experiments definitely rule out the mechanism of Franck and Haber[28] for this system.

The results with N_2O prove also that the role of the positive H^+ ion is not unique and that another, neutral electron scavenger can lead to a similar process.

The present picture involves a thermal electron detachment process from the excited state of the solvated negative ion, leading to the formation of a solvated electron in the aqueous solution. The formation of a thermalized electron is plausible in the case of an excited iodide ion, where the electron in the expanded orbital is acted upon only by the polarization field of the medium.

Franck and Scheibe[29] in their original work postulated a photodetachment process as the primary light absorbtion act of negative ions in solution. Our results show that this occurs only as the result of a secondary thermal process.

Acknowledgment.—This research was sponsored by the Israel Atomic Energy Commission.

(28) J. Franck and F. Haber, *Sitzber. preuss. Akad. Wiss. Physik Math. Klasse*, 750 (1931).

(29) J. Franck and G. Scheibe, *Z. physik. Chem.*, **A139**, 22 (1928).

THE EFFECT OF OXYGEN ON THE PHOTOCHEMISTRY OF THE IODIDE ION IN AQUEOUS SOLUTIONS

By Joshua Jortner, Michael Ottolenghi, and Gabriel Stein

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel

Received December 28, 1961

The effect of O_2 on the photochemistry of aqueous iodide solutions was investigated. O_2 was found to act as a scavenger for both electrons and H atoms. The reaction mechanisms are discussed and kinetic data for the reaction of O_2 with electrons and H atoms are derived. The photochemical results are compared with data from radiation chemistry.

Introduction

Radiation chemical investigations[1] indicate that oxygen dissolved in aqueous solutions acts as an efficient scavenger for both solvated electrons and for H atoms.[1]

Following the preceding work,[2] the effect of O_2 on the photochemistry of the iodide ion was investigated. The investigation of the oxygen effect on this system is of importance for a further insight into the specific scavenging mechanisms of H atoms and their precursors.

Experimental

The experimental technique was similar to that previously employed.[2] Evacuated neutral potassium iodide solutions were equilibrated with air or oxygen for 2–3 hr. The pH was adjusted by acid added just before irradiation, which was carried out as fast as possible to avoid thermal oxidation. The kinetics of the post-irradiation effect in aerated solution were measured by the determination of the time dependence of the I_2 concentration in the reaction vessel after stopping the irradiation. The thermal oxidation was followed by a similar technique.

Results

Some experimental difficulties were encountered in the experimental investigation of this system at low pH. The effect of the thermal oxidation of I^- at pH < 2.5 is appreciable. Short irradiation times (15 sec.) were used, and corrections for thermal oxidation were introduced. The derivation of the experimental results for the initial quantum yields was further complicated by the observation of a post-irradiation effect in aerated solutions. It was assumed that this effect is due to the production of H_2O_2 in irradiated solutions. To confirm this hypothesis a kinetic study of this process was carried out. We measured the dependence of the I_2 concentration (determined as the optical density D_τ) on the time τ after stopping the irradiation. First-order kinetic curves were obtained by plotting ln $(D_\infty - D_\tau)$ as a function of τ (Fig. 1). The experimental values of D_τ were corrected for thermal oxidation. From the first-order rate constants k the second-order rate constants $k/[I^-]$ were obtained, in agreement with the result for thermal oxidation of I^- by H_2O_2.[3] These results indicate that H_2O_2 is produced in the photochemical system.

Table I

Post-Irradiation Effect in Irradiated KI Solutions

$[I^-] = 0.15\ M$, $J = 15 \times 10^{-7}$ einstein sec.$^{-1}$ l.$^{-1}$

pH	k, min.$^{-1}$	$k/[I^-]$, l. mole^{-1} min.$^{-1}$	D_0	D_∞
1.29	0.048	0.75	0.265 ± 0.02	0.48 ± 0.03
0.83	0.22	3.37	0.26 ± 0.02	0.50 ± 0.03

As the thermal oxidation of I^- by H_2O_2 during the short irradiation period is negligible, the initial $[I_2]_0$ concentration corrected for the post-irradiation effect was obtained from extrapolation of log $(D_\infty - D_\tau)$ to $\tau = 0$. We find (Table I) $2D_0 = D_\infty$, *i.e.*, $2[I_2]_0 = [I_2]_\infty$. Thus the quantum yield for H_2O_2 production is equal to that of I_2 during irradiation. The quantum yield at low pH could be evaluated by measuring $\gamma(I_2) + \gamma(H_2O_2)$. This was done by determination of I_2 yield after the completion of the post-irradiation effect about 60 min. after stopping the irradiation.

