

tances but the central one ($C_{\alpha}-C_{\beta}$) are $1.54 \pm 0.02 \text{ \AA.}$; it is very likely that the central C-C bond distance is somewhat longer, $1.58 \pm 0.03 \text{ \AA.}$ and that the C_{α} , C_{β} valence angles are somewhat larger than tetrahedral, $111 \pm 2^{\circ}$.

Summary

The structures of methylenecyclobutane and hexamethylethane have been investigated by means of electron diffraction. The final results are: in methylenecyclobutane the carbon atoms are coplanar, four of them situated on the average at the corners of a square ($1.56 \pm 0.03 \text{ \AA.}$ on side), the fifth on an extension of one of the diagonals

($1.34 \pm 0.02 \text{ \AA.}$ from the carbon atom in the ring); for hexamethylethane the theoretical intensity curves for free rotation, and for the eclipsed and staggered configurations differ by very little, yet agreement with observation is slightly better for the staggered model. However, regardless of which one of these three models one uses, assuming that the central C-C bond is somewhat stretched ($1.58 \pm 0.03 \text{ \AA.}$) improves the correlation with the observed curve. The other distances are: C-C = $1.54 \pm 0.02 \text{ \AA.}$; carbon valence angles $111 \pm 2^{\circ}$; C-H = 1.09 \AA. (assumed).

ITHACA, N. Y.

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[FROM THE INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

Kinetics and Mechanism of 2,6-Di-iodotyrosine Formation¹

BY CHOH HAO LI

Introduction

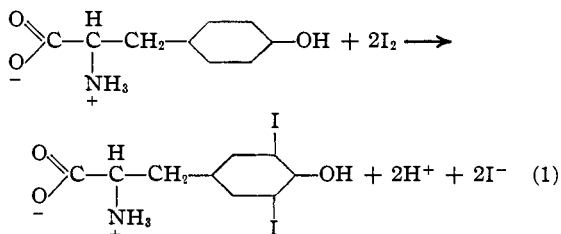
The halogenation of phenols has been examined by many investigators and yet no agreement has been reached with regard to the mechanism of the reactions. Baines^{1a} concluded that the active brominating agent was hypobromous acid but later Francis² showed that the aqueous bromination is due to the free bromine. Soper and Smith³ demonstrated from their chlorination studies that hypochlorous acid reacts with the phenoxide ion but it does not react with the un-ionized phenol or ether. On the other hand, chlorine can chlorinate the ether as well as the phenol.

The mechanism of the iodination of phenols is more confusing. The earlier investigations of Cofman⁴ gave the conclusion that the active iodinating agent was hypoiodous acid, free iodine having apparently no direct iodinating effect. He concluded further that the positive iodine ion is the halogenating agent. Later, Soper and Smith⁵ showed that the iodination of phenol is not caused by the positive iodine ion, but that the main reactions are those between the hypoiodous acid and the ionized and un-ionized phenol. Recently, Hunter and Budrow⁶ were able to iodinate pheno-

lates under anhydrous conditions. In this paper the kinetic data of the di-iodotyrosine formation suggest that the iodination of phenols may involve four paths, namely, (1) iodine and phenol, (2) iodine and phenolate, (3) hypoiodous acid and phenol, and (4) hypoiodous acid and phenolate. The importance of each path is determined by the pH and iodide ion concentrations. Thus, path (4) is the main path in the formation of iodinated phenol in slightly alkaline solution. On the other hand, path (2) leads to the results of Hunter's experiments.

Results

The Rate Law.—Tyrosine is a para substituted phenol; it has a dissociation constant between those of *p*-cresol and phenol.⁷ Its reaction with iodine may be represented by the equation



The product, 2,6-di-iodotyrosine, is shown to be a much stronger acid.⁸ Since the rate of halogenation changes with the pH of the solvent (see below), the reaction must be studied in a buffered

(1) Aided by grants from the Board of Research of the University of California and the Rockefeller Foundation, New York City, and Parke, Davis and Company, Detroit, Michigan

(1a) Baines, *J. Chem. Soc.*, 2810 (1922).

(2) Francis, *THIS JOURNAL*, **47**, 2340 (1925).

