110. *The Kinetics of the Addition of Iodine to β-Phenylpropiolic Acid.*

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RECENT inquiries (*Chem. Rev.*, 1932, **10**, 241; *Phil. Mag.*, 1932, **14**, 112) have revealed the existence of a fairly large number of bimolecular reactions in solution possessing velocities equal to those predicted by the collision theory in its simple form. With the exception of the conversion of ammonium cyanate into urea, the saponification of phthalide, and a few other cases, most of these reactions belong to two groups of chemical changes: (1) $RX + R'ONa \longrightarrow R{\cdot}OR' + NaX$, where X is a halogen atom, and R and R′ are alkyl or aryl groups; (2) $CHRX{\cdot}CO_2H + Y^- \longrightarrow CHRY{\cdot}CO_2H + X^-$, where Y^- is a halide or hydroxyl ion. These reactions are thus somewhat limited in type, and it is desirable to investigate kinetically new examples of bimolecular reactions of a totally different character. The kinetics of the formation of αβ-di-iodocinnamic acid from β-phenylpropiolic acid have therefore been studied in aqueous solution: $CPh{:}C{\cdot}CO_2H + I_2 \longrightarrow CPhI{:}CI{\cdot}CO_2H$. Under ordinary conditions, only one molecule of iodine is added on, the reaction being bimolecular in the presence of potassium iodide (James and Sudborough, J., 1907, **91**, 1037).

EXPERIMENTAL.

Bimolecular Nature of the Reaction.—In order to avoid complications arising from the variable extents of dissociation of phenylpropiolic acid, solutions of the Na salt have been consistently used. Expts. were carried out with equimol. solutions of this salt and I in the presence of a four-fold concn. of KI; the reaction was followed by titrating the total I against standard $Na_2S_2O_3$, with starch as indicator. Examples of bimol. consts. calculated from either of the equations

$$k = \frac{1}{ta}\cdot\frac{x}{a-x} \quad \text{or} \quad k = \frac{1}{t_2 - t_1}\left\{\frac{1}{a-x_2} - \frac{1}{a-x_1}\right\}$$

are given in Table I, the units of *k* being l./g.-mol.-sec. The bimol. character of the reaction has been confirmed at temps. ranging from 15° to 60° and at initial concns. differing by a factor of 200. Concns. exceeding 0·1*M* and temps. greater than 60° were avoided because addition of a second mol. of I tends to take place under these conditions.

TABLE I.

Initial concn. = 0·025*M*. Temp., 24·8°.			Initial concn. = 0·05*M*. Temp., 59·8°.			Initial concn. = 0·0942*M*. Temp., 40·3°.		
t, min.	Titre.	$k \times 10^3$.	*t*, min.	Titre.	$k \times 10^2$.	*t*, min.	Titre.	$k \times 10^3$.
0	25·09		0	25·18		0	27·80	
114	21·30	1·06	3	22·15	1·52	11	21·80	4·54
273	17·72	1·01	6	19·85	1·49	20	18·70	4·41
405	15·50	1·00	10·5	17·20	1·47	32·25	15·62	4·38
662	12·45	1·03	12	16·50	1·46	46	13·15	4·40
1388	7·90	1·03	19	13·60	1·49	60·5	11·32	4·23
1780	6·60	1·07	26	11·60	1·51	75	9·99	4·31
2790	4·55	1·06	35	9·75	1·51			
			47	8·10	1·50			
Mean $k = 1{\cdot}04 \times 10^{-3}$.			Mean $k = 1{\cdot}49 \times 10^{-2}$.			Mean $k = 4{\cdot}38 \times 10^{-3}$.		

The Influence of Dilution upon the Velocity Constant at 24·8°.—Expts. at 24·8°, with equimol. concns. of the reactants and 4 mols. of KI, showed that the velocity is influenced in an unusual way by changing the initial concn. (see Table II, and Fig. 1). At ordinary concns., the bimol. const. is but little affected by the dilution, but when this exceeds 400 l./g.-mol., the velocity const. increases very rapidly as the initial concn. diminishes.

FIG. 1.

Influence of concentration.

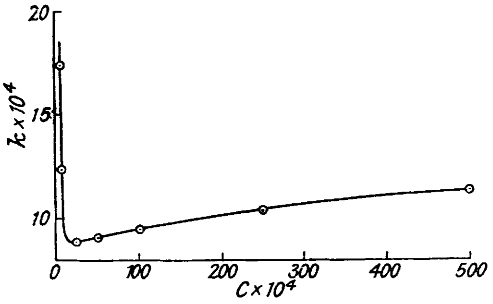

FIG. 2.

