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The Decomposition of Water by XRays in the Presence of the Iodide or Bromide Ion

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The Oxidation of the Ferrocyanide, Arsenite and Selenite Ions by the Irradiation of Their Aqueous Solutions with X-Rays

Gas-free solutions containing the ferrocyanide ion were irradiated with x-rays and were analyzed for hydrogen and oxygen; and for the ferrocyanide ion by potentiometric titration with potassium permanganate. The ferrocyanide is oxidized to ferricyanide and hydrogen is liberated in the equivalent amount. The number of equivalents oxidized is independent of the concentration, from 0.1 to 100.0 millimoles per 1000 cc and of the hydrogen ion concentration from $pH=2.0$ to 11.0, and equals 1.10 microequivalents per 1000 r per 1000 cc. Solutions of arsenite and selenite, which were studied over the same range of concentration and of pH, were transformed by irradiation to arsenate and selenate, respectively, with the production of hydrogen, and the number of equivalents transformed was the same as in the case of the ferrocyanide. Similar results were previously obtained for the nitrite ion.[1]

It is concluded that all these transformations are due to one particular type of x-ray activated water molecule, produced in the amount of 0.55 micromole per 1000 r per 1000 cc. The reactions may be represented as follows:

$2Fe(CN)_6^{--}+(H_2O)_{act.}+H_2O=2Fe(CN)_6^{---}+2OH^-+H_2$

$AsO_3^{---}+(H_2O)_{act.}=AsO_4^{---}+H_2$

$SeO_3^{--}+(H_2O)_{act.}=SeO_4^{--}+H_2$

$NO_2^-+(H_2O)_{act.}=NO_3^-+H_2.$

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[1] H. Fricke and E. J. Hart, J. Chem. Phys. **3**, 365 (1935).

The Decomposition of Water by X-Rays in the Presence of the Iodide or Bromide Ion

We have earlier found[1] that no decomposition of water results from its irradiation with x-rays. We now find that decomposition does occur when the water is irradiated in the presence of either the iodide or the bromide ions.

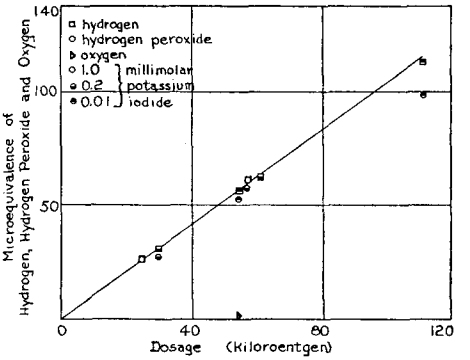

FIG. 1. Decomposition of water in the presence of the iodide ion at $pH=3.0$. Due to the decomposition of the primarily formed hydrogen peroxide, oxygen is produced at the highest dosage.

The action of these ions is catalytic inasmuch as we have been unable to detect any change in their concentrations as a result of the irradiation. In acid solutions, in the presence of sulfuric acid at $pH=3$ and 4, hydrogen and hydrogen peroxide are produced in the amount of 0.55 micromole per 1000 cc and per 1000 r of dosage. In unbuffered solutions or in the presence of sodium hydroxide at $pH=11.0$, the same amount of hydrogen is produced, but instead of hydrogen peroxide, the equivalent amount of oxygen is obtained. The decomposition is independent of the halide ion concentration from 1.0* to 0.01 millimole per liter while for lower concentrations the decomposition decreases. Fig. 1 shows the results obtained for potassium iodide at $pH=3$.

In the presence of the chloride ion, this catalytic decomposition of the water is not obtained.

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[1] H. Fricke and E. R. Brownscombe, Phys. Rev. **44**, 240 (1933).
* For higher concentrations of the potassium iodide, free iodine is formed as a result of the irradiation.

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