

# THE MECHANISM OF THE IODINATION OF PHENOLS

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The transition of organic chemistry from an empirical science to a science having a well-established theoretical foundation has been slow and most incomplete. One of the main factors which has retarded this advance has been a lack of knowledge of the nature of organic reactions. Many theories have been proposed, but proofs of these theories are too often lacking or are quite unsatisfactory. This work was therefore planned to give information concerning the mechanism of one reaction; namely, the iodination of phenols in aqueous solutions.

Appreciable work on the iodination reaction has been done, and the conclusions concerning the mechanism of the reaction have been several. It has been proposed that the  $I_2$  molecule, the  $I_3^-$  ion, the hypoiodous acid molecule, the  $I^+$  ion, or the iodine atom is the substance directly responsible for the substitution of the iodine. With respect to the phenol both the undissociated molecule and the phenolate ion have been suggested as intermediates. It has been further proposed by several authors that the reaction may take place by means of a combination of several of these intermediates. For the most part the proofs of these proposals have not been well-founded, and in several instances they are highly conflicting.

For this paper there has been made a quantitative study of the effects of variation of pH, potassium iodide concentration, and temperature upon the iodination of 2, 4-dichlorophenol. In each individual study all the other factors, including ion concentrations, have been held as nearly constant as possible. The compound 2, 4-dichlorophenol was specifically chosen for study since only one halogen may be readily substituted.

## DISCUSSION

The rate of iodination of 2, 4-dichlorophenol varies markedly with pH. As may be seen in table 1, the rate increases by a factor of about 42 as the pH is increased from 6.0 to 8.0. There are several possible explanations which are listed below.

TABLE 1

*Variation of the calculated rate constants with pH and temperature. Starting conc. of  $I_2$  and 2, 4-dichlorophenol = 0.00183 M. The average deviation for most of the rate values is between  $\pm 1\%$  and  $\pm 3\%$ .*

pH	Added KI m/l	Temp. ° C	k moles <sup>-1</sup> sec <sup>-1</sup>
6.0	0.008	25.6	0.076
6.4	0.008	25.6	0.263
7.0	0.008	25.6	0.99
7.4	0.008	25.6	1.87
8.0	0.008	25.6	3.18
8.0	0.012	25.6	1.09
8.0	0.008	33.5	6.6

1. Assume the phenolate ion is the active intermediate. Then, the variation in rate will depend on the actual concentration of the phenolate ion which in turn will depend on pH.

The ionization constant of phenol may be expressed:

$$K_i = \frac{[\text{H}^+][\Phi\text{O}^-]}{[\Phi\text{OH}]} = \frac{[\text{H}^+][\Phi\text{O}^-]}{a - x - [\Phi\text{O}^-]}$$

where  $K_i$  = ionization constant,  $[\Phi\text{OH}]$  and  $[\Phi\text{O}^-]$  are the phenol and phenolate ion concentrations and  $a - x$  is the sum of the phenol and phenolate ion concentrations at any given time  $t$ .

Then

$$[\Phi\text{O}^-] = \frac{K_i (a - x)}{[\text{H}^+] + K_i}$$

Substituting in the second order rate equation:

$$\frac{dx}{dt} = k [\text{I}_2][\Phi\text{O}^-] = \frac{k K_i}{[\text{H}^+] + K_i} (a - x)^2,$$

where the starting concentrations of  $\text{I}_2$  and total phenol are the same. The iodide ion concentration is assumed to remain constant. Tiessens (1931) has given the ionization constant for 2, 4-dichlorophenol as  $3.1 \times 10^{-8}$ . In like manner, the equilibrium  $\text{I}^- + \text{I}_2 \rightleftharpoons \text{I}_3^-$  will serve to reduce the rate of reaction, and the equation for the correction due to this equilibrium at a constant pH is:

$$\frac{dx}{dt} = \frac{k K_d}{[\text{I}^-] + K_d} (a - x)^2,$$

where  $K_d = 1.4 \times 10^{-3}$  as given by Van Name and Brown (1917).

2. Assume hypiodous acid is the active intermediate. The constant for the hydrolysis of iodine (Bray and Connolly, 1911) has been given as:

$$3 \times 10^{-13} = \frac{[\text{H}^+][\text{I}^-][\text{HOI}]}{[\text{I}_2]}$$

Upon substituting the equation for the dissociation of the triiodide ion into the above equation we obtain:

$$[\text{HOI}] = \frac{4.2 \times 10^{-16} (a - x)}{[\text{H}^+][\text{I}^-]([\text{I}^-] + 1.4 \times 10^{-3})}$$

At an effective iodide ion concentration of 0.0065 M and with  $a - x$  equal to 0.00183 then:

$$[\text{HOI}] = \frac{1.5 \times 10^{-15}}{[\text{H}^+]}$$

$$\frac{dx}{dt} = k [\text{HOI}][\Phi\text{OH}] = \frac{k \times 8 \times 10^{-12}}{[\text{H}^+]} (a - x)^2$$

There will be a change in the iodide ion concentration from the overall reaction:



The above equations will, however, be reasonably quantitative in accuracy.

