

CXLII.—*Studies on Hypophosphorous Acid. Part II.* *Its Reaction with Iodine.*

By ALEC DUNCAN MITCHELL.

IN estimating hypophosphorous acid by means of mercuric chloride according to the method given by Treadwell ("Quantitative Analysis," p. 289), it was found that the oxidation proceeded readily to phosphorous acid, but relatively slowly to phosphoric acid. It was therefore decided to investigate the progress of the reaction, and certain facts were noted in the first stage—the oxidation to phosphorous acid—which are, briefly:

(1) The concentration of mercuric chloride appeared to have no influence on the reaction velocity except when very dilute.

(2) The reaction was accelerated by the addition of hydrochloric acid.

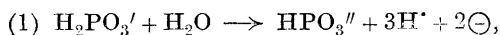
(3) It was therefore auto-catalytic, owing to the hydrochloric acid produced.

(4) The initial velocity was approximately proportional to the product of the concentrations of the hydrogen ions and the hypophosphorous acid.

From these facts, it was concluded that the oxidation to phosphorous acid involved two successive reactions: the first, of measurable velocity, in which the mercuric chloride took no part, and the second, of relatively great velocity, in which the mercuric chloride functioned. No conventional hypothesis appeared adequately to explain these facts.

In order to investigate certain points more fully, an analogous reaction was sought in which the analytical method used would be of greater applicability. The reaction with iodine was found to be accurately comparable, and is here described. That with mercuric chloride will be communicated later, but it may be mentioned that comparative experiments with iodine and mercuric chloride, respectively, showed that the measurable velocity was identical in the two cases, thus lending additional support to the view that only hypophosphorous acid functions in the slower reaction.

Steele (T., 1907, **91**, 1641) had already investigated the reaction with iodine, and obtained the same general results as above. For the reaction $\text{H}_3\text{PO}_2 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 2\text{HI}$ he offered the following explanation: the slow stage is represented by



which proceeds, liberating free ionic charges, if there is also present a

substance capable of utilising them as rapidly as they are formed: (2) $I_2 + 2\ominus = 2I'$. He points out that several hypothetical schemes may be substituted for (1) in order to account for the production of free electrons, but that intermediate compounds containing iodine cannot be formed in this stage. Any equilibrium between hypophosphorous acid and an "active" form would not agree with the facts if it be assumed that equilibrium is instantaneously restored; but it is now shown that, if equilibrium is restored at a finite rate, the existence of an intermediate "active" form adequately agrees with the facts and renders unnecessary the above unconventional hypothesis.

The reaction has now been studied under more diverse conditions, and certain new aspects have been investigated.

Steele ignored two factors, which are here shown to have an important bearing on the problem:

(1) The depression by mineral acids of the ionisation of hypophosphorous acid, which he regarded as "probably slight." Taking this into account by utilising data obtained in the author's paper on the subject (this vol., p. 957), it is shown clearly that the effect is considerable, and that hypophosphorous acid functions as undissociated molecules. Steele obtained higher constants in stronger acid solutions than in weaker, but, instead of attributing this to the increased proportion of molecules, he ascribed it to the fact that he was using more dilute hypophosphorous acid solutions, the behaviour of which he thought anomalous, and suggested the idea that its ions were the active part of the acid.

(2) The part played by the iodine, which is apparently negligible over small ranges at moderate concentration, but becomes relatively great as the concentration decreases. Steele suggested that it played no part in the reaction until about nine-tenths of it had been used up, but that it then took part in an apparently bimolecular reaction. This is now shown to be erroneous. Also, he was led to ascribe certain discrepancies to the above-mentioned anomalous behaviour of hypophosphorous acid in dilute solution, but these are now shown to be regularised when the function of the iodine is considered.

From the data obtained from about thirty experiments now described, actual rates of decrease (ds/dt) of hypophosphorous acid were calculated at the beginning, middle, and end of each experiment, and when these were divided by the concentrations, at time t , of hypophosphorous acid, l_t , and hydrogen ions, h_t , and by the proportion of undissociated hypophosphorous acid molecules, $1 - \alpha_t$, ninety values were obtained for the expression $(ds/dt)/h_t l_t (1 - \alpha_t)$ which were almost constant when the corresponding concentrations

of iodine exceeded $N/50$, but which decreased more and more rapidly with decreasing concentrations of iodine. This behaviour was ultimately found to be represented by the formula

$$[1 + rh_i/a_i](ds/dt) = kh_i l_i (1 - a_i),$$

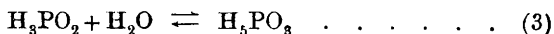
where a_i represents the concentration of the iodine molecules and r and k are constants.