Dependence of γ on pH and O_2 Concentration—In Fig. 2 and 3 we represent the dependence of the initial quantum yield for I_2 production on pH and O_2 concentration. These quantum yields were corrected for thermal oxidation and do not include contribution of the oxidation by H_2O_2. γ_i at

(1) N. F. Barr and A. O. Allen, *J. Phys. Chem.*, **63**, 928 (1959).

(2) J. Jortner, M. Ottolenghi, and G. Stein, *ibid.*, **66**, 2037 (1962).

(3) H. A. Liebhafsky and A. Mohamed, *J. Am. Chem. Soc.*, **55**, 3977 (1933).

$[O_2] = 2 \times 10^{-4}\ M$ in air saturated solution at pH 2.56 and 3.56 was found to be independent of the light intensity J. The pH dependence of $\gamma(I_2)$ in Fig. 2 is represented in the concentration region of O_2 where $\gamma(I_2)$ is independent of O_2 concentration.

At low pH values (below 2) $\gamma_i(I_2)$ is independent of H^+ concentration and attains the limiting value $\gamma_i = 0.29 \pm 0.02$ at 25°, which is again identical with the limiting quantum yield obtained in other scavenger systems.[2]

When the pH is increased $\gamma_i(I_2)$ decreases. The independence of γ on J indicates that this decrease has to be assigned to secondary radical recombination.

At pH 2.56 in air saturated solutions $\gamma(I_2) = 0.26$. This value is identical with the result $\gamma = 0.26$ obtained in the presence of high concentration of alcohols at this pH.[4] Thus it appears that at pH 2.5–3.0 the decrease of the quantum yield is due mainly, as in the case of alcohols, to the formation of the radical pair $(I + H)_{II}$ and the scavenging of the H atom by O_2. However at higher pH values the γ values obtained in the presence of O_2 and alcohols do differ markedly. At pH 3.56 $\gamma(I_2) = 0.16$ in air saturated solutions and $\gamma(I_2) = 0.225$ in the presence of 1 M methanol or isopropyl alcohol.[4] This indicates that in the presence of oxygen an additional mechanism is operating. As radiation chemical studies[1] indicate, O_2 is an efficient scavenger for electrons. Thus at low H^+ concentrations (pH > 3) electron capture by O_2 will occur. This reaction will compete efficiently with electron capture by H^+, leading to the formation of O_2^-. This ion may however reduce an iodine atom to I^- leading to a deactivation back reaction. Alternatively O_2^- can react with H^+ ion yielding HO_2. This scavenging reaction will compete with the back reaction $I + O_2^-$. The hydroperoxy radical yields H_2O_2 by oxidation of another I^- ion.

Reaction Mechanism in the Presence of O_2.—The experimental results for the initial quantum yield in oxygen containing solutions are interpreted in terms of a parallel—consecutive scavenging mechanism

$$(I + e)_I + H^+ \longrightarrow (I + H)_{II} \quad k_{H^+ + e} \quad (1)$$

$$(I + H)_{II} + O_2 \longrightarrow I + HO_2 \quad k_{O_2 + H} \quad (2)$$

$$(I + e)_I + O_2 \longrightarrow (I + O_2^-)_{III} \quad k_{O_2 + e} \quad (3)$$

$$(I + O_2^-)_{III} + H^+ \longrightarrow I + HO_2 \quad k_{H^+ + O_2^-} \quad (4)$$

Followed by

$$I^- + HO_2 \longrightarrow I + HO_2^- \quad (5)$$

$$2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O \quad (6)$$

The radical pairs I, II, and III may also contribute to the residual yield.

