THE PHOTOCHEMICAL PRIMARY PROCESS OF IONS IN AQUEOUS SOLUTIONS.

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The photochemical primary process of negative ions in aqueous solutions, corresponding to their absorption in the ultraviolet, was first investigated by Franck and Scheibe[1] in the case of the halogen ions. They interpreted the primary as an electron affinity spectrum according to: $X^- + h\nu = X +$ electron (X^- halogen ion). By this theory several important features of the photochemical behaviour of these ions could be explained. In 1931 Franck and Haber[2] established a more complete theory which provides a full understanding of the photochemistry of negative ions. This theory was confirmed by experimental work on the halogen ions[3] on sulphites and arsenites[4, 5] and subsequently on sulphides, hydrosulphides and simple mercaptans in alkaline solutions.[6] More recently the photochemistry of simple positive ions was investigated by Weiss and collaborators. They showed that on irradiating with ultraviolet light a solution containing ferrous ions[7] hydrogen gas was given off and that on the other hand ceric ions could decompose water photochemistry[8] yielding molecular oxygen. It will be shown in the following that all the experimental facts can be fully understood on the basis of the Franck-Haber theory and that no modification of this theory is necessary to explain the more recent experimental results.[9]

1. Negative Ions.

(*a*) Iodide Ion.

Photochemical primary process:

$$I^-HOH + h\nu = I + H + OH^- \quad . \quad . \quad . \quad (1.1)$$

followed by:

$$2I = I_2 \quad . \quad . \quad . \quad . \quad . \quad (1.2)$$

$$2H = H_2 \quad . \quad . \quad . \quad . \quad . \quad (1.3)$$

reverse process:

$$\left.\begin{aligned} I + H(+M) &= HI(+M) \\ HI + OH^- &= I^- + H_2O \end{aligned}\right\} \quad . \quad . \quad . \quad (1.4)$$

The photochemical reaction of alkali iodides has been studied by Butkow[3] who observed the formation of I_2, which is formed with a very small quantum yield (in the absence of molecular oxygen). This is due to various types of "reverse processes," such as reactions (1.4)

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[1] Franck and Scheibe, *Z. physik. Chem., A*, 1928, **139**, 22.
[2] Franck and Haber, *Sitz. Preuss. Akad. Wiss.*, 1931, 250.
[3] Butkow, *Z. Physik*, 1930, **62**, 71.
[4] Haber and Wansborough-Jones, *Z. physik. Chem., B*, 1932, **18**, 103.
[5] Goldfinger and Albu, *ibid.*, **16**, 338.
[6] Fishgold and Weiss, *Nature*, 1936, **137**, 71.
[7] Weiss, *ibid.*,, 1935, **136**, 794. Potterill, Walker and Weiss, *Proc. Roy. Soc., A.*, 1936, **156**, 561.
[8] Porret and Weiss, *Nature*, 1937, **139**, 1019.
[9] Farkas and Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1113.

which in solution will be further enhanced through primary recombination.[10]

The photochemical primary process is always represented by reaction (1.1), independent of the cation present. This view is supported by the measurements of Scheibe[11] and Lederle[12] who found that the absorption spectrum of I^- is independent of the metal cation present for iodide concentrations 10^{-4} molar to 1 molar, and by the work of Butkow[3] who observed that the photochemical liberation of iodine is about the same for CsI, KI and NaI solutions. However, Farkas and Farkas[13] found that the photochemical formation of hydrogen gas is greater from acidified solutions than from neutral solutions. This is in agreement with the fact that the photochemical liberation of iodine from iodide solutions (in the presence of oxygen) is favoured by acid solution and probably also in solutions of lithium iodide but decreases roughly in the order: $HI > LiI > NaI > KI$.[14]

The interesting physical explanation put forward by Farkas and Farkas,[9] assuming the neutralisation of the corresponding cation in the primary process (formation of a metal atom), is not in agreement with the experiments, because the primary process has been shown to be independent of the cation. In the case of acid iodide solutions it is possible that some undissociated HI molecules are present which could be split directly into the elements. This explanation has actually been put forward by Warburg and Rump[15] to explain their results on aqueous HI solutions of higher concentrations where the electrolytic dissociation is probably not complete.

