THE PHOTOCHEMISTRY OF THE IODIDE ION IN AQUEOUS SOLUTION

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The photochemistry of evacuated potassium iodide solutions at 2537 Å. was investigated. The dependence of the initial quantum yields on pH, iodide ion concentration and light intensity was investigated. The nature of the residual pH independent yield at $p\text{H} > 3$ is discussed. The pH dependence of the initial quantum yields could be represented by a linear dependence on the square root of H^+ ion concentration. It is shown that this is in agreement with a mechanism based on the theory of diffusion controlled scavenging. The H^+ ion acts as an electron scavenger for a species (electrons or H atoms) formed in the photochemical cage and yield H atoms in the bulk of the solution. The reactivity of H atoms photochemically produced in solution was investigated, and evidence for a pH dependent oxidation mechanism of I^- by H atoms is presented, which may involve the H_2^+aq ion as the actual oxidizing agent.

Introduction

In the ultraviolet region aqueous solutions of iodide show an intense absorption[1] $\epsilon_{2262} = 1.32 \times 10^4$ at 25°, characterized by a high oscillator strength $f = 0.25$. This band has been classified as a charge transfer spectrum.[2,3] For the alkali halides in aqueous solutions the absorption band is typical of the anion and no spectroscopic evidence for ion pair formation has been found.[4] The nature of the excited state has been a matter of controversy.[4,5a,5b]

As has been well known for a long time[6] aerated aqueous iodide solutions liberate free iodine on illumination. More recently the same was shown to occur in deaerated solution.[7,8] The photochemical wave length threshold was shown to coincide with the absorption band onset.[7] Farkas and Farkas[9] showed that the quantum yield was pH dependent, a conclusion supported by Franck and Platzman,[10] who suggest a competition between the decay of the excited state and its interaction with H_3O^+ ion as the reason for the pH dependence. On the other hand Rigg and Weiss[8] conclude that the pH dependence arises out of the competition in bulk between the back reaction of H + I and H_2^+ formation by the reaction between H + H^+. The two theories thus differ in their interpretation of radical formation and the relatively low quantum yield.

Recently the system has been investigated in the whole pH region in the presence of N_2O,[11] and by flash photolysis technique,[12,13] where the existence of the I_2^- ion as intermediate was demonstrated.

The purpose of the present work was to investigate the mechanism of primary radical formation in this system, and the possible specific role of the H_3O^+ ion in this process. Another aspect of this work is the investigation of the chemistry of radicals photochemically produced. It was postulated by Weiss[14] that H atoms in aqueous solutions may act as an oxidizing agent through the intermediate formation of H_2^+. The occurrence of such oxidation reactions is now well established. Using H atoms externally generated it was shown[15] that in the case of the I^- ion the results are consistent with the view that the actual oxidant is the H_2^+ ion. Further independent investigation of this problem appeared desirable in the case of the photochemistry of I^-.

Experimental

Light Source.—The light source was a low pressure mercury lamp operated at 1000 v. drawn from a step up transformer fed from stabilized mains. The current through the lamp (30–150 ma.) was varied by means of a Variac in the primary circuit of the lamp transformer. The output of the lamp was monitored by an I.P. 21 photomultiplier tube connected to a Photovolt instrument. About 90% of the light output is at 2537 Å.

The radiation was filtered through a 5 cm. quartz cell containing $KI-I_2$ aqueous solution permitting the isolation of the strong Hg 2537 Å. line.

Actinometry was carried out by means of the uranyl oxalate actinometer.[16] The chemical change was linear in light intensity as determined by the monitoring photocell. As a check a ferri oxalate actinometer[17] was used. In a typical experiment we obtained for the light intensity, J

J(uranyl oxalate) $J = 6.35 \times 10^{-7}$ einstein l.$^{-1}$ sec.$^{-1}$

J(ferri oxalate) $J = 6.20 \times 10^{-7}$ einstein l.$^{-1}$ sec.$^{-1}$

Agreement between the results was satisfactory.

Reaction Cell.—The reaction cell was adapted from a 4 cm. quartz absorption cell with flat optical windows of 3 cm. optical length for light absorption at 2537 Å. and 4 cm. optical length for spectrophotometry. It was connected to a vacuum system through a valve. The cell orientation reative to the light source was held fixed during all experiments. In this cell 13 cc. of solution was used for each irradiation. Another cell was employed for gasometric analysis, consisting of quartz cylindrical cell with flat optical windows as basis, and 5 cm. optical length holding 60 cc. of solution.