It will be noticed that this equation takes the form

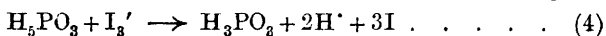
$$ds/dt = kl_i(1 - a_i)h_i a_i / (a_i + rh_i)$$

which the reaction would give if it were simply bimolecular between hypophosphorous acid molecules and iodine, being accelerated by hydrogen ions and retarded by a function, $a_i + rh_i$, of the iodine. Meyerhoffer (*Zeitsch. physikal. Chem.*, 1888, **2**, 585) found that iodine had a retarding effect, proportional to its concentration plus a constant, on the reaction $\text{HBrO}_3 + 6\text{HI} = \text{HBr} + 3\text{H}_2\text{O} + 3\text{I}_2$; but the slightly modified form mentioned above has not been regarded as a valid explanation of the present reaction, since it is difficult to understand why iodine should exert a retarding effect when its concentration is zero, and its acceptance would imply that the hydrogen ions had simultaneously both accelerating and inhibiting effects.

The following hypothesis is found to require the same mathematical expression and to fulfil all the other requirements previously postulated. Hypophosphorous acid molecules are originally in equilibrium with a very small quantity, y , of an "active" form, say H_5PO_3 , in which the action of the hydrogen ions is to accelerate re-establishment of equilibrium:



and the iodine, reacting, as shown later, as the I_3' ion, takes part:



The rate of formation of phosphorous acid, according to (4), will be:

$$ds/dt = k_2 y a_i \quad \dots \quad (5)$$

k_2 being a very large reaction velocity-constant. The equilibrium in (3) is

$$kl_i(1 - a_i)h_i = k_1 y_i h_i \quad \dots \quad (6)$$

k and k_1 being the reaction velocity-constants in the two directions, k_1 being large, but not infinite, and the amount, y_i , being so small as not appreciably to affect the amount of hypophosphorous acid.

Then the rate of increase in y , owing to the tendency to restore equilibrium, is $kl_i(1 - a_i)h_i - k_1 y_i h_i$, from (6), and its rate of decrease is ds/dt ; hence

$$dy/dt = kl_i(1 - a_i)h_i - k_1 y_i h_i - ds/dt \quad \dots \quad (7)$$

Eliminating y_t from (5) and (7), we have

$$(d^2s/dt^2)/k_2 + (ds/dt)^2/k_2\alpha_t + [\alpha_t + k_1h_t/k_2]ds/dt = k\alpha_t l_t(1 - \alpha_t)h_t \quad (8)$$

This expression can be simplified for most reactions, as follows. Since k_2 is very large and k_1 moderately large compared with k , and d^2s/dt^2 and $(ds/dt)^2$ are of a lower order of magnitude than the other terms, and, moreover, are of opposite sign (except in certain cases), the first two terms may be neglected as a first approximation, and one has

$$[\alpha_t + k_1h_t/k_2]ds/dt = k\alpha_t l_t(1 - \alpha_t)h_t$$

or

$$[1 + k_1h_t/k_2\alpha_t]ds/dt = kl_t(1 - \alpha_t)h_t \quad . \quad . \quad . \quad (9)$$

which is identical with the formula obtained experimentally when the constant k_1/k_2 is replaced by the constant r . As the best value of r is found to be 0.012, this explains why the iodine appears not to function until it becomes dilute, when α_t is small.

Now, $l_t = l - s$, $\alpha_t = \alpha - s$, and $h_t = h + ms$, since h_t is found to be a linear function of s . If, therefore, α_t is a simple function of s , the expression can be integrated. In some cases it is a linear function, so that $\alpha_t = \alpha - ns$. Letters without suffixes denote initial values, and m and n are constants for any particular experiment. The expression simplifies to

$$k \cdot dt = ds[1/(l - s)(h + ms)(1 - \alpha + ns) + r/(l - s)(\alpha - s)(1 - \alpha + ns)] \quad (9a)$$

and one obtains, on integration,

$$kt = \frac{1}{(1 - \alpha + nl)(h + ml)[m(1 - \alpha) - hn]} \left[\{m(1 - \alpha) - hn\} \log \frac{l}{l - s} - \right. \\ \left. n(h + ml) \log \frac{1 - \alpha + ns}{1 - \alpha} + m(1 - \alpha + ln) \log \frac{h + ms}{h} \right] + \\ \frac{0.012}{(l - \alpha)(1 - \alpha + ln)(1 - \alpha + na)} \left[(1 - \alpha + ln) \log \frac{\alpha}{\alpha - s} - \right. \\ \left. (1 - \alpha + na) \log \frac{l}{l - s} + n(l - \alpha) \log \frac{1 - \alpha + ns}{1 - \alpha} \right] \quad . \quad . \quad (10)$$