The case of dilute solutions containing hydrogen ions can be explained chemically through some "reverse processes" in which the primarily formed H atoms and I_2 are involved and which in *any* case must be taken into account. Whenever photolysis takes place in an iodide solution hydroxyl ions are formed according to the net process:

$$2I^- + 2H_2O = I_2 + 2OH^- + H_2.$$

If the solution were acid originally these OH^- will be neutralised immediately. If, on the other hand, we start with a neutral solution of an iodide, the solution gradually gets more and more alkaline and the iodine present disappears through the very rapid reaction with OH^- or H_2O according to:

$$I_2 + OH^- \rightleftharpoons HIO + I^- \quad . \quad . \quad . \quad . \quad (1.5)$$
$$I_2 + H_2O \rightleftharpoons HIO + I^- + H^+. \quad . \quad . \quad . \quad (1.6)$$

Both these equilbria are established very rapidly and are in alkaline solutions well on the side of IOH and I^- $\left(\frac{[I_2][OH^-]}{[I^-][IOH]} = 1{\cdot}7 \times 10^{-2} (25^\circ).\right)$ The IOH formed through the reactions (1·5 or 1·6) reacts further to give iodate[16]. It is quite clear that any IOH, HIO_3 or IO_3 present in the solution will act as powerful acceptor for the hydrogen atoms. The

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[10] Franck and Rabinovitch, *Trans. Faraday Soc.*, 1933, **29**, 120.

[11] Scheibe, *Z. Elektrochem*, 1928, **34**, 497.

[12] Lederle, *Z. physik. Chem.*, *B*, 1930, **10**, 121.

[13] Farkas and Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1120.

[14] Schneider, *Z. physik. Chem.*, *B*, 1935, **28**, 311.

[15] Warburg and Rump, *Z. Physik*, 1928, **47**, 305.

[16] Skrabal, *Monatsh. Chem.*, 1911, **32**, 815. Abel, *Z. physik. Chem.*, 1928, **136**, 497.

result is that the quantum yield for the formation of iodine and hydrogen is further decreased.

Since, thus, the primary process is not influenced by the cations present, we can now turn to the consideration of the energy changes involved in the process (1.1). The light quantum absorbed in the case of iodide ions $(h\nu)_I$ is given by :

$$(h\nu)_I = -E_I - D_{H_2O} + E_{OH} + X$$
$$X = (-H_I + H'_{OH})$$

where E_I is the electron affinity of I atom, D_{H_2O} the dissociation energy of water into H and OH, E_{OH} the electron affinity of OH radical, and X' the difference of potential energy of the electron in the initial and final position. This difference is mainly due to the hydration energy of the iodide ion (H_I) being different from that of the OH^- ion which is formed in the reaction. However, according to the Franck-Condon principle the full hydration energy of the hydroxyl ion formed in the reaction cannot be attained because the " heavy " dipoles cannot follow completely the electron jump. In agreement with Farkas and Farkas [9] we shall denote this incomplete hydration energy by H'_{OH}. Farkas and Farkas have introduced the term " electron affinity of the water molecule " for the expression $(E_{OH} + H'_{OH} - D_{H_2O})$. The primary step most probably consists of an attachment of the photo-electron to one of the water molecules in the hydration shell,[7] and therefore this notation seems quite justified.

However, the introduction of these new terms does not alter the actual energy requirement for the primary process.

The energy necessary for the formation of H and I atoms from iodide solutions can be calculated independently from the electrochemical normal potential of the I_2/I^- electrode, the value of which is + 0·54 volt measured against the hydrogen electrode [17] at 25° C. This corresponds to the reaction : *

$$I^-_{aq} + H^+_{aq} = \tfrac{1}{2}I_2 + \tfrac{1}{2}H_2 - 0{\cdot}54 \text{ e. volts,}$$

combined with :

$$\tfrac{1}{2}I_2 = I - 1{\cdot}1 \text{ e.v.}$$
$$\tfrac{1}{2}H_2 = H - 2{\cdot}2 \text{ e.v.}$$
$$H_2O = H^+_{aq} + OH^-_{aq} - 0{\cdot}8 \text{ e.v.}$$

$$I^-_{aq} + H_2O = I + H + OH^-_{aq} - 4{\cdot}65 \text{ e.v.} \qquad (1.7)$$

According to Butkow [3] no decomposition takes place above a wave length of $\lambda \sim 2570$ A. This corresponds to an energy of about 4·8 e.v.

(b) Hydrosulphide and Mercaptan Ions.

