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NOTE

Kinetics of Iodination of Di-substituted Phenols by Iodine Monochloride in Aqueous Methanol

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The kinetics of iodination of di-substituted phenols such as 2,4-dinitro, 2,4-dichloro and 2,4-dibromophenols by iodine monochloride in (70:30% v/v) methanol and water mixture medium shows that the first order dependence each in (ICl) and (substrate), and is overall second order. On the basis of kinetic results, a suitable mechanism has been proposed. Activation energy and other thermodynamic parameters were calculated. The relative order of reactivities of the di-substituted phenols studied are 2,4-dibromophenol > 2,4-dichlorophenol > 2,4-dinitrophenol.

The literature on the use of iodine monochloride for the iodination of phenols[1–3] in acetic acid appears to be scanty. In this paper we report the results of kinetics of iodination of di-substituted phenols such as 2,4-dinitro, 2,4-dichloro and 2,4-dibromophenols by iodine monochloride. To our knowledge this is the second systematic kinetic report on the use of ICl in methanol[4] (70:30% v/v) medium.

All the substrates *viz.* 2,4-dinitro, 2,4-dichloro and 2,4-dibromophenols were used of Sigma or Fluka. Iodine monochloride ampoules of Merck, AR were used after suitable dilution. All other chemicals used were of BDH, AR. The kinetics of the reaction was followed by estimating the unreacted iodine monochloride iodometrically to a stretch end point. The rate constants calculated are reproducible within ±3% error.

The kinetic measurements were carried out by determining the concentration of iodine monochloride iodometrically as a function of time. "The batch method" recommended by Gnanapragasam and Yaddanapalli[5] was adopted since the reaction is faster. In this method the ICl and phenol solution in (70:30% v/v) aqueous methanol (5 mL each) was taken in several iodine flasks and test tubes respectively which were placed in a thermostat bath at the required temperature. When the solution attained the bath temperature, the phenol solution was quickly added to the ICl solution and the mixture was allowed to react for a specific time, soon after the reaction was arrested by quick addition of potassium iodide (10%, 5 mL); the reaction mixture was shaken well and then the liberated iodine was titrated against standard sodium thiosulphate.

The iodination of 2,4-dinitro, 2,4-dichloro and 2,4-dibromo phenols is inves-

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tigated in (70:30% v/v) methanol and water mixture medium with a view to determine the order with respect to the different reactants. the overall order is determined by keeping the concentration of phenol (0.02 M) and that of ICl (0.002 M) *i.e.*, the concentration of phenol is kept ten times more than that of ICl. The reaction is carried out by the addition of appropriate amount of perchloric acid (0.001 M), sodium perchlorate (0.002 M) and sodium chloride (0.002 M), which prevent the rapid hydrolysis of ICl and minimise the effect of the small amount of Cl^- formed during substitution. From the observed results the reaction is of second order overall (Table-1) and the first order dependence of ICl and substrate (Table-2).

TABLE-1
DETERMINATION OF OVERALL ORDER IN (70:30% v/v) MeOH : H_2O MEDIUM AT 30°C BY FRACTIONAL LIFE METHOD

$[NaClO_4] = 0.002$ M; $[NaCl] = 0.002$ M; $[HClO_4] = 0.001$ M
Concentration of phenol is kept ten times more than that of ICl.

Concentration of ICl (mol L^{-1})		Time (sec)		Overall order		
C_2	C_1	t_2	t_1	2,4-dinitro phenol	2,4-dichloro phenol	2,4-dibromo phenol
0.002	0.001	12.0	23.0	1.94	—	—
0.002	0.001	20.0	38.0	1.92	—	—
0.001	0.0005	23.0	50.0	2.10	—	—
0.001	0.0005	38.0	70.0	1.90	—	—
0.002	0.001	2.5	6.0	—	2.2	—
0.002	0.001	5.0	10.0	—	2.0	—
0.001	0.0005	6.0	12.0	—	2.0	—
0.001	0.0005	10.0	19.0	—	1.9	—
0.002	0.001	2.5	5.0	—	—	2.0
0.002	0.001	3.5	7.0	—	—	2.0
0.001	0.0005	5.0	10.0	—	—	2.0
0.001	0.0005	7.0	13.5	—	—	1.9

TABEL-2
INDIVIDUAL ORDERS DETERMINED BY THE INITIAL RATE METHOD IN (70:30% v/v) MeOH : H_2O;
$[NaClO_4] = 0.002$ M; $[NaCl] = 0.002$ M; $[HClO_4] = 0.001$ M

Substrate	ICl	Phenol
2,4-dinitrophenol	1.2	1.1
2,4-dichlorophenol	1.2	1.2
2,4-dibromophenol	1.2	1.1

Similar results have been observed in the iodination of *ortho* and *para*-substituted phenols[4] by iodine monochloride in aqueous methanol.

The effect of temperature on rate constant is determined (by the pseudo first order formula) using the mixture of phenol (0.01 M) and iodine monochloride (0.001 M) over the temperature range 20° to 35°C; the rate constants for the reaction at different temperatures are plotted against 1/T and the activation parameters are calculated (Table-3).