In cases where α_t is not sufficiently nearly a linear function of s , it is better to put $n = 0$, regarding α as constant, and subsequently to employ the average value of $(1 - \alpha)$ for the period concerned in obtaining the value of the constant. Thus one has

$$(1 - \alpha)kt = \left[\log l - l - s + \log \frac{h + ms}{h} \right] / (h + ml) + \\ 0.012 \left[\log \frac{\alpha}{\alpha - s} - \log \frac{l}{l - s} \right] / (l - \alpha) \quad . \quad . \quad (11)$$

The exceptional cases mentioned when simplifying (8) to (9) are those in which the initial hydrogen-ion concentration is relatively

small and the reaction velocity increases at first to a maximum, so that d^2s/dt^2 is not negative until that maximum is passed. These cases give results in fair agreement with the others when formula (11) is used, so that even when both the neglected terms in (8) are positive, their combined effect is very slight.

It is interesting to note that if hydrogen ions actually took part in the reaction (3) in one direction only, and were not merely catalytic, h_i would disappear from the second term on the left of equation (9), and the theory would require results not consistent with practice.

In the calculations, it is assumed that α for the hypophosphorous acid depends only on the initial amount present and on the concentration of the hydrogen ions, and is not affected by the replacement of hypophosphorous acid by phosphorous acid. This assumption is justified, because the ionising powers of the two acids are very similar, and the total of the two acids remains unchanged, so that, according to the "total ion" hypothesis (Arrhenius, *Zeitsch. physikal. Chem.*, 1888, **2**, 285; 1899, **31**, 218; Bray and Hunt, *J. Amer. Chem. Soc.*, 1911, **33**, 781; and Mitchell, this vol., p. 957), for any definite hydrogen-ion concentration there is a definite value of α for each initial concentration of hypophosphorous acid. Also it does not appear that the undissociated molecules of the mineral acids have any appreciable catalytic influence in the concentrations used.

In several experiments (Nos. I, II, and V), possible oxidation to phosphoric acid was checked alkalimetrically (see p. 1332) and found to be negligible. It has, indeed, been shown to be inhibited in an acid medium (Boyer and Bauzil, *J. Pharm. Chim.*, 1918, [vii], **18**, 321), and Federlin (*Zeitsch. physikal. Chem.*, 1902, **41**, 565) could only obtain measurable velocities for the reaction between phosphorous acid and iodine by using concentrated solutions.

In one phase of this work, in order to obtain small yet constant concentrations of hydrogen ions, a "regulator" solution was used, consisting of equimolecular proportions of phosphoric acid and potassium dihydrogen phosphate, so that in the reaction-mixture each was present in molar concentration. Since the concentration of hydrogen ions was constant, the degree of ionisation of hypophosphorous acid was also constant, and, for these experiments, (9) becomes

$$(1 + r'/a_i)ds/dt = k'l_i \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where r' and k' are constants, r' being assigned the value 2.0 as giving most consistent results. Attempts to relate r' to rh and k' to $k(1-\alpha)h$, which they replace, are complicated by lack of

sufficient data for such concentrated solutions, but h is of the order $N/50$ and $(1-\alpha)$ about 0.4, so that it is concluded that both k' and r' are several times greater than would be expected.

Owing to the form of equations (11) and (12), in many cases they gave extremely concordant values of a constant based on the equation $ds/dt = k''l_i\sqrt{a_i}$, which was found not to hold when applied to iodine concentrations of a different order. In experiments XI, XX, and XXV this constant is given, as well as k or k' , as an interesting example of the danger of relying on what happens to be merely a mathematical coincidence.

