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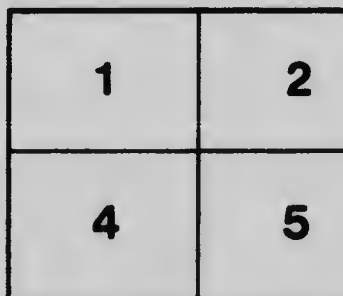
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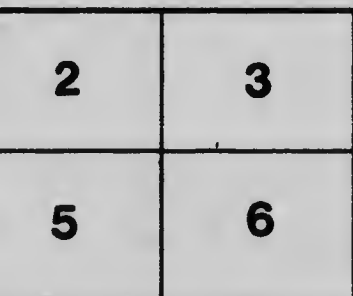
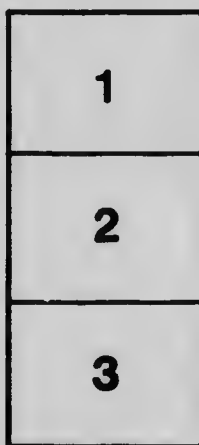
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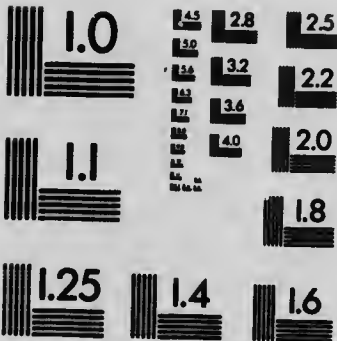
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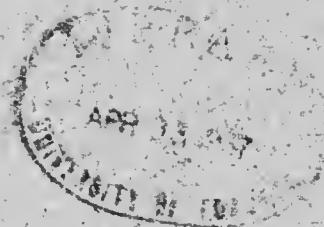
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PAPERS FROM THE CHEMICAL
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NO. 42: THE RATE OF FORMATION OF IODATES
IN ALKALINE SOLUTIONS OF IODINE

BY E. L. C. FORSTER

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THE RATE OF FORMATION OF IODATES IN ALKALINE SOLUTIONS OF IODINE

BY E. L. C. FORSTER

Up to the year 1861, in which Schönbein's "*Beiträge zur nähern Kenntniss des Sauerstoffs und der einfachen Salzbildner*"¹ appeared, it was generally believed that iodine and caustic potash in solution react instantaneously to form potassium iodate. Schönbein showed that the reaction takes place in two stages, and, relying on the close analogy between the chemical behaviour of iodine and chlorine, assumed that the intermediate product was potassium hypoiodite.

With regard to the first stage—formation of hypoiodite—his experiments show that the reaction is incomplete and reversible, leading to an equilibrium between potash, iodine, iodide and hypoiodite; with regard to the second—formation of iodate—which differs from the first in requiring a measurable time for its completion, Schönbein says little, merely pointing out that rise in temperature increases the rate.

In 1894 there appeared a paper by Lonnes² containing measurements of the amount of iodate formed in solutions of iodine and sodium carbonate at measured intervals of time, which show that the rate of the reaction is influenced by the concentrations of the iodide and of the alkali; and in the following year Schwicker³—in the only formal study of the "rate of transformation of potassium hypoiodite" that has as yet appeared—found that the rate was proportional to the square of the concentration of the "iodine," and that increase in the quantity of potash caused a retardation almost proportional to the excess of KOH over that needed to form hypoiodite. In a few experiments in which the iodine was present in slight excess,

¹ Jour. für prakt. Chem. 84, 385 (1861).

² Zeit. anal. Chem. 33, 409 (1894).

³ Zeit. phys. Chem. 16, 303 (1895).

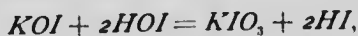


the rate was thought to be proportional to the cube of the concentration of the iodine; no account was taken of the influence of the potassium iodide.

In the opinion of Taylor,¹ Schwicker's results "do not appear to have been altogether satisfactory;" this he ascribes to that author's neglect of the effect due to the potassium iodide in his "iodine" solution. That the rate is in reality largely dependent on the concentration of the iodide, was again shown by Förster and Gyr² in a paper on "the action of iodine on alkalis," published in January of the present year.

