808. *The Photochemistry of Iodide Ions in Aqueous Solution.*

By Tyson Rigg and Joseph Weiss.

The photochemical formation of iodine and hydrogen from aqueous iodide solutions, by irradiation at 2000—2400 Å, has been investigated over a wide range of pH and iodide concentrations, and it has been found that the quantum yield depends markedly on both these factors. The following mechanism gives an adequate account of all the experimental facts:

$$(1a)\ (I^-,H_2O) + h\nu \longrightarrow (I^-,H_2O)^*,$$
$$(1b)\ (I^-,H_2O)^* \longrightarrow I + H + OH^-,$$
$$(2)\ I + H \longrightarrow HI$$

The dependence on pH is attributed to the intervention of hydrogen molecular ions, formed according to (3) $H + H^+ \rightleftharpoons H_2^+$ followed by (4) $H_2^+ + I^- \longrightarrow H_2 + I$, and (5) $2I \longrightarrow I_2$. There is also a second back-reaction, *viz.*, (6) $I_2 + H \longrightarrow HI + I$, which becomes important at higher iodine concentrations.

Franck and Scheibe (*Z. physikal. Chem.*, 1928, *A*, **139**, 22) were the first to interpret the ultra-violet absorption spectra of the halogen ions in solutions as electron-affinity spectra. This was subsequently taken up by Franck and Haber (*Sitzungber. Preuss. Akad. Wiss.*, 1931, 250), who suggested that the electron transfer from the ion (X^-,H_2O) to a water molecule in the hydration shell is represented by the process: $X^-,H_2O + h\nu \longrightarrow X + H + OH^-$.

Farkas and Farkas (*Trans. Faraday Soc.*, 1938, **34**, 1113) questioned some of these conclusions and suggested that the photochemical reaction takes place only by the transfer of the electron from the hydration shell to a hydrogen ion in the solution; this appeared to be confirmed by some observations of an increase in the quantum yield in acid solutions. On the other hand, for positive ions, such as the ferrous ion, according to these authors, the quantum yield should be independent of the hydrogen-ion concentration. However, the latter conclusion is not in agreement with the experimental evidence, for we have shown (*J. Chem. Physics*, 1952, **20**, 1194) that the photochemical formation of hydrogen and of ferric salt from aqueous solutions of ferrous ions is strongly dependent on the hydrogen-ion concentration, which could be interpreted on a quantitative basis by assuming the intervention of the hydrogen molecular ion (H_2^+) in solution, formed by the association of a hydrogen atom with a hydrogen ion.

It has already been suggested that the pH dependence of the iodide-ion photolysis is also due to the formation and reaction of the hydrogen molecular ion (Weiss, *Nature*, 1950, **165**, 728). Hardly any quantitative data are recorded concerning the photochemistry of iodide ions *in the absence of atmospheric oxygen* except a few measurements by Farkas and Farkas (*loc. cit.*) and the qualitative observations by Butkow (*Z. Physik*, 1930, **62**, 71). We have, therefore, carried out a more detailed investigation, particularly with regard to the dependence of the quantum yield on pH and on the iodide-ion concentration.

FIGS. 1 and 2. *Dependence on* pH *of the quantum yield of iodine at constant light intensity* (5·025 × 10^{-5} *einstein/min.* × 100 *ml.*) *and time of irradiation* (6 *min.*).

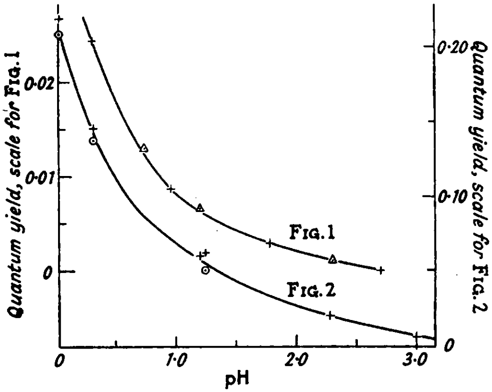
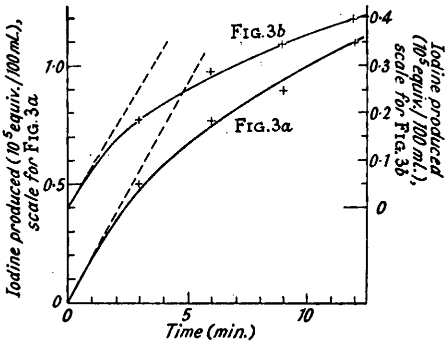