Analysis.—Hydrogen was determined by a microgasometric method. The pressure was determined by a McLeod gauge.

Iodine was determined by its absorption as I_3^-. The spectrophotometric light source was an ordinary 6V 3A tungsten hot wire bulb, with a cut off filter above 400 mμ. An empirical calibration was carried out by introducing a

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

[2] E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 118 (1942).

[3] L. E. Orgel, *Quart. Rev.*, **8**, 422 (1954).

[4] G. Stein and A. Treinin, *Trans. Faraday Soc.*, **55**, 1086, 1091 (1959).

[5] (a) R. L. Platzman and J. Franck, *Z. Physik*, **138**, 411 (1954); (b) M. Smith and M. C. R. Symons, *Disc. Faraday Soc.*, **24**, 206 (1957).

[6] W. H. Ross, *J. Am. Chem. Soc.*, **28**, 788 (1906).

[7] K. Butkow, *Z. Physik*, **62**, 71 (1930).

[8] T. Rigg and J. Weiss, *J. Chem. Soc.*, 4198 (1952).

[9] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1120 (1938).

[10] R. L. Platzman and J. Franck, "Farkas Memorial Volume," Jerusalem, 1952, p. 21.

[11] F. S. Dainton and S. A. Sills, *Nature*, **186**, 879 (1960).

[12] L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1098 (1957).

[13] F. H. C. Edgecombe and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A253**, 154 (1959).

[14] J. Weiss, *Nature*, **165**, 728 (1950).

[15] G. Czapski, J. Jortner and G. Stein, *J. Phys. Chem.*, **63**, 1769 (1959).

[16] E. J. Bowen, "The Chemical Aspects of Light," Oxford University Press, New York, N. Y., 1946.

[17] C. A. Parker, *Proc. Roy. Soc. (London)*, **A220**, 104 (1953).

known amount of I_2 in aqueous iodide solutions, into the reaction cell, and measuring optical densities by means of the IP 21 photomultiplier and the Photovolt instrument. It was found that the optical density was independent of iodide ion concentration above 10^{-2} *M* and a linear dependence of *D* on the iodine concentration up to 1,2 × 10^{-5} mole liter^{-1} was found with an apparent molar absorption coefficient $\epsilon = 9 \times 10^3$ mole^{-1} liter cm.$^{-1}$ (compared to ϵ_{350} = 26500 mole^{-1} liter cm.$^{-1}$). At lower I^- concentrations a similar procedure was employed. The lower limit of iodine detected is about 2 × 10^{-7} mole liter^{-1} and the upper limit was 2.3 × 10^{-5} mole liter.$^{-1}$. This technique enabled an accurate determination of initial reaction yields.

Materials.—All chemicals used were of Analar grade. Solutions were prepared in triply distilled water (ordinary distillation followed by distillation from alkaline permanganate and phosphoric acid). Control experiments were carried out using water purified by irradiation with 200 kv. X-rays and decomposition of the H_2O_2 thus formed by irradiation with the 2537 Å. line of a low pressure Hg lamp. These experiments yielded the same results as obtained in triply distilled water.

Procedure.—A known amount of freshly prepared neutral potassium iodide solution or solid KI was introduced into the reaction vessel and the acid or buffer were added from a separate container, after evacuation, to avoid thermal oxidation. No thermal oxidation could be detected. Erratic results were obtained in solutions containing initial iodine concentration higher than 5 × 10^{-6} *M* causing a decrease of the initial yield. This effect was most important at high *p*H and low I^- concentration. The *p*H below 3.5 was adjusted by H_2SO_4 and above *p*H 3.5 by KH_2PO_4–Na_2HPO_4 buffer (10^{-3} *M*). The *p*H was determined at the end of each run.

The contents of the reaction cell were stirred continuously by a Teflon coated magnetic stirrer. For experiments on deaerated solutions the reaction cell was connected to the vacuum system for 20 seconds every five minutes until, after approximately 3.5 hours, its equilibrium vapor pressure was 1–2 × 10^{-5} mm. The small reaction cell was kept in a thermostated brass compartment in which water was circulated. Experiments were carried out at 25 ± 0.2°.

At suitable intervals after the beginning of irradiation a mechanical shutter separating the cell and the lamp was closed and the amount of free iodine determined. Hydrogen was determined at the end of each run in the large irradiation vessel. These iodine and hydrogen determinations were in satisfactory agreement of about 10%.