The integrated form of (12) is

$$k't = \log \frac{l}{l-s} + \frac{2.0}{l-a} \left(\log \frac{a}{a-s} - \log \frac{l}{l-s} \right) \quad (13)$$

The I_3' Ion.—Considering the equilibrium $I_3' \rightleftharpoons I_2 + I'$ investigated by Jakowkin (*Zeitsch. physikal. Chem.*, 1896, **20**, 19), it can be shown that, for any stage of the reaction,

$$[I_2] = K(a-s)/(p+s-a)$$

to a close degree of approximation, where p is the molar concentration of the potassium iodide (assumed completely ionised), and that $[I_3'] = (a-s)[1 - K/(p+s-a)]$, since p increases by $2s$ and a decreases by s , when s molecules of iodine have been changed to iodide ions. At the beginning of an experiment, when s is zero, $[I_2] = Ka/(p-a)$, and is therefore independent of the concentration. It was at first thought that this would account for the peculiar behaviour of the iodine in apparently not affecting the velocity of the reaction; but $[I_2]$ decreases more rapidly than $a-s$ with increase of s , so that, if the iodine reacted as such, its apparent active mass should fall off more rapidly than $a-s$, whereas actually it changes far less rapidly. Moreover, a comparison was made in experiments XII and I which were identical, except that in XII potassium iodide was added, so that p was equal to $9.78a$, whereas in I it was $3.76a$; if molecular iodine were the active factor, the initial reaction velocities should be in the ratio 2.76 to 8.78, whereas they were almost identical. Experiments XXV and XXVI also illustrate this in presence of the "regulator" solution. The iodine therefore does not react as molecules.

Thus it is the I_3' ion which functions, and, using the constant 0.00135 given by Jakowkin for the equilibrium, it is found that this ion constitutes 99 per cent. of the available iodine in $N/10$ -solutions, but is less in weaker solutions, being only about 65 per cent. in $N/400$ -solutions at the beginning of reactions, and increasing somewhat as the reaction proceeds. This change in the relative concentration of the I_3' ion has been ignored throughout, as the

correction involved only affects the smaller term, and is, moreover, less at the end of a reaction than at the beginning, since the increase of iodide ions outweighs the effect of dilution, and thus increases the proportion of I_3' ions. It would unnecessarily complicate equations, which are evidently sufficiently accurate to demonstrate the validity of the hypothesis.

In conclusion, it may be said that, whatever the nature of the supposed "active" form of hypophosphorous acid, its existence could probably not be detected by chemical means, and, as the indications are that it is less than 1 per cent. of (and in constant proportion to) the acid molecules, its detection by physical means would be difficult. It is also possible that another hypothesis could be found which would require similar mathematical expression, but, if so, it is certainly more complicated than that developed here.

EXPERIMENTAL.

The reactions were carried out in stoppered brown glass bottles in a thermostat at $25 \pm 0.05^\circ$. The iodine solution and hydrochloric acid or "regulator" solutions, when used, were made up to 400 c.c., and when they had acquired the temperature of the thermostat, 1.013, 2.000, or 4.000 c.c. of a concentrated solution of hypophosphorous acid were added from standardised pipettes. At definite times, quantities were withdrawn and run into a large volume of water containing the volume of standard sodium thio-sulphate solution estimated to be necessary, and the final adjustment made at once. Check experiments showed that the hypophosphorous acid did not affect the titrations.

The stock iodine solution was accurately decinormal. As it was subsequently required to know the potassium iodide content of this solution, it was found to be 31.2 grams per litre (or 3.76 molecules per molecule of iodine) by an adaptation of the method with potassium iodate described by Sutton ("Volumetric Analysis," p. 133).

The stock hypophosphorous acid solution was a chemically pure article of commerce (D 1.14) which showed no impurities other than a little phosphorous acid. Its composition was checked by two methods: 25 c.c. of a one-tenth solution gave 1.5124 grams of $Mg_2P_2O_7$, therefore $H_3PO_2 + H_3PO_3 = 5.45$ moles. per litre; 20 c.c. of one-fiftieth solution required 21.80 c.c. of $N/10$ -NaOH with methyl-orange, and 22.60 c.c. with phenolphthalein. Since hypophosphorous acid is monobasic to both indicators and phosphorous acid is monobasic to the former and dibasic to the latter, the former is 5.25 molar and the latter is 0.20 molar, thus giving

a total identical with the gravimetric value. For obtaining the value of l , the solution was regarded as 5.25*N*, and the values of the hydrogen ions were based on a normality of 5.45, since the second hydrogen ion of phosphorous acid can be ignored.