Influence of temperature.

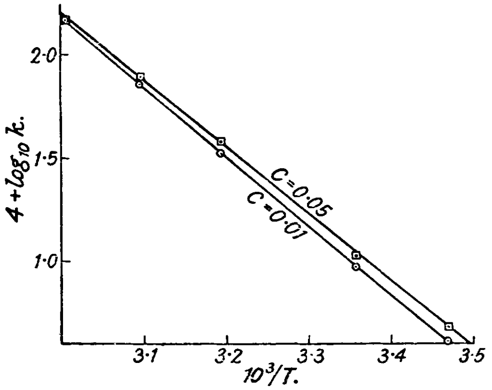

TABLE II.

Initial concn. × 10^4	5	7·5	10	25	50	100	250	500	945
$k \times 10^4$	17·4	12·4	9·75	8·90	9·08	9·45	10·4	11·4	12·6

The Influence of Temperature upon the Velocity Constant.—The effect of temp. on the bimol. const. at various dilutions is summarised in Table III, and in part in Fig. 2.

TABLE III.

	$k \times 10^4$.							
Temp.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
15·2°	4·07	4·04	4·19	4·34	4·74	4·95	6·01	5·72
24·8	9·45	9·48	10·4	10·2	11·4	11·3	12·6	13·1
40·3	33·4	33·6	36·3	36·1	37·8	37·5	43·8	43·4
50·1	72·2	71·9	74·9	75·5	79·2	77·1	87·5	89·2
59·8	149	156	158	152	149	149	—	—
Initial concn.	0·010		0·025		0·050		0·0942	
E (cals./g.-mol.)	15,220		15,170		14,500		14,500	

The Arrhenius equation is accurately obeyed, the critical increment having a slightly lower value in the more conc. solutions.

Ionic Concentrations at 24·8°.—In order to interpret the kinetic measurements relating to solutions of varying compositions, it is necessary to know the exact concentrations of all molecular species at the beginning of the reaction. These can be found from the values of the equilibrium constants of the reactions :

$$\mathrm{I_3^-} \rightleftharpoons \mathrm{I_2} + \mathrm{I^-};\ K_1 = [\mathrm{I_2}][\mathrm{I^-}]/[\mathrm{I_3^-}] \tag{1}$$

and

$$\mathrm{I_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{I^-} + \mathrm{HIO};\ K_2 = [\mathrm{H^+}][\mathrm{I^-}][\mathrm{HIO}]/[\mathrm{I_2}] \tag{2}$$

Application of the data of Jones and Kaplan (*J. Amer. Chem. Soc.*, 1928, **50**, 1845), Bray (*ibid.*, 1910, **32**, 914), and Jones (*ibid.*, 1915, **37**, 24) gives K_1 at 24·8° $= 1{\cdot}405 \times 10^{-3}$, and $K_2 = 2{\cdot}95 \times 10^{-13}$. Since in our experiments the concentration (c) of total iodine was one-fourth of that ($4c$) of total potassium iodide, it follows that

$$[\mathrm{I_3^-}] = \tfrac{1}{2}[5c + K_1 - \sqrt{(5c + K_1)^2 - 16c^2}] \tag{3}$$

$$[\mathrm{I^-}] = 4c - [\mathrm{I_3^-}] \tag{4}$$

$$[\mathrm{I_2}] = c - [\mathrm{I_3^-}] \tag{5}$$

The concentration of hypoiodous acid being small in comparison with these, we may write, from equation (2),

$$[\mathrm{HOI}] = \sqrt{K_2[\mathrm{I_2}]/[\mathrm{I^-}]} \tag{6}$$

The values determined in this way for the initial concentrations corresponding to the experiments summarised in Table III are given in Table IV, $[\mathrm{A^-}]$ representing that of the β-phenylpropiolate ion. It must be pointed out that the calculation of [HOI] by equation (6) ignores the dissociation of water; hence, since the natural hydrogen-ion concentration is commensurate with and in some cases exceeds [HOI], the figures given in the last column of Table IV are liable to serious error. They are subsequently employed, however, in dealing with the kinetics of the reaction in highly dilute solution where the experimental method is capable of yielding results which can only claim to be of a qualitative kind. Under the conditions which have been employed, the calculated value of [HOI] is subject to a maximum error of about 25%. Equation (13) is also approximate, but the error involved is not serious.

TABLE IV.