TABLE-3
ACTIVATION PARAMETERS

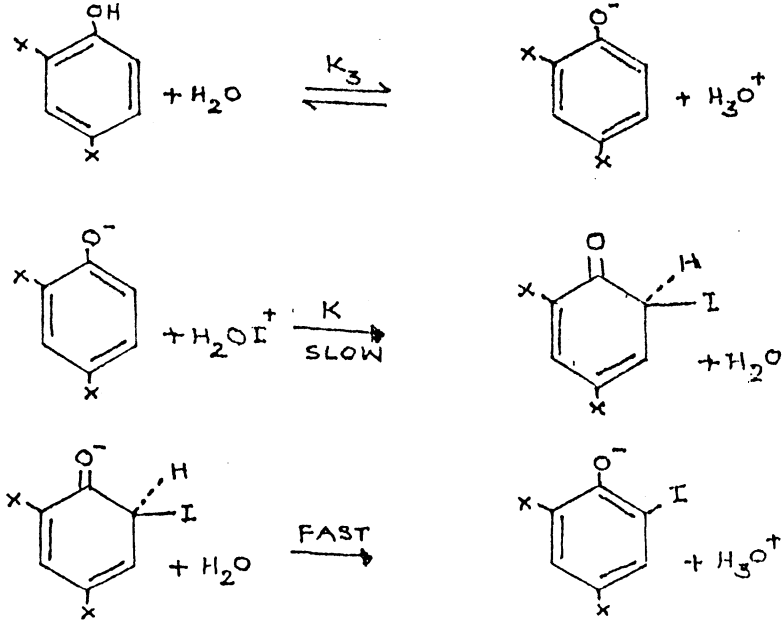
Solvent: MeOH : H_2O (70:30% v/v)
[Substrate] = 0.01 M; [ICl] = 0.001 M ; [$NaClO_4$] = 0.002 M; [NaCl] = 0.002 M; [$HClO_4$] = 0.001 M

Substrate	$K_1 \times 10^4$ (sec^{-1}) at 30°C	E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1} at 30°C	$\Delta S^{\neq}$ kJ mol^{-1} at 30°C	$\Delta F^{\neq}$ kJ mol^{-1} at 30°C	log A
2,4-dinitrophenol	13.43	30.64	28.10	206.25	90.50	2.46
2,4-dichlorophenol	115.15	21.65	18.52	221.05	85.50	1.69
2,4-dibromophenol	184.24	19.61	16.61	223.44	84.31	1.56

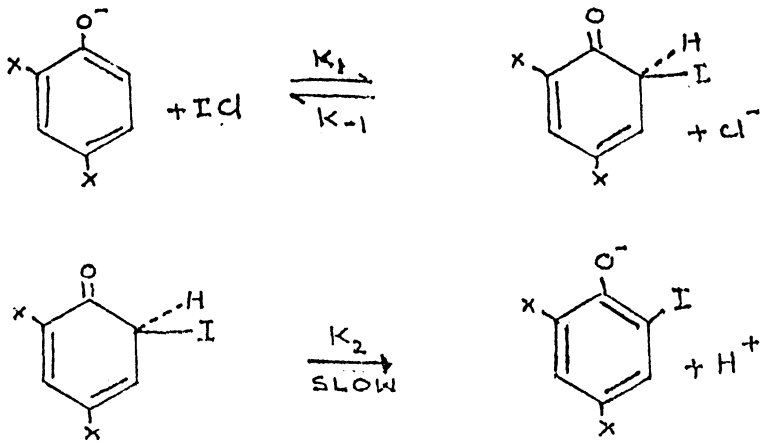
The observed results are in agrement with a reaction between the phenoxide ions and the iodinating species, hypoiodous acidium ion (H_2OI^+). On the basis of this the detailed mechanism is as shown below.

$$ICl_2^- \underset{K_2}{\overset{K_1}{\rightleftharpoons}} ICl + Cl^-$$

$$ICl + H_2O \rightleftharpoons H_2OI^+ + Cl^-$$



However the alternate mechanism given below cannot be neglected.



The comparison of the rate of iodination of various phenols (Table-3) reveals that the reactivities of different di-substituted phenols are in the order, 2,4-dibromophenol > 2,4-dichlorophenols > 2,4-dinitrophenol. This clearly emphasizes that electron releasing groups enhance the reaction rate and electron withdrawing groups retard the rate as has been observed for electrophilic substitution reactions.

The values of activation energy for different phenols (Table-3) show that 2,4-dibromophenol is found to have low activation energy. This small value of energy of activation of 2,4-dibromophenol on comparison with other di-substituted phenols may be due to the rapid rate of iodination of phenol by ICl. The high value of energy of activation for the iodination of 2,4-dinitrophenol, compared with other phenols, may be due to the slow rate of iodination of these phenols by ICl in methanol medium.

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ values (Table-3) agree with those of other electrophilic substitution reactions. The relatively small positive values of $\Delta H^{\neq}$ and large negative values of $\Delta S^{\neq}$ show that the reactions pass through transition states in which bond formations are well advanced. Large negative $\Delta S^{\neq}$ values also indicate the formation of intermediate complex in the rate determining step[6].

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