(3) Soper and Smith, *J. Chem. Soc.*, 1582 (1926).

(4) Cofman, *ibid.*, 1040 (1919).

(5) Soper and Smith, *ibid.*, 2757 (1927).

(6) Hunter and Budrow, *THIS JOURNAL*, **55**, 2122 (1933).

(7) Hitchcock, *J. Gen. Physiol.*, **6**, 747 (1925).

(8) Kirk, Dawson and Schmidt, *J. Biol. Chem.*, **88**, 580 (1930).

medium. In both acetate and phosphate buffers, the rate of reaction (1) is best expressed by the formula

$$dx/dt = k_{\text{obs.}}(a-x)(b-2x) \quad (2)$$

where a and b are the initial concentrations of tyrosine and titratable iodine, respectively, x is the concentration of 2,6-di-iodotyrosine formed in time interval t , and $k_{\text{obs.}}$ is the specific rate constant. By integrating, $k_{\text{obs.}}$ may be calculated by the equation

$$k_{\text{obs.}} = \frac{2.303}{t(b-2a)} \log \frac{a(b-2x)}{b(a-x)} \quad (3)$$

Since most of the experiments were done in the condition that $b = 2a$, $k_{\text{obs.}}$ was obtained by the expression

$$k_{\text{obs.}} = \frac{1}{2t} \frac{x}{a(a-x)} \quad (4)$$

Table I presents a typical run in an acetate buffer indicating the constancy of $k_{\text{obs.}}$ as the reaction went to 70% completion. The rate law was further tested in a phosphate buffer by changing the concentration of a and b as shown in Table II. It is to be noted that the rate does not depend on the ionic strength of the solvent, as may be expected since all the ionic species of the

TABLE I

TYPICAL KINETIC DATA IN THE REACTION OF IODINE AND TYROSINE AT 25°

$b = 2a = 0.0022 M$. $(I^-) = 0.0376 M$. Solvent, 0.2 M acetate buffer + 0.8 M sodium nitrate of pH 5.78.

Time, min.	$x (M \times 10^4)$	$k_{\text{obs.}}$ (g. mole/l./min.)
0.0	0.0	
15.0	1.85	1.39
30.0	3.60	1.48
120.0	9.20	1.36
180.0	11.65	1.42
390.0	15.45	1.38

Av. 1.406

TABLE II

RATE OF REACTION USING DIFFERENT INITIAL CONCENTRATIONS AT 25°

Solvent: phosphate buffer of pH 6.03 and $\mu = 0.1$; $(I^-) = 0.0552 M$.

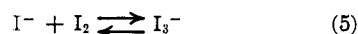
$a, 10^3$ g. mole/l.	$b, 10^3$ g. mole/l.	$k_{\text{obs.}}$ g. mole/l./min.
2.761	5.64	2.240
4.142	5.60	2.298
2.36	2.36	2.684
2.36 ^a	2.36 ^a	2.512
2.761 ^b	3.64 ^b	2.158

Mean 2.378

^a In the presence of $9.22 \times 10^{-4} M$ 2,6-di-iodotyrosine.

^b The ionic strength of the solvent has been increased to 1.32 by adding sodium nitrate.

reactants are in extremely low concentrations, and further the equilibrium



should not be changed with the ionic strength. Hence it is not necessary to introduce the activity coefficients for the specific rate calculations as performed by Soper and Smith.⁵

Reaction in Acetate Buffers.—Determinations of the reaction rate in three acetate buffers^{8a} with different concentrations of iodide ion are summarized in Tables III, IV and V. A plot of $k_{\text{obs.}}$ against $1/(I^-)$, as shown in Fig. 1, reveals the relationship

$$k_{\text{obs.}} = \frac{A}{(I^-)^2} + \frac{B}{(I^-)} \quad (6)$$

where A and B are empirical constants which may be determined from the curve. Table VI presents the estimated values of A and B for these 3 experiments.