$[\mathrm{A^-}] \times 10^4$.	$[\mathrm{I_3^-}] \times 10^4$.	$[\mathrm{I_2}] \times 10^4$.	$[\mathrm{I^-}] \times 10^4$.	$[\mathrm{HOI}] \times 10^8$.
5	2·75	2·25	17·25	19·6
7·5	4·82	2·68	25·2	17·7
10	7·02	2·98	33·0	16·3
25	21·2	3·80	78·8	11·2
50	45·75	4·25	154·0	8·41
100	95·6	4·40	304	6·10
250	245	4·60	755	3·94
500	495	5·00	1505	2·86

The Mechanism of Reaction in the Region of Moderate Concentration.—The velocity of reaction is directly proportional to the total concentration of iodine (p. 424). The figures in Table IV indicate that at concentrations exceeding 5×10^{-3} g.-mol./l. more than 90% of the total iodine is present in the form of $\mathrm{I_3^-}$. The fact that bimolecular velocity constants are found from estimations of the total titratable iodine suggests that the measurable reaction is that occurring between the phenylpropiolate and the tri-iodide ion. In principle, the iodine molecules also may react, but this is improbable for the following reasons: analysis of the experimental results based on this supposition leads to bimolecular constants which alter much more rapidly with the concentration than can be accounted for by the usual electrolytic effect; furthermore, unpublished observations made in this laboratory by Mr. E. J. Bowen (to whom we are indebted for drawing our attention to this reaction) prove that molecular iodine does not attach itself to phenylpropiolic acid in carbon tetrachloride solution. There is much other evidence to show that molecular halogens are not effective in thermal addition reactions of this type. The kinetics of the reaction may thus be formulated on the supposition that the change is entirely ionic: $\mathrm{CPh{\vdots}C{\cdot}CO_2^-} + \mathrm{I_3^-} \longrightarrow \mathrm{CPhI{:}CI{\cdot}CO_2^-} + \mathrm{I^-}$. Denoting by a and c the total concentrations of phenylpropiolate ions and iodine respectively, we have :

$$\text{rate} = k_{\text{obs.}}\, ca \tag{7}$$

and

$$\text{rate} = k_1[\mathrm{I_3^-}]a \tag{8}$$

From equation (1),

$$[\mathrm{I_3^-}] = c[\mathrm{I^-}]/(K_1 + [\mathrm{I^-}])$$

hence,

$$k_{\text{obs.}} = k_1[\mathrm{I^-}]/(K_1 + [\mathrm{I^-}]) \tag{9}$$

The exact expression for the true bimolecular constant k_1, obtained by combining equations (8) and (3) and integrating, would be very complicated and would show the dependence of k upon $[I^-]$ during the course of any given experiment. The fact, however, that the observed bimolecular coefficient is constant removes the necessity for this, and is no doubt due to the relatively small variations in $[I_2]$ shown by the data in Table IV. That the influence of the iodide concentration is very small is clearly seen from the form of the curve in Fig. 1. If the very simple mechanism proposed is the correct one, $k_{obs.}$ should increase to a limiting value with addition of potassium iodide, and the quantity $k_{obs.}\{1 + K_1/[I^-]\}$ should be constant at all dilutions; Fig. 1 amply illustrates the first conclusion. The extent to which the second condition is fulfilled is shown in Table V, the iodide concentrations being the mean of the initial and the final value for each experiment.

TABLE V.

$c \times 10^4$	25	50	100	250	500
$k_{obs.} \times 10^4$	8·90	9·08	9·45	10·4	11·4
$\{[I^-] + K_1\}/[I^-]$	1·157	1·079	1·040	1·016	1·008
$k_{obs.}\{1 + K_1/[I^-]\} \times 10^3$	1·03	0·98	0·98	1·06	1·15

The values in the last line, although varying slightly, change less than the uncorrected values, and alter by no more than 5% over a ten-fold change in the initial concentration. This holds at the other temperatures, k_1 at 40·3° being $3{\cdot}71 \times 10^{-3}$. It has not been possible to allow for the variation of K_1 with the ionic strength.

The Molecular Statistics of the Reaction between Tri-iodide and Phenylpropiolate Ions.—The energy of activation for this reaction is found from the corrected constants (k_1) at various temperatures to be 15,500 cals. The theoretical expression for the bimolecular velocity constant is

$$k = \frac{N_0}{1000}\sigma_{12}{}^2\left\{8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right\}^{\frac{1}{2}} \cdot e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Taking $\sigma_{12} = 5 \times 10^{-8}$ cm., $T = 297{\cdot}8°$, $N_0 = 6{\cdot}06 \times 10^{23}$, $M_1 = 145$, $M_2 = 381$, and $E = 15{,}500$ cals., we have $k_{24\cdot8°} = 4{\cdot}50 \times 10^{-1}$ l./g.-mol./sec., which is 450 times greater than the observed velocity constants (see Table V).