Calculation of Results.—The degrees of dissociation of hydrochloric acid are taken from the results of Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781), and the hydriodic acid is reckoned as hydrochloric acid for this purpose. The degree of dissociation of the hypophosphorous acid in the presence of the mineral acids is obtained by methods based on the author's recent communication on the subject (this vol., p. 957). From table I given therein, a curve is constructed showing the relation between α and the concentration of hydrogen ions, a/v , when no extraneous acid is present. From this it is possible to obtain a series of curves, one for each value of l , showing the relation between α and the concentration of extraneous hydrogen ions (H'_x), as follows: for a definite concentration of hypophosphorous acid, l , the value of α when H'_x is zero can be obtained at once. A slightly lower value, α_1 , is then selected, and the concentration of hydrogen ions in equilibrium with the acid alone at that degree of ionisation is found from the first curve; this must also be the concentration of hydrogen ions in the equilibrium if foreign acid is present, as shown in the paper quoted; from this is therefore deducted $l\alpha_1$, due to the hypophosphorous acid itself, and the remainder is H'_x . A series of corresponding values of α and H'_x is obtained in this way for each value of l , and from the resulting curve the value of α can be obtained for a known H'_x . This method is simpler and of wider applicability than solving the equation developed in the former communication.

In order to avoid small decimals, all concentrations are multiplied by 200, and the value of k should therefore be multiplied by 200 in order to give absolute units. Time, t , is in minutes; $a-s$ shows the iodine concentration in molecules; s shows the number of moles. reduced; $l-s$ the hypophosphorous acid remaining. The column HI shows the original hydrochloric acid (when used) plus $2s$, the hydriodic acid formed. H'_{HI} are the corresponding hydrogen-ion concentrations of the mineral acids, the degree of ionisation (not recorded) being assumed to be unaffected by the presence of the weaker acids. α gives the degree of dissociation of the hypophosphorous and phosphorous acid, and under H'_p is recorded $l\alpha$, the hydrogen ions derived from them, the slight correction necessary for the phosphorous acid initially present having been made throughout. Then follow the total hydrogen-ion concentration, h , and $1-\alpha_M$, the mean value of $1-\alpha$ for the period

(or $1 - \alpha_H$, the value at the middle of the period), for which the constant k is calculated.

Formula (11) is used except where otherwise stated, and in any one experiment the deviations of k from the mean rarely exceed 3 per cent.

The six following experiments were without original hydrochloric acid.

Experiment I.

t .	$a - s$.	s .	$l - s$.	HI.	H'_{HI} .	a .	H'_P .	h .	$1 - \alpha_M$.	$k \times 10^5$
0	4.99	—	10.52	—	—	0.645	7.10	7.10	—	—
5	4.82	0.17	10.35	0.34	0.34	0.640	6.99	7.33	0.355	118
20	4.34	0.65	9.86	1.31	1.28	0.625	6.77	8.05	0.365	114
50	3.29	1.70	8.82	3.40	3.27	0.590	6.44	9.71	0.382	112
80	1.96	3.03	7.48	6.07	5.77	0.553	6.00	11.77	0.400	117
105	0.98	4.01	6.51	8.02	7.58	0.530	5.79	13.37	0.413	118
125	0.19	4.80	5.72	9.59	9.02	0.513	5.58	14.60	0.421	120
145	0.03	4.96	5.56	9.93	9.34	0.510	5.57	14.91	0.422	113

$$m = 1.543. \text{ Mean} = 116$$

The data of the other five experiments gave constants of the same order of agreement, and are here summarised.

Expt.	a .	l .	a .	$H'_P = h$.	m .	$k \times 10^5$.
II.	9.80	20.62	0.552	11.81	1.546	148
IV.	9.92	5.34	0.735	4.07	1.651	134
V.	9.86	10.44	0.645	7.05	1.606	124
VI.	2.43	25.50	0.525	13.91	1.425	139
VII.	2.46	13.00	0.622	8.40	1.507	120

[In experiment VII, the complete formula (10) was used with $n = 0.030$.]

The following experiment is comparable with I, and shows the negligible effect of adding more potassium iodide (see p. 1327):

XII.	4.97	10.44	0.650	7.05	1.566	114
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The next thirteen experiments were with initial hydrochloric acid. Only experiments III and XVI are given in detail, the latter showing the accuracy of the constant at very low concentrations of iodine.