TABLE III

REACTION RATE IN ACETATE BUFFER OF pH 5.23 AT 25°,
 $b = 2a = 0.0044 M$

(I^-) , $M \times 10^2$	$1/(I^-)$	$k_{\text{obs.}}$ g. mole/l./min.
1.76	56.82	2.170
3.76	26.59	0.437
5.76	17.36	.187
7.76	12.86	.102
9.76	10.24	.0656

TABLE IV

REACTION RATE IN ACETATE BUFFER OF pH 5.78 AT 25°,
 $b = 2a = 0.0044 M$

(I^-) , $M \times 10^2$	$1/(I^-)$	$k_{\text{obs.}}$ g. mole/l./min.
1.76	56.82	6.516
3.76	26.59	1.406
5.76	17.36	0.636
7.76	12.86	.341
9.76	10.24	.223

TABLE V

REACTION RATE IN ACETATE BUFFER OF pH 6.02 AT 25°,
 $b = 2a = 0.0044 M$

(I^-) , $M \times 10^2$	$1/(I^-)$	$k_{\text{obs.}}$ g. mole/l./min.
1.76	56.82	10.68
3.76	26.59	3.07
5.76	17.36	1.227
7.76	12.86	0.663
9.76	10.24	0.460

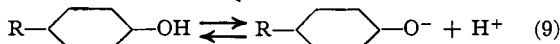
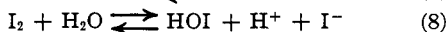
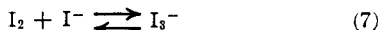
(8a) It is of interest to note that $k_{\text{obs.}}$ obtained in phosphate buffer as shown in Table II is greater than that obtained in acetate buffer under the same condition (see Table V). This cannot be attributed to the difference in ionic strength (see Table II) and must be due to the specific effect of phosphate ion on the rate. A preliminary experiment showed that by increasing 6 times the concentration of phosphate ion concentration without change of pH , the $k_{\text{obs.}}$ increases about two-fold. At the present it is premature to offer any explanations. More data are needed to settle this question.

TABLE VI

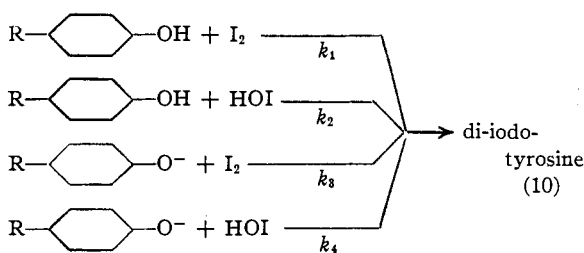
VALUES OF A AND B FOR REACTIONS IN ACETATE BUFFER AT 25°

pH	(H ⁺)10 ⁸	A 10 ⁴	B 10 ⁴
5.23	5.89	6.0	3.0
5.78	1.66	20.0	10.0
6.02	0.955	38.0	17.0

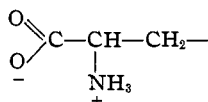
In the reaction mixture, there are three equilibria



from which we may assume that the formation of di-iodotyrosine is obtained through the following paths:



where R is



and k_1, k_2, k_3 and k_4 are the specific rate constants. It follows that

$$dx/dt = k_1(\text{TOH})(I_2) + k_3(\text{TO}^-)(I_2) + k_2(\text{TOH})(\text{HOI}) + k_4(\text{TO}^-)(\text{HOI}) \quad (11)$$

(TOH) and (TO⁻) are the concentrations of tyrosine and tyrosinate, respectively. Since the concentrations of iodine, hypoiodous acid and tyrosinate are determined by equilibria 7, 8 and 9, Eq. (11) becomes

$$\frac{dx}{dt} = (\text{TOH})(I_3^-) \left[\frac{1}{(I^-)K_7} \left\{ k_1 + \frac{k_3K_9}{(H^+)} \right\} + \frac{1}{(I^-)^2K_7} \left\{ \frac{k_2K_8}{(H^+)} + \frac{k_4K_8K_9}{(H^+)^2} \right\} \right] \quad (12)$$

where K_7, K_8 and K_9 are the equilibrium constant of Eqs. 7, 8, and 9 respectively. The total iodine, as determined by the thiosulfate titre, is practically the tri-iodide ion concentration since the ratio $[I^-]/[I_3^-]$ in the reacting mixture is four or more. The tyrosinate concentration is practically negligible as compared with that of tyrosine, so we may write, from (2) and (12)

$$k_{\text{obs.}} = \frac{1}{K_7(I^-)} \left\{ k_1 + \frac{k_3K_9}{(H^+)} \right\} + \frac{1}{K_7(I^-)^2} \left\{ \frac{k_2K_8}{(H^+)} + \frac{k_4K_8K_9}{(H^+)^2} \right\} \quad (13)$$