Fig. 1. $[I^-] = 4\cdot10^{-3}$M. (△, *in presence of* 0·25M-Na_2SO_4.)
Fig. 2. $[I^-] = 2\cdot0$M. (+ *Iodine,* ⊙ *hydrogen determinations.*)

FIG. 3. *Dependence of iodine formation on time of irradiation at constant light intensity* (5·025 × 10^{-5} *einstein/min.* × 100 *ml.*).



(*a*) pH = 0·30, $[I^-] = 4\cdot10^{-3}$M;
(*b*) pH = 3·00, $[I^-] = 2\cdot0$M.

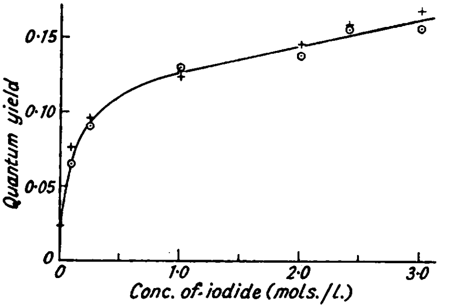


FIG. 4. *Dependence of the quantum yield of iodine* (+) *and hydrogen* (⊙) *on the iodide concentration at constant* pH ≃ 0·30, *constant light intensity* (5·025 × 10^{-5} *einstein/min.* × 100 *ml.*) *and constant time of irradiation* (6 *min.*).

All experiments were carried out under conditions of complete absorption of the incident light, which is the case even at relatively low iodide concentrations, on account of the high extinction coefficient of iodide ions in the region, 2000—2400 Å.

Figs. 1 and 2 represent the results obtained with $[I^-] = 4 \times 10^{-3}$M and $[I^-] = 2\cdot0$M respectively at different hydrogen-ion concentrations (for constant light intensity and time of irradiation); they show that there is a very marked dependence of the quantum yield on pH. Fig. 2 also shows the good agreement between the photochemically produced iodine and the simultaneously produced hydrogen, indicating clearly that there is no interference from any residual oxygen of the air: this is particularly important in the experiments with high iodide- and hydrogen-ion concentrations, as these solutions are very susceptible to autoxidation.

Figs. 3*a* and 3*b* show the dependence of the photochemically produced iodine on the time of irradiation, for constant light intensity for two pH's and for two iodide concentrations. The time dependence is generally non-linear, which indicates the operation of some back reaction.

Similar results have been obtained at other pH and iodide concentrations. Some of the initial yields for constant light intensity are given in Table 1, and it is seen that the

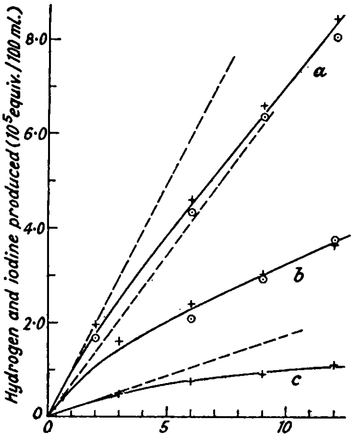
TABLE 1.

pH	Concn. of iodide, mol./l.	Initial rate* (mol./l. min.) × 10^5	pH	Concn. of iodide, mol./l.	Initial rate (mol./l. min.) × 10^5
1·78	0·004	0·316	3·00	2·0	0·95
0·95	,,	0·830	1·20	,,	4·46
0·30	,,	1·93	0·30	,,	10·0

* At constant light intensity.