An exact mathematical treatment of this system is complicated. We attempt to present an approximate treatment applying simplifying assumptions as presented before.[2,4]

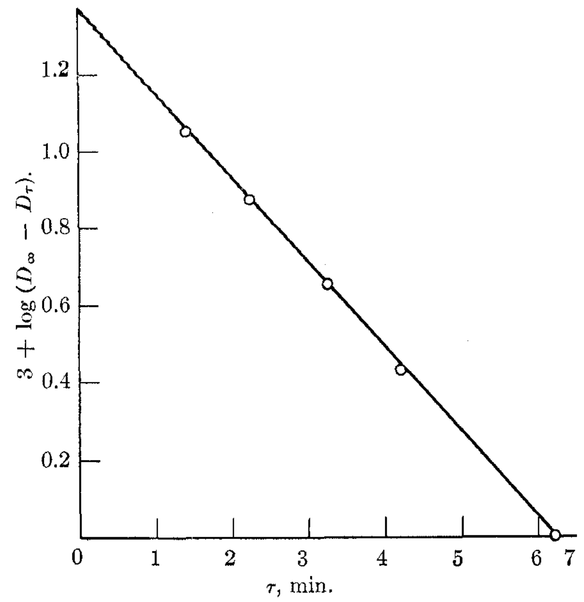

Fig. 1.—Post-irradiation effect of aerated solution: $[I^-] = 0.15\ M$, pH 0.83.

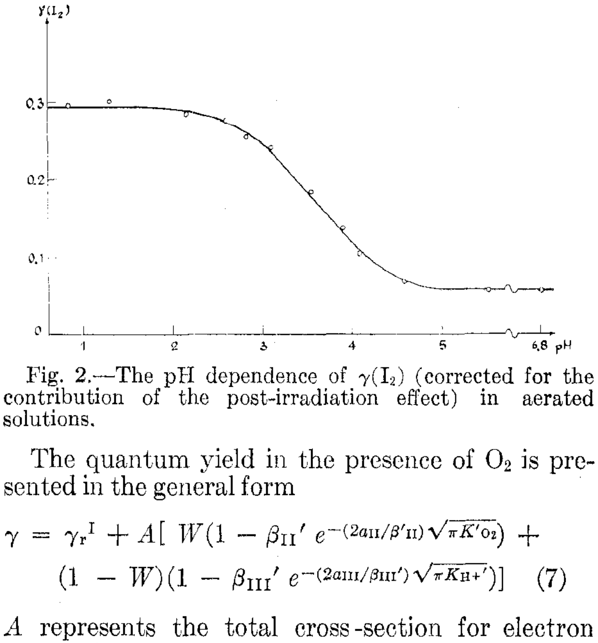

Fig. 2.—The pH dependence of $\gamma(I_2)$ (corrected for the contribution of the post-irradiation effect) in aerated solutions.

The quantum yield in the presence of O_2 is presented in the general form

$$\gamma = \gamma_r{}^I + A[\ W(1 - \beta_{II}{}'\ e^{-(2a_{II}/\beta'_{II})\sqrt{\pi K'_{O_2}}}) + (1 - W)(1 - \beta_{III}{}'\ e^{-(2a_{III}/\beta_{III}{}')\sqrt{\pi K_{H^+}{}'}})] \quad (7)$$

A represents the total cross-section for electron scavenging from cage I by O_2 and H^+. Assuming that the radical pair I yields the residual yield $\gamma_r{}^I$ independent of the two scavenger concentrations we set

$$A = \Gamma[1 - \beta_I{}'e^{-(2a_I/\beta_I{}')\sqrt{\pi K_{O_2} + K_{H^+}}})] - \gamma_r{}^I \quad (8)$$

The constants K in eq. 7 and 8 are defined by

$$K_{O_2} = K_{O_2 + e}[O_2]$$

$$K_{O_2}{}' = k_{O_2 + H}[O_2]$$

$$K_{H^+} = k_{H^+ + e}[H^+]$$

$$K_{H^+}{}' = k_{H^+ + O_2^-}[H^+]$$

W represents the fraction of radicals from cage I scavenged by H^+, *i.e.*, $W = K_{H^+}/(K_{H^+} + K_{O_2})$; thus the cross-section for the formation of cage II is WA.