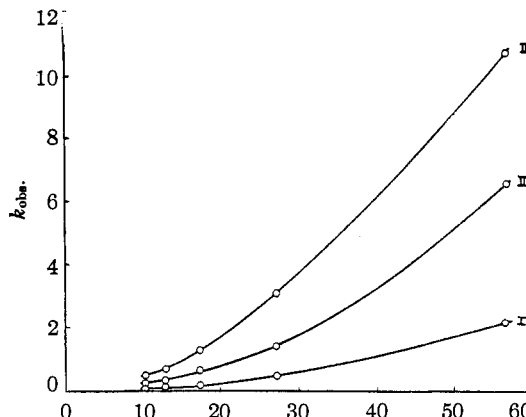


Fig. 1.—The change of reaction rate with iodide ion concentration in different pH acetate buffers at 25°: I, pH 5.23; II, pH 5.78; III, pH 6.02.

From Eq. 6

$$A = 1/K_7 \left\{ \frac{k_2K_8}{(H^+)} + \frac{k_4K_8K_9}{(H^+)^2} \right\} \quad (14)$$

$$B = 1/K_7 \left\{ k_1 + \frac{k_3K_9}{(H^+)} \right\} \quad (15)$$

From the equilibrium constants:^{7,9,10} $K_7 = 715, K_8 = 3 \times 10^{-13}, K_9 = 8.5 \times 10^{-11}$ at 25° and the data in Table VI with the assumption that $a_{H^+} = (H^+)$ we obtain the specific rate constants for each path of Eq. 10. Results are summarized in Table VII. Thus, in a reaction mixture of known hydrogen ion and iodide concentrations, the observed specific rate constant can be calculated from the expression

$$k_{\text{obs.}} = \frac{1}{(I^-)} \left[2.1 \times 10^{-5} + \frac{1.63 \times 10^{-9}}{(H^+)} \right] + \frac{1}{(I^-)^2} \times \left[\frac{3.23 \times 10^{-9}}{(H^+)} + \frac{3.56 \times 10^{-16}}{(H^+)^2} \right] \quad (16)$$

TABLE VII

SPECIFIC RATE CONSTANTS OF PATHS LEADING TO THE IODINATION OF PHENOL IN ACETATE BUFFER AT 25°

Specific rate constants	G. mole/l./min. 10 ²
k_1	1.5
k_2	7.7×10^8
k_3	1.37×10^6
k_4	1×10^{12}

Table VIII presents some calculated and observed specific rate constants from experiments studied in acetate buffers. In every case, the agreement between the calculated and observed constants is within the experimental error, indicating that expression 16 is satisfied for experiments in acetate buffers.

(9) Bray and MacKay, THIS JOURNAL, 32, 914 (1910).
 (10) Bray, *ibid.*, 32, 932 (1910).

TABLE VIII

A SUMMARY OF SOME CALCULATED AND OBSERVED SPECIFIC RATE CONSTANTS FOR REACTIONS IN ACETATE BUFFERS AT 25°

(H ⁺) 10 ^a	(I ⁻) M × 10 ²	<i>k</i> _{obs.} , g. mole/l./min.	<i>k</i> _{calcd.} , g. mole/l./min.
5.89	3.76	0.437	0.432
5.89	5.76	.187	.185
5.89	10.24	.0657	.0659
1.66	7.76	.341	.344
1.66	5.76	.636	.620
1.66	9.76	.223	.220
1.66	1.76	6.516	6.514
0.955	7.76	0.663	0.643
0.955	9.76	0.430	0.414