Photochemical primary process :

$$SH^-HOH + h\nu = SH + H + OH^- \qquad (1.8)$$

recombination $$2SH = S_2H_2 \qquad (1.9)$$

reverse process $$SH + H = SH_2 \qquad (1.10)$$

dismutation $$2SH = SH_2 + S. \qquad (1.11)$$

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* Here and in the following thermochemical equations the subscript " *aq* " denotes the fully hydrated ions. In some cases the total energies (heats of formation) have been used instead of the free energies. However, at room temperature this difference never exceeds ± 0·5 e.v.

[17] Gurney, *Ions in Solution* (Cambridge, 1936).

Similarly in the case of simple mercaptans (*e.g.*, ethyl mercaptan) in alkaline solution :

$$C_2H_5S^{-}HOH + h\nu = C_2G_5S + H + OH^{-} \quad . \quad . \quad (1.12)$$
$$2C_2H_5S = C_2H_5S\,.\,S\,.\,H_5C_2 \quad . \quad . \quad (1.13)$$
$$C_2H_5S + H = C_2H_5SH. \quad . \quad . \quad . \quad (1.14)$$

The formation of disulphides and molecular hydrogen and sulphur, formed according to the above reactions has been observed experimentally by Weiss and Fishgold.[6] They are formed with a low quantum yield. This is due to the reverse processes (1.10 and 1.14) and in particular to the dismutation process in the case of SH (reaction 1.11).

According to a recent theoretical discussion [18] the dismutation processes assume great importance in the case of radicals with a large dipole moment (*e.g.*, SH) because the coulombic repulsion interferes with the recombination process.

The light quantum needed for the photochemical decomposition of hydrosulphide according to reaction 1.8 is given by the equation :

$$-(h\nu)_{SH} = -E_{SH} - D_{H_2O} + E_{OH} + X = -6{\cdot}56 \text{ e.v.} + H'_{OH}$$
$$X = -H_{SH} + H'_{OH}$$
$$H'_{OH} = 6{\cdot}56 \text{ e.v.} - (h\nu)_{SH} = 2{\cdot}06 \text{ e.v.}$$

where E_{SH} is the electron affinity of SH radical = 2·65 e.v.,[19] D_{H_2O} the dissociation energy (into H and OH) = 5·0 e.v., E_{OH} the electron affinity of OH radical = 3·7 e.v.,[20] and H_{SH} the hydration energy of SH^{-} ion = 2·61 e.v.[19]

The wave-lengths necessary to decompose SH^{-} ions in solution was found to be $\lambda \sim 2700$ A.[6, 21] This corresponds to an energy $(h\nu)_{SH} \sim 4{\cdot}5$ e.v. and leads to the value of $H'_{OH} \sim 2{\cdot}06$ e.v. The full hydration energy of OH^{-} ions is 3·8 e.v.[22] so that 54 per cent. of it is utilised in the above process.

2. Positive Ions.

(*a*) Ferrous Ion.

On irradiation in the ultraviolet, hydrogen gas is evolved and an equivalent amount of ferric ions formed :

photochemical primary process :

$$Fe^{2+} + HOH + h\nu = Fe^{3+} + OH^{-} + H \quad . \quad . \quad (2.1)$$
$$2H = H_2$$

reverse process : $Fe^{3+} + H = Fe^{2+} + H^{+}$. . . . (2.2)

The low quantum yield which is practically independent of the hydrogen ion concentration [7] is due to the reverse process (2.2). This is further illustrated by the fact that in solutions which contain even a very small amount of ferric ions at the beginning no evolution of hydrogen takes

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[18] Weiss, *Trans. Faraday Soc.*, 1935, **31**, 966.

[19] West, *J. Physic. Chem.*, 1935, **39**, 493.

[20] Weiss, *Trans. Faraday Soc.*, 1940, **36**, 856.

[21] Ley and Arends, *Z. physik. Chem.*, *B*, 1931, **15**, 311.