In the experiments described in the present paper, I have examined the effect of changing the quantities of potash, iodine, and potassium iodide, on the rate of formation of potassium iodate in alkaline solutions of iodine. When the potash is present in large excess — colourless solutions — the results are simple, and can be expressed with a fair degree of accuracy by saying that the rate is proportional to the concentration of the iodion \bar{I} , the hypoiodion \overline{OI} , and the hypoiodous acid HOI . In brown solutions, on the other hand, where the iodine is in excess, the relations are more complex; and, until the numerical values of certain constants have been determined, it cannot be asserted that the laws suggested by the experiments with colourless solutions are valid for all.

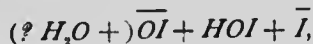
My measurements show that Förster's equation



which in that author's opinion "corresponds in all details" with the reaction itself, must be rejected equally with the older theory adopted by Schwicker and others



and that in all probability it must be replaced by some equation of which the left member is



¹ Chem. News, 76, 17 (1897).

² Zeit. Elektrochemie, 9, 1 (1903).

and of which the right can be filled in, for the present, only by a draft on the imagination.

I. Colourless Solutions

The solution of potash was mixed with the water in a 400 cc Erlenmeyer flask and brought to zero by immersion in a well-stirred bath of ice and water; the mixed solutions of iodine and potassium iodide, also at zero, were then quickly poured in, the whole well shaken and the time noted. After two minutes the first analysis was made; 10 cc was pipetted into a mixture of 50 cc water with 20 cc of a half-saturated solution of ammonium bicarbonate, by which further formation of iodate was prevented, and the residual "iodine" (hypoiodite) was then determined by $n/100$ sodium arsenite with starch as indicator, 0.5 cc of N KI being added to make the end-point distinct; $n/100$ iodine was used to "titrate back", and a correction of 0.1 cc was applied to the reading, being the amount of iodine needed to give the blue colour.

The stock solutions used in all the experiments described in this paper, with the exception of those of Tables XIII and XIV were: 1.092-normal potash, freed from carbonate by lime, 1.151- F potassium iodide, and 0.0936-normal iodine, the latter being prepared by dissolving about 12.7 grams of iodine in 100 cc of the 1.151- F KI and diluting to a liter. They were standardized in the usual manner, with sulphuric acid, silver, and sublimed iodine respectively. The volumetric solution of sodium arsenite was 0.01025-normal (against iodine) and the thiosulphate was 0.0104-normal (against the arsenite).

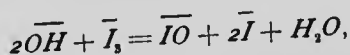
The potassium iodide employed contained small quantities of potassium iodate and potassium carbonate; these were removed by acidifying with sulphuric acid, boiling to expel CO_2 , adding sodium thiosulphate until the solution just gave no blue with starch, and finally neutralizing with caustic potash freed from carbonate by lime. The water used in making up the reacting mixtures was freed from CO_2 by boiling for fifteen minutes, and was protected by soda lime.

¹ One formula-weight in grams per liter.

The pipettes were calibrated by weighing the distilled water discharged; 30 seconds being allowed for draining.

At the head of each table is given the volume of each of these stock solutions employed. Under θ is entered the time in minutes reckoned from the first analysis (for which $\theta = 0$); under As , the number of cc of the volumetric arsenite solution required to remove the iodine in 10 cc of the reacting mixture, and under $K_2 \times 10^4$ the value of $10^4(I/As - I/As_0) \times I/\theta$.

Adopting Schönbein's assumption, that when iodine is dissolved in a solution of potash, potassium hypoiodite is formed, the quantities of the constituents \overline{OH} , \overline{I} , and \overline{OI} may be determined by means of the equation



the quantity of \overline{I}_3 in colourless solutions obviously being zero.