3. Assume both the phenolate ion and hypiodous acid are the reactants. Then, the rate of reaction will roughly vary inversely with the square of the hydrogen ion concentration.

In table 2 there are compared the calculated concentrations of the phenolate ion, the calculated concentrations of hypiodous acid, and the observed reaction rate constants. In figures 1 and 2 these values are graphed. The plot of the phenolate ion concentrations against the observed rate constants is a straight line and indicates a direct proportion between these values. No such relationship exists between the hypiodous acid concentrations and the rate constants. Therefore it may be concluded that the reaction takes place as a result of the interaction of the phenolate ion and the iodine molecule.

TABLE 2

*Variation of the reaction rate with pH. A comparison of the calculated phenolate ion and hypiodous acid concentrations with the observed rate constant values. Temperature 25.6°; added KI concentration 0.008 M; starting concentration of I<sub>2</sub> and 2, 4-dichlorophenol = 0.00183 M.*

pH	k m <sup>-1</sup> sec <sup>-1</sup>	Calc. Starting [C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> O <sup>-</sup> ] m/l x 10 <sup>5</sup>	Calc. Starting [HOI] m/l x 10 <sup>8</sup>
6.0	0.076	5.5	1.5
6.4	0.263	13.2	3.7
7.0	0.99	44.	25.
7.4	1.87	80.	37.
8.0	3.18	138.	150.

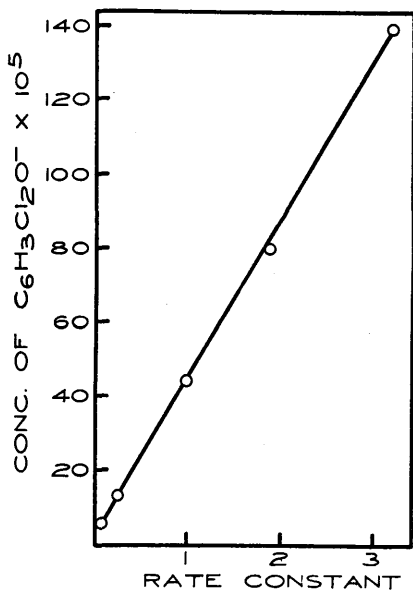


Figure 1

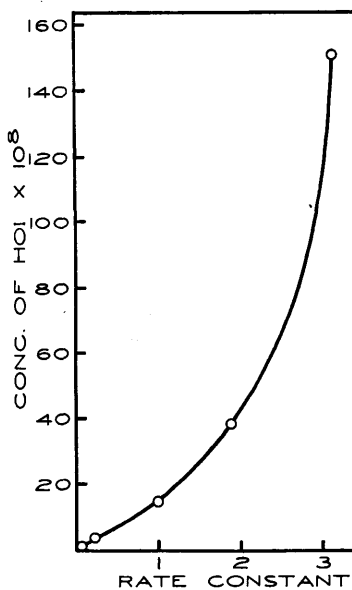


Figure 2

FIGURE 1. A graph showing the linear relationship of the starting concentration of the 2, 4-dichlorophenolate ion in moles per liter and the observed reaction rate constants in moles<sup>-1</sup> sec<sup>-1</sup>.

FIGURE 2. A graph showing the lack of linear relationship between the starting hypiodous acid concentration in moles per liter and the observed reaction rate constants in moles<sup>-1</sup> sec<sup>-1</sup>.

Two series of experiments were run in which the iodide ion concentration was varied. Table 3 gives the observed rate and compares the calculated  $I_2$  and HOI concentrations as predicted from the previously derived equations. It may be observed that neither equation quantitatively predicts the marked decrease in rate.

The activation energy has been roughly determined. The value from data in table 1 is 17 kcal/mole.