[22] Van Arkel and de Boer, *Die chemische Bindung als elektrostatische Erscheinung* (Hirzel, 1931).

place at all. The energy necessary for the primary process according to reaction (2.1) is given by:

$$(h\nu)_{\mathrm{Fe}} = -\, I_{\mathrm{Fe}^{2+}} - D_{\mathrm{H_2O}} + E_{\mathrm{OH}} + X$$
$$X = (-\, H_{\mathrm{Fe}^{2+}} + H'_{\mathrm{OH}} + H'_{\mathrm{Fe}^{3+}}.$$

This energy can also be calculated from the Fe^{3+}/Fe^{2+} electrochemical potential, the value of which is + 0·75 volts[17] measured against the hydrogen electrode (at 25°). This corresponds to the reaction:

$$\mathrm{Fe^{2+}{}_{aq} + H^{+}{}_{aq} = Fe^{3+} + \tfrac{1}{2}H_2 - 0{\cdot}75\ e.v.}$$

combined with

$$\mathrm{\tfrac{1}{2}H_2 = H - 2{\cdot}2\ e.v.}$$
$$\mathrm{H_2O = H^{+}{}_{aq} + OH^{-}{}_{aq} - 0{\cdot}8\ e.v.}$$

$$\mathrm{Fe^{2+}{}_{aq} + H_2O = Fe^{3+}{}_{aq} + OH^{-}{}_{aq} + H - 3{\cdot}76\ e.v.} \qquad (2.3)$$

The photochemical decomposition requires 4·5 e.v.[7] The difference of 0·8 e.v. must be attributed to the incomplete hydration of the OH^- and Fe^{3+} formed in the reaction.

Farkas and Farkas[4] have correctly deduced the energy requirement of 4·5 e.v. for the reaction ($Fe^{2+}{}_{aq} = Fe^{3+}{}_{aq}$ + electron). However, they assume that this reaction represents the actual photochemical process which takes place on irradiation, because they compare this value of 4·5 e.v. with the experimentally observed one. This is, of course, not the case; the actual photochemical process which takes place is represented by reaction (2.3), which only requires 3·76 e.v. and there is an excess energy of 0·74 e.v. available to balance the incomplete hydration.

It is of interest to compare with this the energy changes involved in the thermal evolution of hydrogen which takes place in the acid solutions of chromous and titanous ions. Both these reactions are accelerated in the presence of platinised platinum.

(*b*) Chromous and Titanous Ions.

The Cr^{3+}/Cr^{2+} normal potential, measured against the hydrogen electrode is — 0·38 e.v. (25° C.) therefore we have the reactions:

$$\mathrm{Cr^{2+}{}_{aq} + H^{+}{}_{aq} = Cr^{3+}{}_{aq} + \tfrac{1}{2}H_2 + 0{\cdot}38\ e.v.}$$
$$\mathrm{\tfrac{1}{2}H_2 = H - 2{\cdot}2\ e.v.}$$

$$\mathrm{Cr^{2+}{}_{aq} + H^{+}{}_{aq} = Cr^{3+}{}_{aq} + H - 1{\cdot}82\ e.v.} \qquad (2.4)$$

This reaction is fairly endothermic and it is doubtful whether it can take place at all in homogenous solution. It is not impossible that it proceeds, even under ordinary conditions as a wall reaction.

In the presence of platinised platinum the reaction is greatly accelerated. The reason for this may be found in the fact that the hydrogen atoms formed in reaction (2.4) are not formed free in solution but are adsorbed on the surface of the platinum. We thereby gain the adsorption energy given by:[23]

$$\mathrm{H = (H)_{ads} + 2{\cdot}5\ e.v.}$$

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[23] Lennard-Jones, *Trans. Faraday Soc.*, 1932, **28**, 341.

and obtain for the reaction in the presence of the heterogenous catalyst:

$$Cr^{2+}{}_{aq} + H^{+}{}_{aq} = Cr^{3+}{}_{aq} + H_{ads} + 0{\cdot}68 \text{ e.v.} \qquad (2.5)$$

followed by the recombination of the adsorbed hydrogen atoms to give H_2.

Similar considerations hold for the case of thermal evolution of hydrogen from acid solutions containing Ti^{3+} ions.

(*c*) Ceric Ion.

The photochemical behaviour of Fe^{2+} ion is in a way similar to that of negative ions. In both cases the primary process corresponds to an electron affinity spectrum: the electron is detached under the influence of a light quantum and decomposes the water.

The photochemical behaviour of ceric ion belongs to a different category.