Let A , B , and C represent the numbers of gram-molecules of KOH , KI , and KI_3 before mixing, multiplied in each case by 10^5 . Thus for example, in Expt. 1:

50 cc potash: $A = 10^5 \times 0.050 \times 1.092 = 5460$

20 cc iodine: In making this up there was used

$10^5 \times 0.020 \times 0.1151$ units of potassium iodide, of which

$10^5 \times 0.020 \times 0.0936 \times 0.5 = 93.6 = C$ was converted into KI_3 , leaving

$10^5 \times 0.020 \times 0.0683 = 136.6 KI$

20 cc iodide: containing $10^5 \times 0.020 \times 1.151 = 2302 KI$, to which must be added 136.6 in the iodine solution, giving 2439 = B .

Then after mixing, when all the triiodion, \overline{I}_3 , has been converted into hypoiodion, \overline{OI} , but before the formation of iodate has commenced,

the \overline{OH} present = $A - 2C = 5560 - 187 = 5273$

“ \overline{I} “ = $B + 2C = 2439 + 187 = 2626$

“ \overline{OI} “ = $C = 94.6$

In the calculation it has been assumed that, owing to the

large excess of potash, the concentration of the HOI might be neglected in comparison with that of the \overline{OI} ions.

In addition to the experiments recorded in the tables, others were carried out which showed that the presence of a small quantity of potassium iodate (one gram in 100 cc) has no effect on the rate, and that the possible absorption of carbonic acid from the air during the progress of an experiment was likewise without influence on the result. In a few measurements the reacting mixture was exposed to direct sunlight; the same figures were obtained as in duplicates made in the diffuse light of the laboratory.

In Table VI, the initial compositions of the solutions in the experiments of Tables I to V are given in the terms of \overline{OH} , \overline{I} , and \overline{IO} , together with the average values of K_2 . The initial rate, R_0 , is obtained by multiplying α'_2 into the square of the initial concentration of the hypoiodion,

$$R_0 = dx/d\theta(x=0) = K_2 C^2.$$

From the constancy of K_2 in each of the Tables I-V, it is apparent that the rate is proportional to the square of the concentration of the \overline{OI} ; this conclusion is confirmed (within 10 percent) by comparison of Tables I and II (see also Table VI).

TABLE I.

Potash, 50 cc ; Iodide, 20 cc ; Iodine, 20 cc ; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	9.06	—
3	8.52	23.3
10	7.54	22.2
15	7.24	25.1
19	6.40	24.1
22	5.99	25.6
		Av. 24.1

TABLE II.

Potash, 50 cc ; Iodide, 20 cc ; Iodine, 40 cc ; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	17.25	—
4	14.70	25.1
9	11.77	29.9
13	10.06	31.8
17	8.68	33.6
22	7.53	34.0
27	7.27	29.4
		Av. 30.6

TABLE III.

Potash, 100 cc ; Iodide, 20 cc ; Iodine, 20 cc ; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	8.75	—
4	8.37	13.2
8	8.18	10.0
12	7.62	14.1
16	7.60	10.9
20	7.09	13.4
24	6.93	13.9
		Av. 12.5

TABLE IV.

Potash, 25 cc ; Iodide, 20 cc ; Iodine, 20 cc ; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	9.09	—
4	7.95	39.5
8	6.80	46.2
18	5.08	48.0
22	4.50	55.0
26	4.00	53.8
		Av. 48.5

TABLE V.

Potash, 50 cc ; Iodide, 10 cc ; Iodine, 20 cc ; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	8.95	—
6	8.48	10.3
9	8.27	10.2
13	7.88	11.6
17	7.25	15.4
		Av. 11.8

TABLE VI.

Table	\overline{OH}	\overline{I}	\overline{OI}	$K_2 \times 10^4$	R_0	$K^1 \times 10^4$
1	5273	2626	93.6	24.1	21.1	47
2	5086	3050	187.2	30.6	107.3	51
3	10733	2626	93.6	12.5	11.0	50
4	2543	2626	93.6	48.5	42.5	46
5	5273	1475	93.6	11.9	10.4	43

Further comparison of the experiments, which is facilitated by the summary given in Table VI, shows that within the same limits (8 to 10 percent) the rate is directly proportional to the concentration of the \overline{I} , and inversely to that of the \overline{OH} . Since the product of \overline{H}^+ and \overline{OH} concentrations is constant, and since the concentration of the HOI is proportional to the product of those of \overline{H}^+ and \overline{OI} , this is equivalent to saying that the rate is proportional to the concentrations of \overline{OI} , \overline{I} , and HOI .