By rearrangement of Eq. 13 it becomes

$$k_{\text{obs.}} = \frac{k_1}{K_7(I^-)} + \frac{1}{(H^+)} \left[\frac{k_2 K_8}{K_7(I^-)^2} + \frac{k_3 K_9}{K_7(I^-)^2} \right] + \frac{1}{(H^+)^2} \frac{k_4 K_9 K_8}{K_7(I^-)^2} \quad (17a)$$

or

$$k_{\text{obs.}} = \frac{2.1 \times 10^{-5}}{(I^-)} + \frac{1}{(H^+)} \left[\frac{1.63 \times 10^{-9}}{(I^-)} + \frac{3.23 \times 10^{-9}}{(I^-)^2} \right] + \frac{1}{(H^+)^2} \frac{3.56 \times 10^{-16}}{(I^-)^2} \quad (17b)$$

It may therefore be expected that the reaction rate depends on the hydrogen ion concentrations in solvents containing the same iodide concentration with the relationship as expressed in Eq. 17a. Table IX summarizes the observed specific reaction rate constant in different pH of an acetate buffer together with the calculated *k* using Eq. 17b.

TABLE IX

THE OBSERVED AND CALCULATED REACTION RATE IN ACETATE BUFFERS OF DIFFERENT pH AT 25°, *b* = 2*a* = 4.4 × 10⁻³ M; (I⁻) = 2 × 10⁻² M

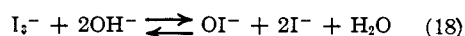
pH	(H ⁺) 10 ^a	1/(H ⁺) 10 ⁻⁴	<i>k</i> _{obs.}	<i>k</i> _{calcd.}
4.55	28.18	3.55	0.282	0.292
4.99	10.23	9.76	0.885	0.805
5.23	5.89	17.00	1.52	1.416
5.57	2.69	37.10	3.40	3.152
5.78	1.66	60.20	4.95	5.233
6.02	0.96	104.26	8.40	9.45

Reaction in Sodium Hydroxide pH Solutions.^{10a}—When 0.0022 mole of tyrosine, 0.0044 mole of iodine and 0.044 mole of iodide were dissolved in 50 cc. of 0.05 *N* sodium hydroxide no loss of iodine was found. However, approximately 48% of the tyrosine was iodinated if the concentration of sodium hydroxide was decreased to 0.01 *N*. These results are surprising and are not in accordance with our expectation since, as shown in

(10a) I am indebted to Professors T. D. Stewart and W. C. Bray for their invaluable suggestions on the iodination reactions in sodium hydroxide solution.

acetate buffer experiments, it was expected that phenols were rapidly and completely iodinated in alkaline solution.

In alkaline solution, iodine is rapidly hydrolyzed as indicated in Eq. 8, and the resultant hypoiodous acid is expected to be neutralized to some extent. If the solution is sufficiently basic, the reaction becomes



It is known that the hypoiodite ion decomposes into iodate ion which does not react with phenols. Thus it is apparent that in 0.05 *N* sodium hydroxide the iodine must be changed completely into iodate ion so that when the tyrosine is added no iodination reaction is found.

If the hypoiodous acid or hypoiodite ion is partly converted into iodate ion, the addition of phenols would use up the former ions and leave the latter unchanged. Hence the rate of iodate ion formation^{10b} can be determined by titrating the iodate ion in acid solution after the phenols have been added. A typical experiment, carried out in 0.9171 *M* sodium hydroxide, summarized in Table X, indicates that iodine will react instantaneously with tyrosine if the phenol is added immediately after the addition of the free iodine into the sodium hydroxide solution. In the last column of the table a bimolecular rate constant is calculated by assuming

$$-d\Sigma(I_2)/dt = k_2\Sigma(I_2)^2 \quad (19, 20)$$

TABLE X

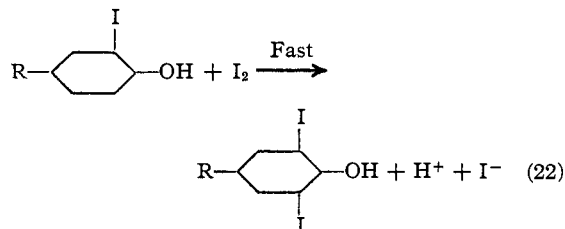
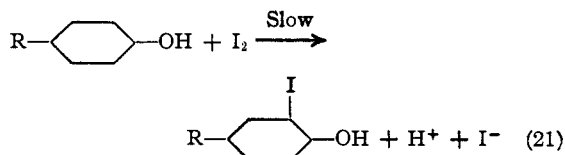
RATE OF DISAPPEARANCE OF HYPOIODITE ION IN 0.9171 *M* SODIUM HYDROXIDE AT 25°, $\Sigma(I_2) = 0.00645$ M; (I⁻) = 0.05 *M*