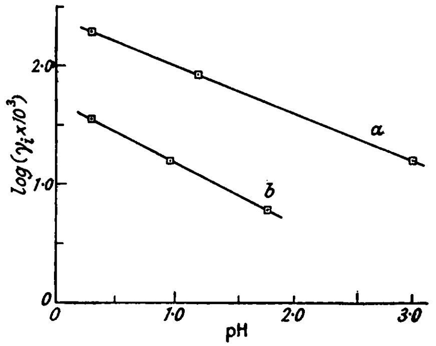
quantum yield increases markedly at the higher iodide concentrations. This is demonstrated more clearly by Fig. 4, which shows the dependence of the quantum yield on the iodide concentration in the range 0·004—3·0 mols./l. (at constant pH, light intensity, and time of irradiation). The quantum yield shows a rapid increase at comparatively low concentrations of iodide, followed by a relatively slow increase between 0·5 and 3·0 mols./l.

FIG. 5. *Dependence of iodine* (+) *and of hydrogen* (⊙) *formation on time of irradiation at constant light intensity* (5·026 × 10^{-5} *einstein/min.* × 100 *ml.*) *in* 1N-H_2SO_4 (pH ≃ 0·30).



(*a*) 2·0M-, (*b*) 0·1M-, (*c*) 4 × 10^{-3}M-*potassium iodide.*

FIG. 6. *Logarithmic plot of* initial *quantum yield* (γ_i) *against* pH, *for two different iodide concentrations.*



(*a*) 2·0M, (*b*) 4 × 10^{-3}M-*potassium iodide.*

Fig. 5 shows that the rate of iodine formation, under otherwise similar conditions, is greatly increased at higher iodide concentrations.

Discussion.—The modification of the theory as suggested by Farkas and Farkas (*loc. cit.*) introduces into the photochemistry of iodide ions a dependence of the quantum yield on the pH. These authors suggested that the actual chemical process is initiated by reaction of the " excited " ions with hydrogen ions which can be represented by : $I^- + h\nu \longrightarrow (I^-)^*$, followed by $(I^-)^* + H^+ \longrightarrow I + H$, with the following process of deactivation : $(I^-)^* \longrightarrow I^- +$ energy. This mechanism would lead to the following expression :

$$\text{quantum yield} = \text{const.} \times [H^+]/(1 + \text{const.} \times [H^+])$$

according to which the quantum yield should be independent of the iodine concentration and should approach *unity* with increasing hydrogen-ion concentration. This expression is, however, not in agreement with the experimental results.

On the other hand, if one introduces H_2^+ into the mechanism, the experimental results can be satisfactorily interpreted on the basis of a photochemical primary process somewhat similar to that suggested by Franck and Haber (*loc. cit.*).

Derivation of the Kinetics.—The following elementary processes have to be considered :

light absorption: $(I^-,H_2O) + h\nu \longrightarrow (I^-,H_2O)^*$ (I_a = light absorbed per unit of time) . (1*a*)

" dissociation " of the " excited ion ": $(I^-,H_2O)^* \longrightarrow I + H + OH^-$ . . . (1*b*)

$$I + H \xrightarrow{k_2} HI \tag{2}$$

$$H + H^+ \underset{k'_3}{\overset{k_3}{\rightleftarrows}} H_2^+ \tag{3)(3'}$$

$$I^- + H_2^+ \xrightarrow{k_4} I + H_2 \tag{4}$$

$$2I \xrightarrow{k_5} I_2 \tag{5}$$

$$I_2 + H \xrightarrow{k_6} HI + I \tag{6}$$

$$I_2 + I^- \rightleftarrows I_3^- \text{ (equilibrium constant } K_T \simeq 1{\cdot}36 \times 10^{-3} \text{ at } 25°) \tag{7}$$

In the case of positive ions, *e.g.*, ferrous, we have concluded that most of the excited ions undergo a process of deactivation. This apparently does not apply to the excited iodide ions, where the electron transferred to the hydration shell seems to have a much greater tendency to " split " a water molecule according to (1*b*), which is similar to the primary process suggested by Franck and Haber. However, the intermediate formation of an " excited " iodide ion is made probable by the recent considerations by Platzman and Franck (personal communication) concerning the absorption spectrum of iodide ions in solution.