The assumptions upon which equation (10) is based are that reaction occurs whenever the ions collide with sufficient violence, and that the total number of collisions is given by the gas formula. Now the low efficiency of activating collisions between tri-iodide and phenylpropiolate ions which is suggested by the factor 1/450 may be apparent only, due to the necessity for ternary collisions, involving these ions and a molecule of water. The frequency of encounters in which molecules of solvent take part decreases with a rise in temperature, a circumstance which necessitates a correction in the critical increment. The supposition may be tested provided that the number of ternary collisions can be calculated. The exact equation is not known, but a sufficiently close approximation to it may be obtained in the following manner, by considering in the first instance the total number of collisions occurring per second between water molecules and solute ions of one kind (mass = m_A, diameter = σ_A, concentration = n_A mols. per c.c.). This is related to the viscosity (η) of the solvent by the expression (see J., 1932, 95) :

$$Z_{A,W} = 3\pi\eta\sigma_A n_A/2m_A.$$

The chance that an ion of the second kind (B) shall take part in such a collision is approximately $v_B/(v_A + v_B + v_W)$, where v is the actual volume of each molecular species per c.c., v_W being that of water. In dilute solution, this reduces to v_B/v_W, or, neglecting the differences in the diameters, to n_B/n_W, n_B and n_W being the number of ions of B and of molecules of water respectively in 1 c.c. The frequency of ternary collisions is therefore given approximately by the equation

$$Z_{A,B,W} = 3\pi\eta\sigma n_A n_B/2m_A n_W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If this is combined with the expression for the bimolecular constant (in g.-mol./l.) (*Phil. Mag.*, 1932, **14**, 112), the theoretical value of k is

$$k = \frac{N_0}{1000} \cdot \frac{3\pi\eta\sigma}{2m_A n_W} \cdot e^{-E'/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The corrected energy of activation (E'), found by plotting log $k_{\text{obs.}}/\eta$ against $1/T$, becomes 19,200 cals. At 24·8°, with $\eta = 9{\cdot}0 \times 10^{-3}$ g./cm.-sec., $\sigma = 5 \times 10^{-8}$ cm., $m_A = 2{\cdot}39 \times 10^{-22}$ g., and $n_W = 3{\cdot}37 \times 10^{22}$, the calculated value of k becomes $1{\cdot}16 \times 10^{-3}$, which is in very close agreement with the observed value.

The Mechanism and Molecular Statistics of the Reaction in the Region of High Dilution.—Over the complete range of concentration which has been examined (0·0005—0·1M), the reaction retains its bimolecular character. When c exceeds 0·0025M, the velocity alters but little with the initial concentrations, but below this limit, $k_{\text{obs.}}$ increases rapidly with the dilution. So also does the concentration of hypoiodous acid (see Table IV), and it was therefore suspected that these two facts were related. On examination, the hypothesis that reaction follows a collision between a hypoiodous acid molecule and a β-phenylpropiolate ion accounted for all the phenomena.

The observed bimolecular constant (k) corresponding to an initial concentration of $8{\cdot}75 \times 10^{-4}$ g.-mol./l. was found to be $1{\cdot}11 \times 10^{-3}$ (see Fig. 1). The contribution due to the tri-iodide reaction is $8{\cdot}9 \times 10^{-4}$, hence the component of the velocity due to HOI is $2{\cdot}2 \times 10^{-4}$. The concentration of HOI in these circumstances [equation (6) and Table IV] is $1{\cdot}74 \times 10^{-7}$, so the bimolecular constant in terms of hypoiodous acid and phenylpropiolate ions is

$$k_2 = 2{\cdot}2 \times 10^{-4} \times 8{\cdot}75 \times 10^{-4}/1{\cdot}74 \times 10^{-7} = 1{\cdot}11.$$

If the explanation offered is correct, the velocity of the reaction in absence of potassium iodide should be much greater than in its presence. This has been found to be the case. In water at 24·8°, the bimolecular constant relating to an initial concentration of iodine and propiolate of 0·0005 is $1{\cdot}30 \times 10^{-2}$. The concentration of hypoiodous acid under these conditions is given approximately by the relation

$$[\text{HOI}] = \sqrt[3]{K_2[\text{I}_2]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Since $K_2 = 2{\cdot}95 \times 10^{-13}$ and $[\text{I}_2] = 5{\cdot}0 \times 10^{-4}$, $[\text{HOI}] = 5{\cdot}28 \times 10^{-6}$. The velocity of reaction being ascribed entirely to hypoiodous acid, the bimolecular constant becomes $k_2 = 1{\cdot}30 \times 10^{-2} \times 5 \times 10^{-4}/5{\cdot}28 \times 10^{-6} = 1{\cdot}23$, which is in fair agreement with that found for the results obtained in the presence of potassium iodide. Similar results referring to another temperature are given below. It is seen that at both temperatures, k_2 is reasonably constant over a forty-fold range in the initial concentration of hypoiodous acid.