Time, min.	$\Sigma(I_2) 10^3$	<i>k</i> ₂
5	5.08	8.36
10	4.25	8.04
20	3.11	8.34
35	2.15	8.85
65	1.45	8.24
		Mean 8.36

Discussion

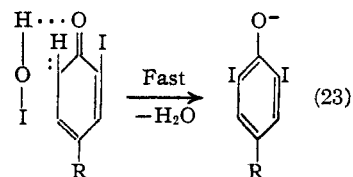
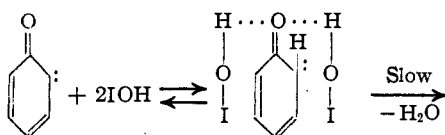
As the rate law indicated, the rate-determining step in iodinating phenols is the formation of a mono-iodo compound

(10b) The velocity of iodate ion formation in high alkali solution has been studied by Forster [*J. Phys. Chem.*, **56**, 324 (1903)] and Chapin [*THIS JOURNAL*, **56**, 2211 (1934)]. They both used arsenious oxide in determining the concentration of hypoiodite ion. By using the same method, Miss C. White and the present author are not able to obtain a good rate constant. However, as shown in Table X, the phenol method gives a good and reproducible *k*₂. The decomposition of hypoiodite ion is now being reinvestigated and results will be published shortly.



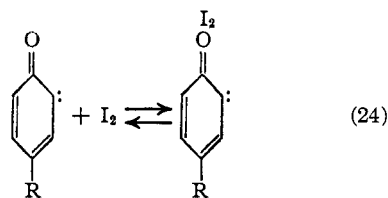
This implies that as soon as the first iodine atom enters the benzene ring, the second one reacts instantaneously. There are three more pairs of reacting species giving similar schemes (21) and (22). As shown in Table VII, the most reactive pair is phenolate and hypoiodous acid, while phenol and iodine are the least reactive couple. In view of the fact that the $-\text{O}^-$ group behaves as a stronger *o-p*-directing group than the $-\text{OH}$ group, it is obvious that phenolate ion is far more reactive than the phenol. The results of Soper and Smith^{3,5} also lead to the conclusion that the phenolate ion is halogenated more readily than undissociated phenol or a phenolic ether. From Table VII, we obtain: $k_3/k_1 = 9.1 \times 10^5$ and $k_4/k_2 = 1.3 \times 10^3$; it follows that in cases where iodine is the halogenating agent, the reactivity of the tyrosinate is about 10^6 times that of the tyrosine while in the case of hypoiodous acid, the phenolate ion is about 10^3 times more reactive than the undissociated phenol.

Several mechanisms may be suggested to satisfy the above rate law; the following two seem most probable. If we assumed the existence of the hypothetical complexes between the resonated phenolate ion and the hypoiodous acid or iodine, and if we assume further as soon as the carbon and iodine bond is formed the second iodine enters the ring immediately, it is easily understood that the rate law requires only the first order of iodine concentration:

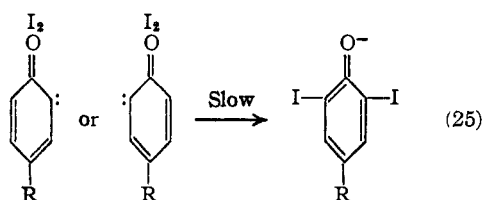


It may also be seen that the hypoiodous acid is more reactive than the free iodine since hydrogen bonds are involved in the hypoiodous acid-phenolate complex formation which seems to be more stable.

