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THE PHOTOCHEMISTRY OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE CONTAINING N_2O

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When an aqueous solution of potassium iodide for which $3.5 < pH < 11$ and containing N_2O is irradiated by light of wavelength 2537 Å the following reactions occur.
(* and ‡ denote photo excited ions).

$$I^-_{aq} + h\nu \rightarrow * \rightarrow ‡ \quad (\text{return to } I^-_{aq}: 0)$$

$$‡ + I^- \xrightarrow{1} H + OH^- + I_2^-$$

$$H + N_2O \xrightarrow{2} N_2 + OH \qquad \text{slow}$$

$$HO + I^- \xrightarrow{3} HO^- + I \qquad \text{fast}$$

$$I + I^- \xrightarrow{4} I_2^- \qquad \text{fast}$$

$$2\,I_2^- \xrightarrow{5} I_2 + 2I^- \text{ or } I_3^- + I^-$$

$$H + I_2^- \xrightarrow{6} H^+ + 2\,I^-$$

Consequently $\Phi(N_2) = \Phi(I_2)$ increases with concentration of N_2O and KI to a limiting value of 0.165, which is the maximum attainable yield of hydrogen atoms as a result of the first two processes, and k_1/k_0 can be evaluated from the experimental results. At low $[N_2O]$ the rate of reaction tends to become proportional to $(I_a[N_2O])^{2/3}$, and the rotating sector technique can be used to obtain the values of k_2, k_3 and k_4.

Change of pH below 3.5 and above 11 has dramatic effects. The sharp decline in $\Phi(I_2)$, the constancy of $\Phi(N_2)$ and the appearance of oxygen in yields such that $\Phi(N_2) = \Phi(I_2) + 2\,\Phi(O_2) = 0.16$ when the pH is increased above pH 11 is caused by a simple competition between reaction 3 and reaction 7.

$$HO + OH^- \xrightarrow{7} O^-aq$$

The striking decrease of $\Phi(N_2)$, the increase of $\Phi(H_2)$ from zero and the minimum in $\Phi(I_2)$ which occur when the pH is decreased below 3.5 are due to two causes. Firstly, H^+ competes with N_2O for H forming H_2^+ in reaction 9, which

$$H + H^+ \xrightarrow{9} H_2^+$$

always oxidizes iodide according to equation 10. Consequently

$$H_2^+ + I^- \xrightarrow{10} H_2 + I \qquad \text{fast}$$

over this pH range $\Phi(I_2) = \Phi(H_2) + \Phi(N_2)$ and $\Phi(H_2)/\Phi(N_2) = k_9(H^+)/k_2(N_2O)$. Secondly, small concentrations of H^+ interfere with reaction (1) so that Φ_H decreases as the pH changes from 3.0 to 1.2 but larger concentrations of H^+ facilitate the formation of H, presumably via a reaction which may be written according to equation 11, so that Φ_H increases as the pH is further reduced.

$$\bullet + H^+ \xrightarrow{11} H + I$$

The numerical values of k_2, k_5, k_6 and k_9 and of the ratios k_0/k_1 and k_8/k_7 will be discussed.

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