Experiment III.

t .	$a - s$.	s .	$l - s$.	HI.	H'_{HI} .	a .	H'_P .	h .	$1 - \alpha_M$.	$k \times 10^5$.
0	4.93	—	10.44	11.30	10.59	0.496	5.38	15.97	—	—
5	4.33	0.60	9.84	12.51	11.68	0.485	5.26	16.94	0.510	(139)
10	3.89	1.04	9.40	13.38	12.47	0.478	5.18	17.65	0.513	126
15	3.34	1.59	8.85	14.48	13.47	0.470	5.10	18.57	0.517	129
20	2.80	2.13	8.31	15.56	14.44	0.463	5.02	19.46	0.520	130
25	2.31	2.62	7.82	16.55	15.35	0.457	4.95	20.30	0.524	129
30	1.81	3.12	7.32	17.55	16.24	0.450	4.88	21.12	0.527	130
35	1.40	3.53	6.91	18.37	16.97	0.445	4.82	21.79	0.530	127
40	0.95	3.98	6.46	19.25	17.75	0.439	4.76	22.51	0.533	128
45	0.57	4.36	6.08	20.02	18.44	0.434	4.70	23.14	0.535	128
50	0.28	4.65	5.79	20.60	18.95	0.430	4.66	23.58	0.537	128
55	0.11	4.82	5.62	20.94	19.26	0.428	4.64	23.90	0.538	128
60	0.04	4.91	5.53	21.12	19.41	0.426	4.62	24.03	0.539	130

$$m = 1.644. \text{ Mean} = 128$$

Experiment XVI.

<i>t.</i>	<i>a - s.</i>	<i>s.</i>	<i>l - s.</i>	HI.	H _{HI} .	<i>a.</i>	H _P .	<i>h.</i>	1 - <i>a_M</i> .	<i>k</i> × 10 ⁵
0	0.499	—	2.670	14.10	13.13	0.515	1.43	14.56	—	—
2	0.460	0.039	2.631	14.18	13.20	—	1.42	14.62	0.486	(135)
7	0.389	0.110	2.560	14.32	13.33	—	1.42	14.75	—	116
12	0.319	0.180	2.490	14.46	13.47	—	1.42	14.89	—	116
16	0.267	0.232	2.438	14.57	13.56	—	1.41	14.97	—	116
22	0.196	0.303	2.367	14.71	13.68	—	1.40	15.08	—	116
28	0.141	0.358	2.312	14.82	13.79	—	1.40	15.19	—	116
44	0.043	0.456	2.214	15.01	13.96	0.503	1.39	15.35	0.491	116
<i>m</i> = 1.73. Mean = 116										

Expt.	<i>a.</i>	<i>l.</i>	HI.	H _{HI} .	<i>a.</i>	H _P .	<i>m.</i>	<i>k</i> × 10 ⁵
XIV.	0.76	10.30	11.10	10.41	0.498	5.33	1.647	128
XV.	0.250	2.670	28.20	25.66	0.409	1.13	1.830	136
XVII.	0.250	2.670	14.10	13.13	0.515	1.43	1.764	132
XVIII.	0.986	1.040	28.0	25.5	0.415	0.45	1.66	123
XIX.	0.958	20.20	10.86	10.19	0.459	9.64	1.572	145
XX.	0.985	2.080	28.0	25.5	0.412	0.9	—	122
XXI.	0.985	2.080	11.20	10.47	0.550	1.20	1.81	112
XXII.	0.493	1.040	28.0	25.5	0.415	0.44	—	137
VIII.	4.97	2.67	113.0	96.0	0.25	—	—	137
IX.	2.485	2.67	56.5	51.0	0.30	—	—	129
XI.	2.485	2.67	113.0	96.0	0.25	—	—	131

Where no value is given for *m*, *h* is regarded as constant, and in the last three experiments the value of H_P has been neglected, as not appreciably affecting the total value of *h*. Also, in the last three experiments, *a* was obtained by extrapolation, and is therefore only approximate.

In experiment XI, eight values, all between 300 and 312, were obtained for the constant *k*'' × 10⁴ mentioned on p. 1327. In experiment XX, similarly all ten values were between 107 and 112.

The following seven experiments were in a solution molar with respect to both phosphoric acid and potassium dihydrogen phosphate as "regulator" (see p. 1326). Formula (13) is used in each case. Experiment XXIII is given in detail.

Experiment XXIII.