In addition to a similar scheme like (23) for the iodine-phenolate reaction, a rearrangement mechanism may be possible. It is known that the acidic property of iodine is responsible for many iodine compounds such as the R_3NI_2 . In a solution of iodine and phenol, the following equilibrium may be set up rapidly

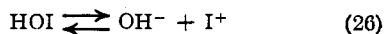


There follows the migration of iodine to ortho positions



It is obvious that this mechanism also satisfies the observed rate law, which demands the first order of iodine and phenol concentrations. The results of Hunter and Budrow⁶ may then be explained solely by this scheme.

Since both bromination and chlorination reactions are possible for the interpretation that the active halogenating agent is the positive halogen ion, it may be inferred that the iodination process also follows the same mechanism. This hypothesis already has been disproved by Soper and Smith. Their arguments involve the assumption that if the reaction is due to the positive iodine ion, the effects of free iodine and hypoiodous acid on phenols are expected to be qualitatively the same in view of the equilibria



which leads to the fact that

$$\frac{K_{27}}{K_{26}} = \frac{(\text{HOI})(\text{I}^-)(\text{H}^+)}{(\text{I}_2)(\text{OH}^-)(\text{H}^+)} = \frac{K_8}{K_w} = 30$$

From this ratio it would imply that the hypiodous acid is only slightly more reactive than the free iodine if we assume that the active iodinating agent is the positive iodine ion. However, as shown in the results of Soper and Smith, and those described in this paper, the hypiodous acid is far more reactive than free iodine. This is not only true in the case of phenols: the work of Moelwyn-Hughes and Legard¹¹ in the iodine addition to β -phenylpropionic acid and that of Griffith and McKeown¹² in the reaction between iodine and oxalic acid also confirm this view. Thus, it seems unlikely that the positive iodine ion is participating in the iodination reactions in the experiments herein reported.

Experimental

Materials.—Tyrosine, the c. p. preparation, was recrystallized from water and dried in the desiccator for many weeks before use. Acetate and phosphate buffers were made according to the direction of Clark.¹³ After the acid and base were mixed, the sodium nitrate was added so that the final concentration of sodium nitrate became 0.8 molal. The $p\text{H}$ of the final solution was determined with a glass electrode. The observed value was never more or less than 0.02 unit of the desired $p\text{H}$.

Procedure.—The phenol and iodine (in known concentration of potassium iodide) solutions were prepared by dissolving the weighed quantities in two 25-cc. volumetric flasks separately with the buffer solution. After the solutions came to the temperature of the thermostat ($25.0 \pm 0.02^\circ$), they were mixed in a glass-stoppered flask. The time of mixing was taken as 0 time: 5 cc. of this solution

was transferred at known time intervals to 10 cc. of 1.0 N hydrochloric acid which stopped the reaction. The free iodine was titrated with 0.010 N thiosulfate solution which was prepared every day from a 0.10 N solution. The starch solution, which served as the indicator, was also prepared daily. The reaction followed in all cases up to at least 60% completion. A 10-cc. micro-buret was used for titrations.

The reaction in 0.9171 M sodium hydroxide was carried out as follows. After 5 cc. of 0.129 N iodine solution (in 0.5 M potassium iodide) was mixed with 45 cc. of 1.019 M sodium hydroxide, a 5 cc. sample of the mixture was pipetted into 1 cc. of tyrosine solution (containing 5.0 mg. of tyrosine) at certain time intervals. This 6 cc. of mixture was then poured slowly into 10 cc. of 2 M sulfuric acid solution; the liberated free iodine was titrated with 0.01 N thiosulfate solution as described above.

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Summary

1. The rate of 2,6-di-iodotyrosine formation has been studied in acetate buffers at 25° and found to be a bimolecular reaction as shown in the expression: $\text{rate} = 1.5 \times 10^{-2}(\text{TOH})(\text{I}_2) + 1.37 \times 10^4(\text{TO}^-)(\text{I}_2) + 7.7 \times 10^6(\text{TOH})(\text{HOI}) + 10^{10}(\text{TO}^-)(\text{HOI})$.

2. A mechanism has been proposed for the iodination of phenols. It is shown to be in agreement with the experimental observations.

3. In high alkaline solution the iodination reaction is instantaneous if the concentration of hypiodous acid or hypiodite ion is maintained. The iodate ion does not react, on the other hand, with phenol. Thus phenol is proved to be very suitable in determining the rate of hypiodite ion decomposition.

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