Enthalpy of activation (ΔH*)	8.384 kJ/mol
4	Entropy of activation (ΔS*)	-0.1807 kJ/K

When the molecular chlorine was used as a chlorinating agent the polarization of the electrophile, viz. the chlorine molecule takes place due to the inductive effect of substrate ring



Chlorine in aqueous solution was extensively hydrolyzed to hypochlorous acid, but HOCl was known to be a much slower chlorinating agent than molecular chlorine. Since the hydrolysis equilibrium was established rapidly, the chlorination may be regarded as effectively by molecular chlorine only.

3.1 The mechanism of the reaction of 2-nitrophenol, 3-nitrophenol and 4-nitrophenol with chlorine:



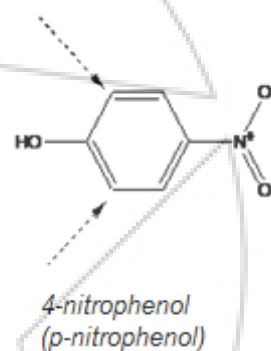
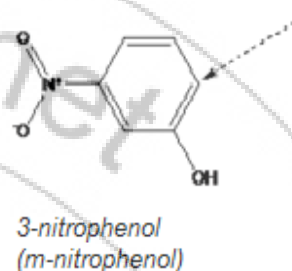
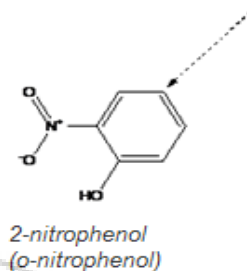
3.2 Comparative kinetic study of isomers of Nitrophenol

It was observed that the reactivity order was decreased from 2-nitrophenol to 4-nitrophenol to 3-nitrophenol. All the isomers contain common -OH group which is ortho-para orienting. In this case the stereo-specificity decides the reactivities of these isomers towards chlorination. The incoming electrophile was having more steric-hindrance in case of 3-nitrophenol than 2-nitrophenol than 4-nitrophenol.

The path of incoming electrophile (Cl⁺) was shown in figure by dotted arrows to its respective positions.

Due to less steric-hindrance the chlorination of ortho isomer was fastest; having specific reaction rate was 16.67 M⁻¹ s⁻¹. The para isomer at same concentration of chloride ion gives

specific reaction rate 14.17 M⁻¹ s⁻¹. The meta isomer at same concentration of chloride ion gives specific reaction rate 10.40 M⁻¹ s⁻¹.



4. Conclusion

The relative reactivities of the isomers of nitrophenol considered in these reactions have been speculated only qualitatively on stereo chemical principles but direct kinetic measurements for a quantitative assessment was lacking presumably due to the rapidity of these reactions. Such verification was provided by the study of the kinetics of the chlorination of the three isomers of nitrophenol by molecular chlorine in aqueous solution. Though these reactions were rapid and could not be studied by conventional methods, the RPE has been used to monitor the progress of these reactions to evaluate the specific reaction rates.

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