<i>t.</i>	<i>a - s.</i>	<i>s.</i>	<i>l - s.</i>	<i>k</i> ' × 10 ⁴ .
0	4.996	—	10.50	—
2	4.596	0.400	10.10	274
6	3.898	1.098	9.40	267
10.2	3.246	1.750	8.75	268
15	2.578	2.418	8.08	272
20	1.996	3.000	7.50	274
25	1.522	3.474	7.03	274
33	0.950	4.046	6.40	276
45	0.432	4.564	5.94	276

Mean 272

3 C* 2

Expt.	a .	l .	$k' \times 10^4$.
XXIV.	4.970	5.224	271
XXV.	2.494	5.250	254
XXXI.	0.4992	1.050	264
XXXII.	0.2496	1.050	291
XXXIII.	0.4992	0.525	266
XXXIV.	0.4994	5.250	240

For XXV, all eight values of $k'' \times 10^4$ (p. 1327) are between 600 and 626.

Experiment XXVI was exactly comparable with XXV, except that it contained potassium iodide in the proportion of 15.8 molecules to each molecule of iodine; XXV, and all other experiments except XII, have the proportion 3.76. The constant, $k' \times 10^4$, was 255; the agreement with 254, obtained in XXV, shows that iodine functions as the I_3' ion.

Experiment XXVII, at 11.6° , gave a constant, $k' \times 10^4 = 54.8$, and as it is exactly parallel with XXV, the temperature-coefficient is 4.64 for 13.4 degrees. Logarithmic proportion reduces this to 3.14 for 10 degrees and 2.22 for 7 degrees. Steele found 3.1 for 10 degrees for solutions without added acid or "regulator." Since the term involving r' , the ratio between two rapid reaction velocities (see formula 12), accounts for more than half the value of the constants, it appears that this ratio is practically unaltered over the range of temperature employed.

The agreement between the constants obtained in this series of "regulator" experiments shows clearly that the iodine must function in the manner shown in the equations used. The effect of neglecting it is very much more apparent in this series than in the earlier experiments.

In order to detect possible oxidation to phosphoric acid, the following procedure was adopted. If phosphorous acid only is produced, each molecule of iodine reduced gives rise to 2 molecules of hydriodic acid, and also changes 1 molecule of monobasic hypophosphorous acid to 1 molecule of dibasic phosphorous acid, phenolphthalein being used as indicator; whereas, if phosphoric acid is produced, 2 molecules of iodine give rise to 4 molecules of hydriodic acid, and still only raise the basicity by unity. Therefore, in the former case, the increase of acidity should be 1.5 times the number of equivalents of iodine consumed, and in the latter case the ratio should be 1.25. In every case tested, the ratio has been very close to 1.5, so that the production of phosphoric acid is very slight.

Expt. I.—At t_{145} , 20 c.c. required 14.84 c.c. of $N/10$ -NaOH more than at t_0 ; iodine consumed = 9.93 c.c. of $N/10$ - $Na_2S_2O_3$; ratio = 1.495.

Expt. II—Increase of alkali titre at $t_{50}=14.63$ c.c.; iodine consumed = 9.75 c.c.; ratio = 1.501.

Expt. V.—Increase of alkali titre at $t_{150}=19.58$ c.c.; iodine consumed = 13.10 c.c.; ratio = 1.495.

For the same purpose in the "regulator" series, an experiment (XXVIII) was carried out exactly parallel with XXV, except that hypophosphorous acid was replaced by the same concentration of phosphorous acid. In three hours, less than one-half per cent. of the iodine was reduced, whereas in experiment XXV, 50 per cent. was reduced in twenty-two minutes.

Experiment X was carried out with hypophosphorous acid which was previously neutralised (to methyl-orange), and is comparable with I. In five hours, less than 5 per cent. of the iodine was reduced; as the second hydrogen ion of the phosphorous acid, originally present to a slight extent, would be sufficient to start the reaction, and so provide more hydrogen ions, it is probable that reaction in neutral solution is extremely slow, and that the $\text{H}_2\text{PO}_2'$ ion does not react, except, possibly, in the presence of hydrogen ions, in which case reaction is evidently so slow as not greatly to affect the constancy of values obtained on the assumption that it does not take place at all.

The following experiments of Steele's are quoted, after conversion to the units used herein, to show how the irregularities observed by him are largely accounted for in the light of the present work. The first two columns are derived from his data; the remainder are obtained as in the author's results. The constants obtained by each method are shown, those of Steele being designated by K_s . The letter S after the Roman numerals indicates his experiments.