According to our findings, the reason why the quantum yield is relatively low here is not the deactivation of the excited iodide ions, but the very efficient back-reaction (2) between the hydrogen and the iodine atoms, which is probably enhanced by the Franck–Rabinovitch " cage effect."

The experimental results indicate that at higher iodine concentrations a second back-reaction (6) between molecular iodine and hydrogen atoms has to be taken into account. This reaction should be relatively less important at higher iodide concentrations, on account of the formation of tri-iodide ions, according to the equilibrium (7) from which the " true " concentration of $[I_2]$ in terms of the total (*analytical*) concentration of iodine (I_2) is given by :

$$[I_2] = (I_2)K_T/(K_T + [I^-]) \tag{I}$$

From equations (1)—(6) one obtains for the stationary state of the unstable intermediates the equations :

$$d(I^-,H_2O)^*/dt = 0 \tag{IIa}$$

$$d(I)/dt = 0 \tag{IIb}$$

$$d(H)/dt = 0 \tag{IIc}$$

$$d(H_2^+)/dt = 0 \tag{IId}$$

This leads to the equation

$$I_a - k_2[H][I] - k_5[I]^2 = 0 \tag{IIIa}$$

Substituting for [H] from the above equations for the stationary state, one obtains

$$[H] = (k_5/\Gamma)[I]^2 \tag{IIIb}$$

where

$$\Gamma = \{k_3k_4[H^+][I^-]/(k_3' + k_4[I^-])\} + k_6[I_2] \tag{IIIc}$$

and with equation (III*a*) this gives

$$I_a - k_5[I]^2 - (k_2k_5/\Gamma)[I]^3 = 0 \tag{IIId}$$

Thus one obtains for the rate of formation of molecular iodine (or hydrogen) :

$$\begin{aligned} d(I_2)/dt = d(H_2)/dt &= k_5[I]^2 - k_6[H][I_2] \\ &= k_5[I]^2\{1 - k_6K_T(I_2)/\Gamma(K_T + [I^-])\} \end{aligned} \tag{IVa}$$

As shown in Figs. 3*a* and 3*b*, in general, there is a non-linear dependence of the yield on the time of irradiation (for constant light intensity).—However, the first term in (IV*a*) would normally lead to a linear dependence as the pH and $[I^-]$ can be regarded as practically constant. Thus it appears that, in order to account for the experimental facts, it is necessary to take into account a back-reaction. Reaction (6) meets all the necessary requirements. The treatment of the complete equation (IV*a*) leads to complicated expressions; therefore, in the following discussion mainly the *initial* yields have been considered.

In the calculation of the stationary iodine atom concentration from (III*d*) it is obvious that only the cubic term depends on the hydrogen-ion concentration, whereas the quadratic term by itself would lead to a rate which increases only very slowly with increasing acidity and, initially, would be completely independent of pH.

On the other hand, the strongest dependence on pH is obtained if one neglects the quadratic term in (III*d*), *i.e.*, if

$$k_2[I] \gg \Gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (V)$$

which, for the *initial* formation of iodine, leads to the rate equation

$$d(I_2)/dt|_i \simeq k_5[I]^2 \simeq k_5(I_a\Gamma/k_2k_5)^{2/3} \quad . \quad . \quad . \quad . \quad . \quad (VIa)$$

and for the initial quantum yield (γ_i) from (VI*a*) and (III*d*)

$$\gamma_i = (1/I_a)d(I_2)/dt \propto k_5\{k_3k_4[H^+][I^-]/(k_3' + k_4[I^-])\}^{2/3} \quad . \quad . \quad . \quad (VIb)$$

The dependence of the quantum yield (γ) on the pH at constant light intensity and time of irradiation is shown by Figs. 1 and 2, for two widely different iodide concentrations.