---

[4] J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **66**, 2029 (1962).

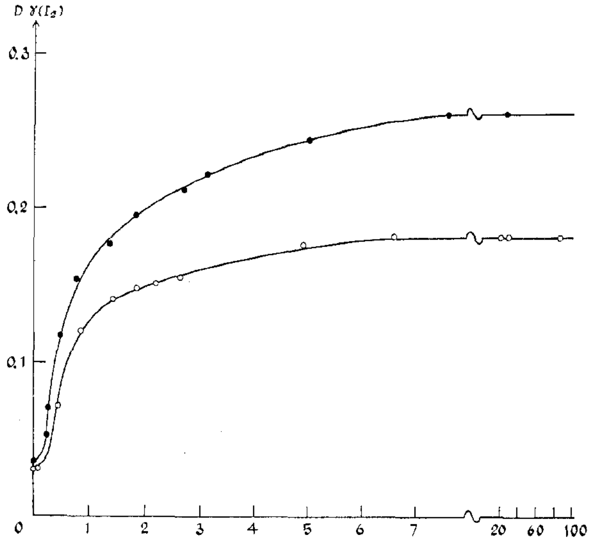

Fig. 3.—Dependence of $\gamma(I_2)$ and O_2 concentration: ●, pH 2.56; ○, pH 3.56.

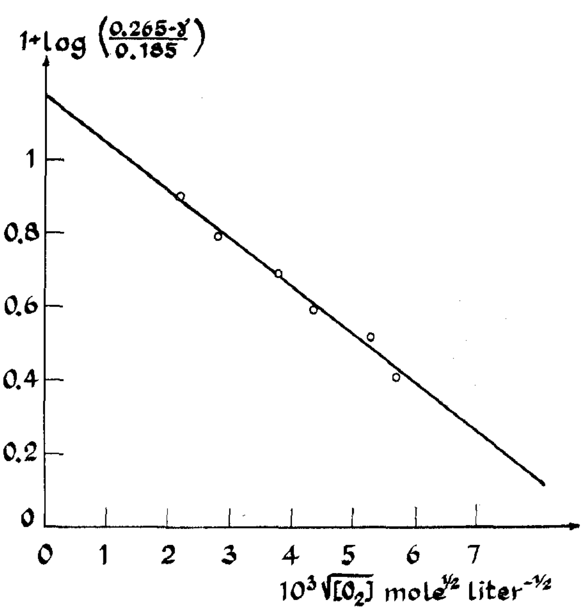

Fig 4.—Scavenging of H atoms by O_2 at pH 2.56.

Equation 7 can be transformed into the form

$$\gamma = \gamma_r{}^{I} + A[1 - W\beta_{II}{}'\, e^{-(2a_{II}/\beta_{II}')\sqrt{\pi K_{O_2}{}'}} - (1 - W)\beta_{III}{}'\, e^{-(2a_{III}/\beta_{III})'\sqrt{\pi K_{H^+}{}'}}] \quad (7')$$

Scavenging of H Atoms by O_2.—At sufficiently high H^+ concentrations, at pH < 3, we assumed that the reaction path involves scavenging by H^+ (reaction 1) and the contribution of reaction 3 is negligible. Equation 7′ is reduced to the form

$$\gamma = \gamma_r{}^{I} + [\Gamma(1 - \beta_I{}'\, e^{-2a_I/\beta_I'\sqrt{\pi K_{H^+}}}) - \gamma_r{}^{I}] \times (1 - \beta_{II}{}'\, e^{-(2a_{II}/2\beta_{II}')\sqrt{\pi K_{O_2}}}) \quad (9)$$

This equation was applied for the treatment of the dependence of $\gamma(I_2)$ on O_2 concentration at pH 2.56. At limiting high O_2 concentration the quantum yield is (Fig. 3)

$$\Gamma(1 - \beta_I{}'\, e^{-(2a_I/\beta_I')\sqrt{\pi K_{H^+}}}) - 0.26$$

The rate constant $k_{O_2 + H}$ was evaluated by plotting $\log [(0.26 - \gamma)/(0.26 - 0.08)]$ as a function of $\sqrt{[O_2]}$. From Fig. 4 we obtain $\beta_{II} \sim 1$ and $2a_{II} \times \sqrt{\pi k_{H + O_2}} = 260$ mole$^{-1/2}$ l.$^{1/2}$.