The ceric ion is first raised to an excited state by the light absorption and the excited ceric ion (Ce^{4+*}) is then capable of extracting an electron from one of the water molecules in its hydration shell, which is thereby oxidised finally yielding molecular oxygen and hydrogen ions.
Photochemical primary process:

$$\begin{array}{lrcll}
 & Ce^{4+} + h\nu & = & Ce^{4+*} & (2.8) \\
 & Ce^{4+*} + H_2O & = & Ce^{3+} + H^{+} + OH & (2.9) \\
 & 2OH & = & H_2O + O \, . & (2.10) \\
 & 2O(+ M) & = & O_2(+ M), . & (2.11) \\
\text{reverse process:} & Ce^{3+} + OH & = & Ce^{4+} + OH^{-}. & (2.12)
\end{array}$$

It may be that it is not permissible to separate the reaction (2.8 and 2.9) and that they both occur in one act. The formation of excited ceric ions of any lifetime depends on whether or not ceric ions in solution show any marked fluorescence (corresponding to the reverse process ($Ce^{4+*} \rightarrow Ce^{4+} + h\nu$). However, it is not to be expected that aqueous ceric salt solutions show fluorescence, because H_2O molecules are very efficient in quenching this fluorescence by reacting with the excited ion according to reaction (2.9) before it has time to emit fluorescence.

The energy for the net process can be again calculated from the known electrochemical potential Ce^{4+}/Ce^{3+} which is $+ 1{\cdot}55$ volts[17] (against the hydrogen-electrode, at 25°).

$$\begin{array}{rcl}
Ce^{3+}{}_{aq} + H^{+}{}_{aq} & = & Ce^{4+}{}_{aq} + \tfrac{1}{2}H_2 - 1{\cdot}55 \text{ e.v.} \\
H + OH & = & H_2O + 5{\cdot}0 \text{ e.v.} \\
\tfrac{1}{2}H_2 & = & H - 2{\cdot}2 \text{ e.v.} \\
\hline
Ce^{3+}{}_{aq} + H^{+}{}_{aq} + OH & = & Ce^{4+}{}_{aq} + H_2O + 1{\cdot}35 \text{ e.v.} \qquad (2.6)
\end{array}$$

The absorption spectrum of ceric ions in solution has been determined by Porret and Weiss.[8] The long wave absorption limit was found at $\lambda \sim 5100$ A., corresponding to an energy of 2·4 e.v.; the difference of about 1 e.v. arising again out of the incomplete hydration during the electron jump.

A similar calculation can be carried out for the thermal formation of O_2 by cobaltic ions which was studied by Foerster and Oberer.[24] The experimental data lend support to the view that the cobaltic ions interact

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[24] Oberer, *Dissertation*, Zurich, 1903.

with OH^- ions directly because the velocity of the reaction decreases with increasing H^+ concentration. The normal potential of the Co^{3+}/Co^{2+} is + 1·8 volts[17] (against the hydrogen-electrode, at 25°).

$$\begin{aligned} Co^{2+}{}_{aq} + H^+{}_{aq} &= Co^{3+}{}_{aq} + \tfrac{1}{2}H_2 - 1{\cdot}8 \text{ e.v.} \\ H + OH &= H_2O + 5{\cdot}0 \text{ e.v.} \\ \tfrac{1}{2}H_2 &= H - 2{\cdot}2 \text{ e.v.} \\ H_2O &= H^+{}_{aq} + OH^-{}_{aq} - 0{\cdot}8 \text{ e.v.} \\ \hline Co^{2+}{}_{aq} + OH &= Co^{3+}{}_{aq} + OH^-{}_{aq} + 0{\cdot}2 \text{ e.v.} \end{aligned} \qquad (2.7)$$

Ceric ions require at least 1·35 e.v. in order to decompose water into H^+ ions and OH radicals, whereas cobaltic ions can discharge hydroxyl ions in a reaction which is endothermic with only 0·2 e.v., and, therefore, can go on even at room temperature.

Summary.

1. More recent experimental work on the photochemical primary process of the following ions has been discussed :

I^-, SH^-, RS^- (mercaptan ions) Fe^{2+}, Ce^{4+}.

2. The photochemical primary processes are adequately described by the theory of Franck and Haber but a number of chemical factors have to be taken into account for the secondary reactions. For instance, in the case of iodide ions the reaction of iodine molecules with OH^- or H_2O is capable of explaining the different behaviour of acidified solutions.

3. The energy necessary for the photochemical decompositions have been calculated independently from the corresponding electrochemical oxidation-reduction potentials (ferrous/ferric, cerous/ceric etc.).

4. The thermal formation of hydrogen gas from chromous solutions and the thermal formation of molecular oxygen from cobaltic solutions are discussed from a similar point of view.

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