For a more quantitative comparison the *initial* yields, at constant iodide concentration, for different pH have been taken from Table 1, and in Fig. 6 log γ_i is plotted against pH. From a generalisation of (VI*a*) it follows that

$$\gamma_i \propto [H^+]^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (VIIa)$$

with $0 \leqslant n \leqslant 0{\cdot}66$, where the lower limit would correspond to the case where the inequality (V) is reversed. Thus

$$d \log \gamma_i/d\,pH = -n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (VIIb)$$

Experimentally one finds from Fig. 6 :

$$d \log \gamma_i/d\,pH = -0{\cdot}52 \pm 0{\cdot}04 \text{ (for } [I^-] = 4 \times 10^{-3}\text{M)} = -0{\cdot}40 \pm 0{\cdot}04 \text{ (for } [I^-] = 2{\cdot}0\text{M)}$$

which are both nearer the maximum value of $-0{\cdot}66$. It is clear that if condition (V) does not hold very well, the cubic equation (III*d*) would have to be solved completely for a more detailed discussion. This is, however, not possible without some independent knowledge of some of the rate constants involved.

As the experimental error in the actual determination of the *initial* yields is certainly not more than ±10%, the slopes in Fig. 6 are accurate to within the limits stated.

The fact that the slope (n) decreases with increasing iodide concentration follows immediately from equation (III*d*), as Γ generally increases with increasing iodide concentration and thus the cubic term becomes less important relative to the quadratic term, which is independent of pH. Although the iodide concentration in the two cases considered above differs by a factor of 500, the decrease in the slope at the higher iodide concentration is relatively small; this can also be deduced from equations (III*d*) and (III*c*), which show that Γ will increase only relatively *slowly* with increasing iodide-ion concentration.

Some further semiquantitative confirmation of the theory can be obtained from a consideration of the initial rates at different iodide concentrations at constant pH. There is a marked increase of the initial yield with increasing iodide concentration, as shown by Fig. 5 which represents the yield for constant pH and constant time of irradiation, over a wide range of iodide concentration; at low concentrations there is a rapid increase of the yield which, however, increases only relatively slowly beyond a certain iodide concentration. The general character of the curve is well represented by an equation of the form

$$\gamma_i \simeq \{K_1[I^-]/(1 + K_2[I^-])\}^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (VIII)$$

which is suggested by the theoretical equation (VI*b*), where K_1 and K_2 are independent of the iodide concentration.

However, in the theoretical evaluation of the experiments at high iodide concentrations, there is also the difficulty that there is a very considerable change in the ionic strength, and for a more quantitative treatment some definite information regarding the activity coefficients would also be required. Furthermore, it must be borne in mind that at the higher iodide concentrations practically complete light absorption occurs in a very thin layer, and this may also modify somewhat the course of the reaction. Nevertheless, the initial yields of the experiments given in Fig. 4 are fairly well represented by a relation of the type of equation (VIII), the upper limit being taken for the exponent, as shown by the data in Table 2. Although these figures are primarily of qualitative significance, on the whole there is satisfactory agreement between the theory and the experimental results.

TABLE 2.

Concn. of iodide, mols./l.	Initial rate * $[d(I_2)/dt]_i$, (mols./l. × min.) × 10^5: Found	Calc. from $\{2 \times 10^{-5} [I^-]/(1 + 20[I^-])\}^{\frac{1}{2}}$
2·0	10·0	9·85
0·1	7·0	7·58
0·004	1·8	1·76

* At constant light intensity.

EXPERIMENTAL

The source of radiation was a low-pressure mercury discharge tube of about 500 watts, used in conjunction with a voltage stabiliser (Ferranti). Unfiltered radiation was used under conditions of complete absorption. The apparatus was on conventional lines. A spherical silica flask, filled with triply distilled water, was used as a condenser. In this way, and with a small centrifugal blower, the temperature in the reaction vessel could be kept constant at $20° \pm 1°$.