Scavenging of O_2^- by H^+.—For high pH $K_{O_2} \gg K_{H^+}$ and at high O_2 concentration where $A = \Gamma - \gamma_r{}^{I}$ we set $W = 0$ and thus obtain from eq. 7′, for the scavenging reaction of O_2^- by H^+

$$\ln\left(\frac{\Gamma - \gamma}{\Gamma - \gamma_r{}^{I}}\right) = \ln \beta_{III}{}' - \frac{2a_{III}}{\beta_{III}{}'}\sqrt{\pi k_{H^+ + O_2^-}}\,[H^+] \quad (10)$$

We have assumed that eq. 10 is applicable for pH > 3.5. From the experimental results in this high pH region we obtained $\beta_{III}{}' = 1$ and $2a_{III} \times \sqrt{\pi k_{H^+ + O_2^-}} = 60 \pm 20$. This result indicates that the rate constant $k^{H^+ + O_2^-}$ is high, in agreement with kinetic data[5] which indicate that the rates of neutralization of bases in solution are diffusion controlled.

Semiquantitative Treatment of Experimental Results in the Presence of O_2.—The numerical values for $\beta_{II}{}'$, $\beta_{III}{}'$, $2a_{II}\sqrt{\pi k_{H + O_2}}$, and $2a_{III} \times \sqrt{\pi k_{O_2^- + H^+}}$ obtained from the above approximate treatments may be substituted now in eq. 7′ yielding

$$\gamma = 0.08 + [0.29\,(1 - 0.725e^{-50\sqrt{[H^+] + \alpha[O_2]}}) - 0.08] \times \left[1 - \left(\frac{e^{-260\sqrt{[O_2]}}}{1 + \alpha([O_2]/[H^+])} - \frac{e^{-60\sqrt{[H^+]}}}{1 + ([H^+]/\alpha[O_2])}\right)\right] \quad (11)$$

where $\alpha = k_{O_2 + e}/k_{H^+ + e}$. For the parameters specifying electron scavenging by H^+, appearing in A, we chose $\beta_I = 0.725$ and $(2a_I/\beta_I{}')\sqrt{\pi k_{H^+ + e}} = 50$. This value is somewhat lower than that obtained in the presence of alcohols,[4] but is consistent with the results for competitive scavenging of electrons by H^+ and N_2O.[2]

The experimental results do not make possible the exact evaluation of α. However, reasonable agreement of the experimental results with eq. 11 is obtained for $\alpha = 1-5$ showing that the efficiency of O_2 and H^+ as electron scavengers is of the same order of magnitude.

The comparison of the experimental results with those obtained from eq. 11 is presented in Table II.

The good agreement of the calculated and experimental results should be accepted with some reservation. The general treatment presented in this work is too approximate for a quantitative treatment of this complicated system.

Discussion

The Residual Yield in O_2 Solutions.—The quantum yield obtained at pH > 4.5 in air and oxygen saturated solutions is independent of pH. This

---

[5] M. Eigen and K. Kusten, *J. Am. Chem. Soc.*, **82**, 5952 (1960).