II. Brown Solutions

In presence of a large excess of iodine, the plan of analysis described on page 642 would give very inaccurate results; it was therefore abandoned in favor of a direct determination of the iodate formed, according to the following method.

The iodine and hypoiodite were destroyed and the reaction stopped by pouring in a slight excess of fifth-normal sodium arsenite. The contents of the flask were then emptied into a beaker, 100 cc of water added, and then a measured quantity of

$$^1 R_0 \times (OH) = K \times (I) \times (OI)^2$$

hydrochloric acid diluted with 100 cc of water; the iodine which was thereupon liberated from the iodate was determined by sodium thiosulphate. Under x in the tables of this section is entered the number cc of 0.0104- n thiosulphate needed, and under θ the interval in minutes between mixing the reagents and adding the arsenite. By working quickly, using as little arsenite as possible, and adding in each case a definite excess (5 cc of 2- n HCl) of hydrochloric acid over that needed to neutralize the potash in the reacting mixture and the sodium bicarbonate in the arsenite solution, it was found possible to determine the iodate before any iodine was liberated by arsenic acid. It would have been better to remove the excess of arsenite before acidifying, but blank experiments show that the error arising from its presence is small.

A series of experiments analogous to those of Tables I-V were first carried out, but as no "constant" could be found, recourse was had to the "method of constant rates," the solutions being so made up that the changes in concentration during the progress of an experiment were almost negligible. In Tables VII-XII the rates (R) were obtained by dividing x (which is proportional to the amount of iodate formed) by the duration of the reaction in minutes. Duplicate experiments showed that the value of R so obtained was rather greater when θ was 3 or 4 minutes than when it was one; this suggests that the formation of hypiodite may require an appreciable interval of time for its completion, but I have not examined the matter further.

TABLE VII.

Potash varies; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
		2	2.1
1	Brown	1	11.3
2	Brown	1	8.7
5	Light brown	1	4.2
10	Green yellow	1	2.9
15	Light green	2	2.1
20	" "	4	1.6
25	" "	5	

¹ See Bray, Jour. Phys. Chem. 7, 92 (1903).

TABLE VIII.

Potash varies; Iodide, 40 cc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
2	Brown	1	4.2
5	Yellow brown	1	11.1
10	Yellow green	1	9.3
15	Green yellow	1	6.0
20	" "	1	3.8
25	" "	3	3.4

TABLE IX.

Potash varies; Iodide, 60 cc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
2	Brown	4	1.9
5	"	1	8.4
10	"	1	11.6
15	Yellow brown	1	10.7
20	Yellow green	1	6.4
25	Green yellow	1	5.0

TABLE X.

Potash varies; Iodide, 20 cc; Iodine, 40 cc; Volume, 200 cc

KOH	θ	x	R
1	2	10.6	5.3
2	1	22.9	22.9
3	1	44.1	44.1

TABLE XI.

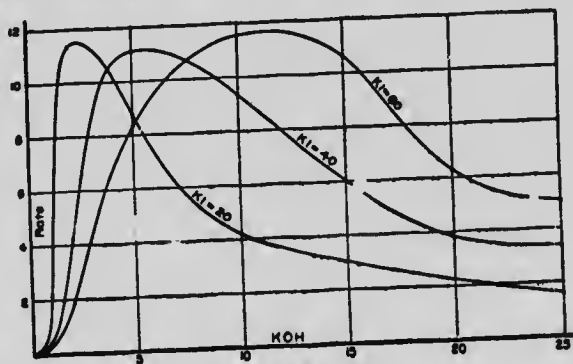
Potash varies; Iodide, 40 cc; Iodine, 40 cc; Volume, 200 cc

KOH	θ	x	R
1	2	3.3	1.6
2	1	9.6	9.6
3	1	23.1	23.1

TABLE XII.
Potash varies; Iodide, 60 cc; Iodine, 40 cc; Volume, 200 cc

KOH	θ	x	R
1	3	2.2	0.7
2	1	4.5	4.5
3	1	12.3	12.3

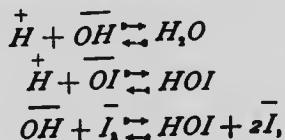
From Tables VII-XII it appears that, in presence of a large excess of iodine, the rate of formation of iodate is increased by increasing the concentration of the iodine or of the potash, and decreased by increasing that of the iodide—the effect in the last two cases being the opposite of that produced when the potash is in excess. The existence of maximum rates, which is necessitated by this circumstance, is well shown by the curves.