Actinometry.—The total light output in the ultra-violet region was measured actinometrically by means of chloroacetic acid. This was chosen since its absorption spectrum shows a good overlap with that of iodide ions in aqueous solutions, and the error involved should not amount to more than about 10% which was adequate for the purpose of the present investigation.

The value $0{\cdot}62 \pm 0{\cdot}04$ used for the quantum efficiency of chloroacetic acid photolysis is due to Kuechler and Pick (*Z. physikal. Chem.*, 1940, *B*, **45**, 116), who carried out a very careful investigation of this reaction. The light absorbed by the solution was $5{\cdot}025 \times 10^{-5}$ einstein/(min. × 100 ml.).

Preparation of Solutions.—The water used was ordinary distilled water redistilled from permanganate and then from dilute phosphoric acid. It was boiled out in a stream of carbon dioxide, and after cooling in the gas stream it could be syphoned out of its container as required.

The procedure adopted in making up the solutions was as follows. Some of the carbon dioxide-saturated water was acidified with sulphuric acid to the extent required, and 100 ml. were introduced into the reaction vessel which was already *in situ* on the evacuation apparatus. A fairly vigorous stream of carbon dioxide was then passed through the solution for some minutes to sweep out all the air, and then pumped out with an oil-pump and a liquid-air trap.

In the experiments with dilute solutions, the potassium iodide was introduced into the reaction vessel immediately before pumping out. The method of preparing the concentrated solutions (up to 3M) was somewhat different: the requisite amount of solid potassium iodide was dropped *via* a specially designed orifice into the acidified water in the vessel after deaeration (carbon dioxide bubbling through continuously), and the solution was then immediately pumped out as above. In this way, it was found possible to prepare even 3M-solutions of potassium iodide in 1M-sulphuric acid without any measurable autoxidation occurring.

De-aeration of the Solutions.—All experiments were carried out in evacuated solutions. The first stage of evacuation is described in the preceding section, a " Hyvac " oil-pump being used to pump out the gas *via* a liquid-air trap. More carbon dioxide was then admitted, and the vessel again pumped out. Evacuation was finally completed and checked on the gas-analysis apparatus where the solutions were evacuated by means of a Toepler pump. The vapour phase in equilibrium with the solutions was also tested for oxygen by means of a trypaflavine gel and it was shown that the oxygen pressure did not exceed 10^{-5} mm. Hg. No effects due to residual oxygen could be observed in any of the experiments after using the above procedure.

Quantitative Estimations.—In the experiments with dilute solutions (4×10^{-3}M) the vessel was cooled in ice and filled with carbon dioxide after irradiation, the contents being quickly titrated in a slow stream of carbon dioxide with thiosulphate and starch indicator. In the more concentrated solutions the yield of hydrogen and iodine was large enough to enable the former to be measured also. Up to 1 ml. of gas was obtained in these experiments and was shown to be pure hydrogen by diffusion through a palladium tube after no contraction could be observed on passage over a heated platinum spiral. After the gas had been removed, the vessel was filled with carbon dioxide and the contents were titrated with thiosulphate.

In the determination of the small amounts of iodine in the presence of more than 0·1M-potassium iodide some difficulty was experienced, since a purplish-red colour was produced with the starch indicator instead of the usual intense blue colour. This red iodine complex seemed to react only slowly with the thiosulphate, but reliable results could be obtained by adding initially an excess of thiosulphate and back-titrating with iodine solution.

Blank experiments were always carried out but no detectable amounts of iodine could be observed under the conditions described above. This is also confirmed by the fact that, in those cases where hydrogen and iodine determinations were carried out, the agreement was always satisfactory, as will be seen from Figs. 2, 4, and 5.

Normally, the accuracy of the iodine titrations was ±0·5%, but in the 2M-iodide solutions, where the difficulties described above arise, the titration is accurate only within ±5%. However, in these solutions the hydrogen measurements are correspondingly more accurate (±2%) owing to the increased yields.

All reagents used in the course of this investigation were of " AnalaR " grade.

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UNIVERSITY OF DURHAM, KING'S COLLEGE,
NEWCASTLE-ON-TYNE, 1.

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