TABLE 3

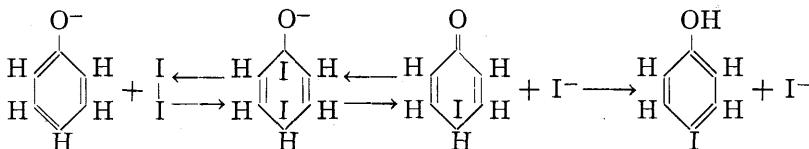
*Variation of the reaction rate with iodide concentration. A comparison of the calculated concentrations of molecular iodine and hypiodous acid with the observed rate constant values. Temperature 25.6°; pH 8.0; starting concentration of  $I_2$  and 2, 4-dichlorophenol = 0.00183 M.*

Added KI m/l	Approx. Effective [I <sup>-</sup> ] m/l	k m <sup>-1</sup> sec <sup>-1</sup>	Calc. [HOI] m/l x 10 <sup>7</sup>	k/ /[HOI] x 10 <sup>8</sup>	Calc. [I <sub>2</sub> ] m/l x 10 <sup>4</sup>	k/ /[I <sub>2</sub> ] x 10 <sup>4</sup>
0.008	0.0065	3.18	1.5	2.1	3.2	1.0
0.012	0.0104	1.09	6.3	1.7	2.2	0.50

## CONCLUSIONS

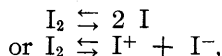
From the data concerning the variation of rate with pH it may be concluded the reaction of  $I_2$  with phenols occurs by the direct reaction of the  $I_2$  molecule and the phenolate ion.

The reason for the very marked effect of potassium iodide is not clear. Possibly another as yet undetermined equilibrium is involved. A possible mechanism is the following:



The equilibrium formation of the I<sup>-</sup> in the second step would tend to be reversed by the presence of excess iodide ion. This equilibrium in addition to the  $I_3^- \rightleftharpoons I^- + I_2$  equilibrium might explain the marked effect of the variation of iodide concentrations. This work with varying iodide ion concentrations clearly indicates that the mechanism of this reaction cannot be completely outlined from the data in this paper.

The low activation energy of 17 kcal. would seem to preclude equilibria of the nature



since much larger amounts of energy are required to transform the  $I_2$  molecule either to I atoms or  $I^+I^-$  ions. This value of 17 kcal/mole undoubtedly does not represent the activation energy for the reaction,  $I_2 + \Phi O^- \rightarrow$  products, since both pH and potassium iodide concentration affect the effective concentrations of the reactants. The activation energy should decrease with decreasing iodide ion concentrations and decrease with increasing pH. (This conclusion is based on unpublished work on the periodate-glycol reaction by Jay E. Taylor and B. Soldano.) Thus the true activation energy should be appreciably lower than the value given.

It is well known that ICl is an iodinating agent instead of a chlorinating agent. In view of the above evidence the most likely explanation is that the ICl molecule is polar (and not ionic) with the I atom having a partial plus charge. Upon attacking the phenolate ion the I is oriented to the ortho or para positions and the Cl to the carbon holding the O<sup>-</sup> group. The Cl<sup>-</sup> is then split out leaving the I substituted in the benzene ring.

Work is now being continued with this reaction, and it is hoped that a more complete view of the mechanism can be given in the near future.

#### EXPERIMENTAL

All chemicals used were of C.P. grade except the 2, 4-dichlorophenol which was recrystallized with much difficulty from a mixture of benzene and petroleum ether. It was necessary to carry out the recrystallization under anhydrous conditions as the phenol tended to absorb moisture from the atmosphere; this prevented the formation of crystals. It was kept in a dessicator.

The buffer solutions were made from varying amounts of hydrochloric acid and a constant amount of dipotassium hydrogen phosphate. The concentration of K<sub>2</sub>HPO<sub>4</sub> added to each reaction mixture was equal to five times the concentration of phenol.

The 2, 4-dichlorophenol solution was made by weighing the solid.

The iodine solutions were standardized against standard sodium thiosulfate. A weight burette was used for greater accuracy and convenience.

To make a given run the equivalency of 1.814 ml or KI + I<sub>2</sub> solution (measured from a micro pipette) was determined. An equal quantity of the iodine solution was then placed in a small glass bucket. The bucket was set in a weighing bottle, and the bottle was then put into a constant temperature bath. An equivalent quantity of the phenol solution (about 18 ml) and the prescribed amount of buffer were placed in a 100 ml glass-stoppered flask which was then set in a constant temperature bath. After the reactants had come to temperature the iodine was dropped into the phenol solution and mixed. After a measured amount of time 3 ml of 5% phosphoric acid was added to stop the reaction, and the remaining iodine was titrated with standard thiosulfate.

#### REFERENCES

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- Bray, W. C., and E. L. Connoly.** 1911. The hydrolysis of iodine and bromine. A correction. *Jour. Amer. Chem. Soc.*, 33: 1485.
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