Temp.	Total [KI] × 10³.	[HOI] × 10⁶.	k_2.	Mean	Temp.	Total [KI] × 10³.	[HOI] × 10⁶.	k_2.	Mean
24·8°	0	5·28	1·23	1·17	40·3°	0	9·83	5·60	5·81
,,	3·50	0·163	1·11		,,	5·00	0·247	6·01	

These data may be summarised in the form $k_2 = 1{\cdot}35 \times 10^{14} . e^{-19{,}100/RT}$. Comparison with the theoretical velocity given by equation (10) shows that the reaction between the organic ion and hypoiodous acid is highly efficient, in that at least 100 molecules are transformed for every activating collision. How far this can be taken as evidence that a chain mechanism is at work is doubtful, for the values of K_2 are not very precise, and equations (6) and (13) are both approximations.

Halogens in solution frequently react in the more reactive form of the hypohalous acid; such is definitely the case, *e.g.*, in the reaction between the halogens and oxalic acid (Griffith and McKeown, *Trans. Faraday Soc.*, 1932, **28**, 757), arsenious acid, and hydrogen peroxide in aqueous solution (Bray, *Chem. Rev.*, 1932, **10**, 161), and probably also with bromine and cinnamic acid in ethyl-alcoholic solution (Williams, J., 1932, 979).

The general equation for the velocity of the addition of iodine to phenylpropiolic acid in aqueous solution takes the form

$$-d[I_2]/dt = k_1[A][I_3^-] + k_2[A][HOI]$$

or

$$-\frac{d[I_2]}{dt}\cdot\frac{1}{[A]} = \frac{k_1}{K_1}[I_2][I^-] + k_2 \, . \, K_2\frac{[I_2]}{[H^+][I^-]} \quad . \quad . \quad . \quad . \quad (14)$$

This accounts for all the known facts, including a minimum velocity dependent upon the concentration of iodide ion, but mathematical difficulties are too great to allow us to calculate the position of the minimum point.

There are two remaining facts which are not completely understood. By extrapolating the nearly horizontal portion of the curve in Fig. 1 to infinite dilution, and plotting log $k_{obs.}/k_\infty$ against the square root of the ionic strength, the slope of the resulting curve corresponds more closely to that of a reaction of zero ionic type than to one between two electrically charged molecules.

The addition of hydrogen ion to solutions in the very dilute range of concentrations diminishes the rate, but not to the same extent as does the addition of iodide ion. The difference in the two effects is noteworthy, but is no doubt due in part to the subsidiary effect produced by hydrogen ion upon the dissociation of phenylpropiolic acid.

By selecting a concentration (*viz.*, 0·01), where the reaction due to hypoiodous acid is negligible, it has been found that the reactivity of the undissociated phenylpropiolic acid, HA, is lower than that of its anion, A^-; *e.g.*, at 40·3°, with $[A^-] = 0{\cdot}01$, $k_{obs.} = 3{\cdot}34 \times 10^{-3}$; with $[HA] + [A^-] = 0{\cdot}01$, $k_{obs.} = 2{\cdot}49 \times 10^{-3}$; the addition of 0·0344$M$-$H^+$ further reduces the velocity to $1{\cdot}64 \times 10^{-3}$. As, however, the temperature coefficient of the dissociation constant of phenylpropiolic acid is not known, this aspect of the problem has not been pursued beyond the qualitative stage.

SUMMARY.

The kinetics of the addition of iodine to β-phenylpropiolic acid in aqueous solution have been investigated at five temperatures, and at dilutions ranging from 10 to 2000 litres.

At moderate concentrations, the reaction appears to occur entirely between the tri-iodide ion and the organic ion. Only one in 450 of the binary collisions results in chemical change, but the assumption that ternary collisions involving water molecules are necessary leads to agreement between theoretical and experimental velocities.

At concentrations below $2{\cdot}5 \times 10^{-4}M$, the reaction is apparently initiated by collisions between molecules of hypoiodous acid and phenylpropiolate ions, each activating collision now resulting in the transformation of over 100 organic molecules.

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