TABLE II

QUANTUM YIELDS IN THE PRESENCE OF OXYGEN. CALCULATED RESULTS FROM EQUATION 11 WITH $\alpha = 3$

pH	$[O_2]$, mole l.$^{-1}$	$\gamma(I_2)$, expt.	$\gamma(I_2)$, calcd.
1.0	2.3×10^{-4}	0.290 ± 0.005	0.290
2.15	2.3×10^{-4}	$.285 \pm .005$	.275
2.6	2.3×10^{-4}	$.260 \pm .005$	.270
2.8	2.3×10^{-4}	$.246 \pm .005$	.250
3.9	2.3×10^{-4}	$.133 \pm .005$	.155
4.1	2.3×10^{-4}	$.110 \pm .005$	.140
2.56	6.6×10^{-5}	$.250 \pm .005$	.240
2.56	3.95×10^{-5}	$.230 \pm .005$	.235
2.56	2.5×10^{-5}	$.207 \pm .005$	.210
2.56	1.32×10^{-5}	$.190 \pm .005$	.175
2.56	0.83×10^{-5}	$.150 \pm .005$	.170
3.56	6.6×10^{-5}	$.180 \pm .005$	.171
3.56	3.95×10^{-5}	$.167 \pm .005$	.168
3.56	2.5×10^{-5}	$.150 \pm .005$	.153
3.56	1.32×10^{-5}	$.137 \pm .005$	.142
3.56	0.83×10^{-5}	$.122 \pm .005$	.133

quantum yield, $\gamma = 0.065 \pm 0.01$, represents the experimental determination of the residual yield. In the presence of oxygen the residual yield represents the sum of the residual yields γ_r^{I} and γ_r^{III}. As indicated by the experimental results in the presence of alcohols at high pH[2] hydrogen atom scavengers are not efficient for the residual yield in neutral solution. On the other hand, O_2 is an efficient scavenger for electrons. The residual yield in the presence of O_2 is about equal to the extrapolated values of $\gamma_r^{I} = 0.07$ and 0.08 obtained[2,4] from the pH dependence in the presence of alcohols and from scavenging by N_2O. These results indicate that the residual yield from cage I involves solvated electrons and not H atoms diffusing into the bulk.

Relative Rate Constants for the Reactivity of H Atoms.—The experimental results from the scavenging experiments make possible the evaluation of relative rate constants for the reactivity of various scavengers with H atoms and electrons. The relative rate constants for the reactivity of H atoms with various scavengers are shown in Table III and compared with kinetic data obtained from radiation chemical investigations.[6] These radiation chemical investigations were carried out at low pH to assure that H atoms as such are involved in these reactions.[6] The agreement between the photochemical and radiation chemical data is fair and indicates the consistency of the mechanisms derived.

TABLE III

KINETIC DATA FOR THE REACTIVITY OF H ATOMS

Scavenger	$2a_{II}\sqrt{\pi k}$, mole$^{-1/2}$ l.$^{1/2}$	$\frac{k_{H+S}}{k_{H+O_2}}$ (photochemical data)	$\frac{k_{H+S}}{k_{H+O_2}}$ (radiation-chemical data)[6]
Methanol	3.88	16×10^{-5}	8.5×10^{-5}
Isopropyl alc.	20	5×10^{-3}	2.6×10^{-3}
H^+	2.6	10^{-4}	...
O_2	260		

The Reactivity of Electrons.—Molecular oxygen in the photochemical system was found to act as an efficient scavenger for electrons. The rate constant for the reaction

$$O_2 + e_{aq} \longrightarrow O_2{}^-{}_{aq} \qquad (12)$$

is about equal to the rate constant for the reaction

$$H^+{}_{aq} + e_{aq} \longrightarrow H \qquad (13)$$

This result is in complete agreement with a recent radiation chemical investigation of the pH dependence of the decomposition of H_2O_2 in the presence of O_2.[7]

Czapski and Allen[7] concluded that for the reducing radicals produced from the radiolysis of neutral aqueous solutions, the rate constants for reactions 12 and 13 are equal within a few per cent. In a similar way agreement was obtained[2] between photochemical and radiation chemical data for the relative rate constants for scavenging electrons by H^+ and N_2O. These results indicate the identity of H atom precursors formed by thermal electron detachment from the excited state of the iodide ion, with the reducing species formed from the radiolysis of neutral aqueous solutions.

Acknowledgment.—This research was sponsored by the Israel Atomic Energy Commission.

---

[6] J. Rabani, *J. Phys. Chem.*, **66**, 361 (1962).

[7] G. Czapski and A. O. Allen, BNL. 5576, 1961; *J. Phys. Chem.*, **66**, 262 (1962).