Tables 7, 8, and 9

It would be interesting to know whether in the experiments of this section, as in those with colorless solutions, the rate is even roughly proportional to the concentrations of \overline{OI} , \overline{I} , and \overline{HOI} ; in brown solutions, however, where only part of the iodine is converted into hypiodites, it is not easy to determine the amounts of these three constituents.

Assuming the chemical equations:—



and the corresponding conditions of equilibrium:—

$$\begin{aligned}(\overset{+}{H})(\overline{OH}) &= W \\(\overset{+}{H})(\overline{OI}) &= D(HOI) \\(\overline{OH})(\overline{I}) &= E(HOI)(\overline{I})^2,\end{aligned}$$

(where the symbols in brackets signify the amounts of the reagents in a fixed volume of solution, and W , D , and E are constants) and representing the initial quantities of potash, iodide, and iodine by A , B , and C as before, the following equations

$$\begin{aligned}Wy &= Dz(A - 2y - z) \\(A - 2y - z)(C - y - z) &= Ez(B + 2y + 2z)^2,\end{aligned}$$

determining y , the concentration of the \overline{OI} ions, and z that of undissociated HOI (before the formation of \overline{IO}_3 has begun) may be obtained. These equations may be solved for y and z , and the results substituted in the expression for the rate of formation of iodate,

$$R = Kyz(B + 2y + 2z),$$

but without knowledge of the numerical values of D and E the relation so obtained cannot be compared directly with the experiments. I hope to determine these constants during the present winter; in the meantime the experiments of this section, though perhaps not so accurate as those in which the potash was in excess, and not leading to such simple results, serve to show how much the brown solutions differ from the colourless in respect to the influence exerted by the amounts of iodide and of potash on the rate of formation of potassium iodide.

Temperature Coefficient

A few experiments were undertaken at 30.3° in order to test the influence of the temperature on the rate; those with the colourless solutions are given in Table XIII, and those with brown solutions in Table XIV. In neither case is the temperature coefficient as great as usual, but as in all probability the dissociation of HOI and the equilibrium constant E (see above) change with the temperature, abnormal results are not to

be wondered at. The experiments of Table XIII were carried out with solutions of potassium iodide that had not been freed from carbonate, and are therefore not directly comparable with the other experiments of this paper.

TABLE XIII. (Colourless)

Potash, 25 cc (0.929-*n*); Iodide, 20 cc (0.956-*F*); Iodine 20 cc (0.089-*n*); As (0.0101-*n*) Volume, 200 cc

θ	As(0°)	K ₂ × 10 ⁴ (0°)	As(30.4°)	K ₂ × 10 ⁴ (30.4°)
0	—	—	6.28	457.0
7	6.78	45.0	2.32	396.8
10	6.32	40.6	1.68	437.9
14	5.56	44.3	—	—
20	4.80	45.1	—	—
		Av. 43.7		Av. 431.

TABLE XIV. (Brown)

Potash, 1.0 cc; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

θ	<i>x</i>	R(0°)	θ	<i>x</i>	R(30.3°)
2	4.2	2.1	1	32.3	32.3

Summary

In the presence of a large excess of potash, the rate of formation of potassium iodate is, approximately, proportional to the concentrations of \overline{OI} , \overline{I} , and HOI .

In presence of a large excess of iodine, the rate is increased by increasing the amount of potash or iodine, and decreased by adding to that of the potassium iodide.

On continually increasing the amount of potash, so that the solution changes from brown to colourless, the rate increases through a maximum.

The temperature coefficient is smaller than is customary.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this investigation was undertaken, and under whose supervision it has been carried out.

University of Toronto,
October, 1903.