Results and Discussion

Dependence of Initial Yields on *p*H and Light Intensity.—An initial quantum yield γ_i was obtained from the expression

$$\gamma_i = \frac{1}{J}\left(\frac{d[I_2]}{dt}\right)_0$$

where *J* is the light intensity. The dependence of γ_i in evacuated solutions on *p*H, iodide ion concentration and light intensity was investigated.

Figure 1 presents the dependence of the yield of I_2 at constant light intensity on irradiation time. The initial slopes could be determined and hence γ_i was approximately evaluated.

The *p*H dependence of γ_i is shown in Fig. 2. Above *p*H 3.5 a residual *p*H independent quantum yield is observed. This is consistent with recent observations.[13] The pronounced dependence of γ_i in acid solutions is in qualitative agreement with previous investigations.[8]

The initial quantum yield is independent of light intensity. This observation was confirmed with reasonable accuracy for a low *p*H region (*p*H 0.8). These data are presented in Fig. 3, and are consistent with other recent results.[11]

The Nature of the Absorption Act and Primary Products.—There is good agreement between the experimental spectroscopic results and their recent theoretical interpretations regarding the nature of the primary absorption act. Both the theory of Smith and Symons[18,19] and that of Stein and Treinin[4,20] agree in that they postulate as did Platzman and Franck[5] a symmetrical excited state in which the electron is not bound to a single solvent molecule[9] but rather is bound in the field formed by the oriented water molecules of the solvent medium. In spite of detailed differences, concerning the structure of the excited level, both groups recently have concluded[19,20] that in the excited state the electron probably is confined to the first hydration layer of water molecules.

The restrictions imposed by the Franck–Condon principle on the optical electron transfer process have to be considered. The life time of the spherically symmetrical excited state of the iodide ion,[5] is of the order of the relaxation time of the solvent molecules. After a period of 10^{-10} to 10^{-11} sec. an iodine atom and an electron are formed. There is no experimentally observed fluorescence in aqueous iodide solutions. The life time of an

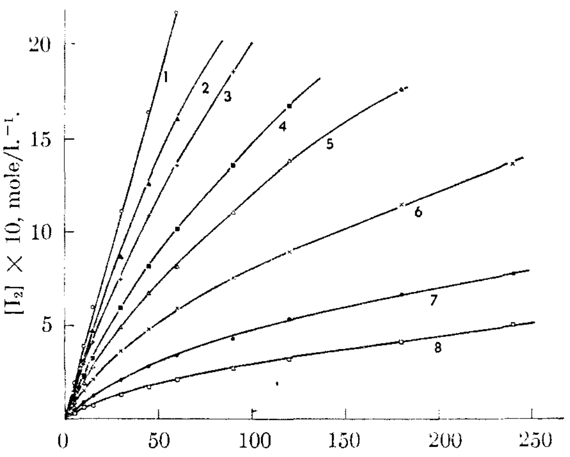

Fig. 1.—Photo-oxidation yields of iodide solutions at constant light intensity, I^- = 0.15 *M*, *J* = 9.7 × 10^{-1} einstein liter^{-1} sec.$^{-1}$: Curve 1, 0.74 *M* H_2SO_4; 2, *p*H 0.65; 3, *p*H 0.90; 4, *p*H 1.10; 5, *p*H 1.36; 6, *p*H 1.78; 7, *p*H 2.2; 8, *p*H 2.6.

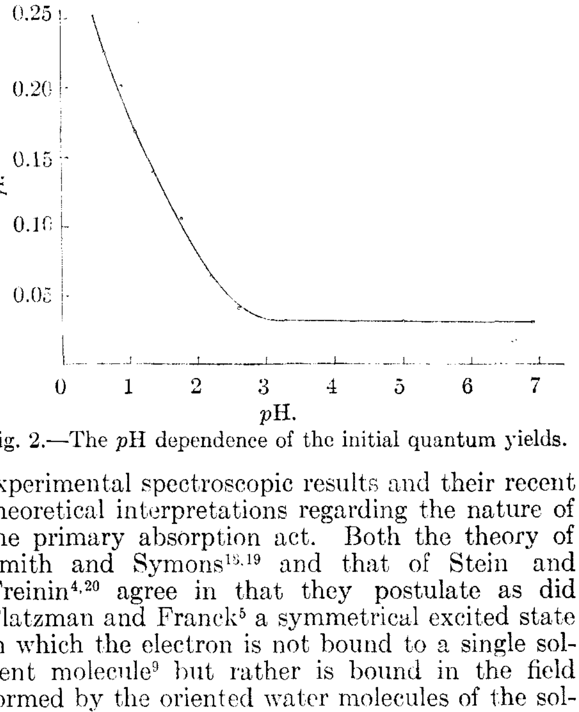

Fig. 2.—The *p*H dependence of the initial quantum yields.