The value 119 obtained for $k \times 10^5$ in X(S) is in agreement with the author's results, and shows less falling off with time than does K_s . Moreover, for the three experiments, the results are far more concordant than those obtained on Steele's hypothesis. The fact that Steele used a very pure specimen of hypophosphorous acid may account for the slightly lower values in his experiments.

Expt.	α .	l .	α .	$\text{H}^+_{\text{P}} = h$.	$k \times 10^5$.	$K_s \times 10^3$.
X(S)	2.00	20.00	0.555	11.10	119	94
XI(S)	0.500	5.00	0.734	3.67	92	45
XII(S)	0.200	2.00	0.841	1.68	83	24.5

Although the agreement is not so good as in the other results, it is evidently far better than in the results obtained by Steele's method, so that the present hypothesis, which attributes a definite part to the iodine molecules, is apparently more justified by results than that which ignores the iodine and attributes the great decrease

in the constant to a decreased activity of hypophosphorous acid at low concentrations.

This is further supported by a reconsideration of Steele's experiment II, for which he could not obtain a constant without assuming the degree of ionisation to be 0.20 instead of the actual 0.775, which was again supposed to be due to decreased activity. According to the present method, one obtains moderate constancy.

Experiment II(S) at 18°.

<i>t.</i>	<i>a - s.</i>	<i>s.</i>	<i>l - s.</i>	$H^{III}.$	<i>a.</i>	$H^I_P.$	<i>h.</i>	$1 - a_H.$	$k \times 10^5.$
0	4.50	—	4.00	—	0.775	3.11	3.11	—	—
390	4.20	0.30	3.70	0.60	0.750	3.00	3.60	0.235	(25.3)
570	3.98	0.52	3.48	1.02	0.735	2.94	3.96	0.245	(28.1)
1440	2.42	2.08	1.92	4.00	0.660	2.64	6.64	0.280	38.3
1710	2.04	2.46	1.54	4.68	0.643	2.56	7.24	0.290	37.7
1830	1.84	2.66	1.34	5.04	0.636	2.54	7.58	0.295	39.2
2805	0.80	3.70	0.30	6.96	0.597	2.38	9.34	0.340	41.5
3240	0.68	3.82	0.18	7.24	0.592	2.36	9.60	0.355	39.8

$$m = 1.675. \quad \text{Mean} = 39.3$$

If the temperature-coefficient for seven degrees is taken as 2.22 (see p. 1332), this gives the low value of 87 for 25°, but, that the experiments correspond in general is seen from the following summary of experiments, for which the data can be utilised:

Experiment.	III(S).	IV(S).	V(S).	VIII(S).	XIII(S).	XV(S).	XXI(S)
$k \times 10^5$	108	115	119	105	107	113	119
$K_s \times 10^4$	355	400	425	430	425	505	555

Steele's $K_s \times 10^4$, given for comparison, clearly shows the inadequacy of his hypothesis.

The method of treatment now presented obviously places the question on a more systematic basis, although the slight variation of the "constant" from one experiment to another is not accounted for; but the several small approximations made, together with the uncertainty in the choice of the value of the constant r , the large influence, in certain cases, of a difference, $l - a$, which is sometimes very small, and the alteration in the proportion of the iodine which is present as the I_3' ion, may easily account for the variation of 10 per cent. from the mean value, 128×10^{-5} . It is also probable that the H_2PO_2' ions react slowly, and account partly for the variations, since the three highest constants are given by the three greatest concentrations of hypophosphorous acid.

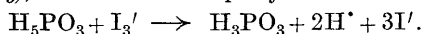
Summary.

(1) The previous attempt to explain the reaction had suggested an hypothesis involving the presence of free ionic charges. By taking

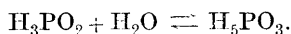
into consideration certain factors which had been ignored, this is shown to be unnecessary, and most discrepancies disappear.

(2) These factors were: (i) the influence of the iodine concentration on the measurable velocity, this influence being slight at moderate dilution, but relatively large at greater dilution, and (ii) the effect of hydrochloric and hydriodic acids on the ionisation of hypophosphorous acid.

(3) The following hypothesis is advanced to explain all the anomalies formerly noted. The hypophosphorous acid *molecules* are in equilibrium with a very small proportion of an "active" form (say H_5PO_3), which reacts rapidly with the iodine,



The restoration of the equilibrium thus displaced is accelerated by hydrogen ions, and forms the measurable reaction,



UNIVERSITY OF LONDON,
SOUTH KENSINGTON, S.W.

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