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(18) M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, **54**, 338 (1958).

(19) T. R. Griffiths and M. C. R. Symons, *ibid.*, **56**, 1125 (1960).

(20) G. Stein and A. Treinin, *ibid.*, **56**, 1393 (1960).

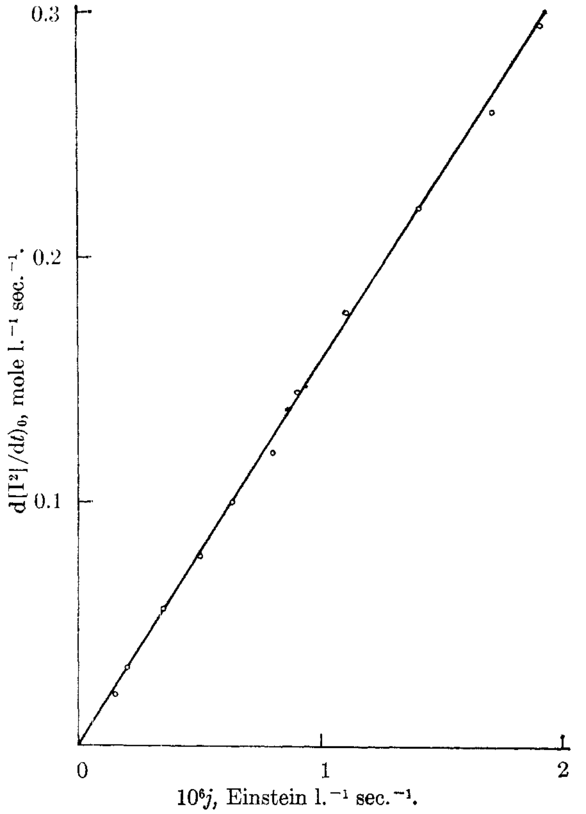

Fig. 3.—The dependence of the initial photo-oxidation yields of 5×10^{-2} *M* KI solutions on light intensity at *p*H 0.8.

excited state required before fluorescent radiative transition to the ground state occurs is of the order of 10^{-8} sec. or longer. Therefore in systems like that of aqueous iodide after 10^{-11} to 10^{-10} sec. the process of thermal degradation of the excited state may lead to an intermediate state, in which the electron is less confined, and may undergo a quasi random walk process in the vicinity of the iodine atom over the water molecules. A dissociative electron capture of this electron by a water molecule may result in the formation of an H atom by a *p*H independent mechanism. This may occur by localization of the electronic charge on a prestretched H–OH bond. The kinetic scheme will be presented in the form

$$I^-_{aq} \xrightarrow{h\nu} I^-_{aq}{}^* \longrightarrow (I + e)_{I} \longrightarrow (I + H)_{II} \quad (1)$$

where ( ) represents the solvent cage. The radical pairs in I or in II may undergo primary recombination, which is kinetically equivalent to a thermal deactivation of the excited state. The radical pairs which escape primary recombination may undergo diffusive secondary recombination with their original partners.[21] The radicals escaping recombination diffuse into the bulk. The residual *p*H independent yield observed in evacuated solutions above *p*H 3.5 indicates the operation of this mechanism. This model for the "*residual yield*" is actually a modification of the original Franck–Haber mechanism,[22] taking into account the Franck–Condon principle.

The Residual Yield.—Independent evidence derived from the investigation of the chemistry of hydrogen atoms in iodide solutions[15] indicates that at *p*H above 3 no oxidation reaction of I^- ion by H atoms occurs. Thus in this *p*H region the possible reactions of the radicals in bulk will be hydrogen atom recombination

$$2H \longrightarrow H_2 \quad (2)$$

and iodine formation by the mechanism proposed by Grossweiner and Matheson[12]

$$I + I^- \rightleftarrows I^-_2 \quad (3)$$

$$2I^-_2 \longrightarrow I^-_3 + I^- \quad (4)$$

$$I^-_2 + I \longrightarrow I^-_3 \quad (5)$$

$$2I \longrightarrow I_2 \quad (6)$$

These back reactions are possible

$$H + I \longrightarrow H^+ + I^- \quad (7)$$

$$H + I^-_2 \longrightarrow H^+ + 2I^- \quad (8)$$

As these experiments were carried out at relatively high $[I^-]$ concentration, it is reasonable to assume that every iodine atom introduced into the bulk is converted into the I^-_2 ion. This assumption is consistent with the results of Grossweiner and Matheson.[12] Including reactions 2,3,4 and 8 in the kinetic scheme the steady-state treatment for the intermediates I, I^-_2 and H readily leads to

$$\left(\frac{d[I_2]}{dt}\right)_0 = \frac{k_4 \alpha J}{2k_4 + k_8(k_4/k_2)^{1/2}} \quad (I)$$

where α is the quantum yield for the introduction of radicals into the bulk.

The relation between the experimental residual yield $\gamma_i{}^r$ and α will be considered for two limiting cases

$$(a) \quad k_2 = k_4 = k_8 \qquad \gamma_i{}^r = \frac{1}{3}\alpha$$

$$(b) \quad k_3 = k_4 >> k_8 \qquad \gamma_i{}^r = \frac{1}{2}\alpha$$

As both reactions 2 and 4 are diffusion controlled[23,24] these are the relevant cases. Thus α is of the order of $2\gamma_i{}^r - 3\gamma_i{}^r$.

In Fig. 4 the photochemical curves at various I^- concentrations at *p*H 5.5 are presented. From the initial slopes the residual yield is obtained $\gamma_i{}^r = 0.03 \pm 0.005$. The initial residual yield is independent of I^- concentration.

Graphical Evaluation of Initial Yields.—In the photochemical system the iodine yield *versus* time curves (Fig. 1) are departing from linearity indicating an efficient back reaction. This effect causes a considerable inaccuracy in the estimation of the initial quantum yields. This difficulty is mainly manifested at high *p*H and low I^- concentrations.

The initial yields were calculated on the basis of the assumption, to be discussed later, that at relatively low *p*H below 2.0 hydrogen atoms in the bulk act as oxidizing agents for I^- ions; or alternatively may reduce I_2. Disregarding for the moment the actual oxidation and reduction mech-

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[21] J. C. Roy, W. H. Hamill and R. R. Williams, *J. Am. Chem. Soc.*, **77**, 2953 (1955).

[22] J. Franck and F. Haber, *Sitzungsber. Preuss. Akad. Wiss.*, 250 (1931).

[23] N. Davidson, *J. Chem. Phys.*, **19**, 1311 (1951).

[24] H. L. Friedman and A. H. Zeltman, *ibid.*, **28**, 1113 (1958).

anisms the rate of formation of I_2 can be represented by

$$\frac{d[I_2]}{dt} = \frac{\alpha J}{2}\left(1 + \frac{k_{ox}[I^-] - k_r[I_2]}{k_{ox}[I^-] + k_r[I_2]}\right) = \frac{\alpha J k_{ox}[I^-]}{k_{ox}[I^-] + k_r[I_2]} \qquad \text{(II)}$$

where k_{ox} and k_r are the composite rate constants for oxidation of I^- and reduction of I_2 by H atoms. In the *p*H region below 2 it is assumed that the rate of introduction of radicals into the bulk is equal to the initial photo-oxidation yield.

Integration of equation II for the initial stages of the reaction experimentally investigated when I^- can be considered as effectively constant, leads to the result

$$\frac{t}{[I_2]} = \frac{1}{\alpha J} + \frac{1}{2\alpha J}\frac{k_r}{k_{ox}[I^-]}[I_2] \qquad \text{(III)}$$

The plots of $t/[I_2]$ *versus* $[I_2]$ are presented in Fig. 5 and 6 for various H^+ and I^- concentrations. The plots are linear up to $[I_2] = 2 \times 10^{-5}$ *M*, in good agreement with equation III.

From the intercepts in Fig. 5 and 6 the initial photo-oxidation yields are obtained. The initial quantum yields at various *p*H obtained by this method are presented in Table I. These results are compared with the initial yields obtained directly from the initial slopes of the curves in Fig. 1. The results thus obtained by the extrapolation method are about 5–20% higher, although they show the same general *p*H dependence as the initial yields directly obtained. These results clearly indicate that in the low *p*H region the initial quantum yield is *p*H dependent.

TABLE I

INITIAL QUANTUM YIELDS FOR PHOTO-OXIDATION OF EVACUATED 0.15 *M* KI SOLUTIONS

*p*H	γ_i From Fig. 1	γ_i From intercepts of Fig. 5
0.65	0.226	0.240
0.9	.200	.212
1.1	.167	.187
1.36	.139	.163
1.78	.105	.138

The *p*H Dependence of γ_i.—The *p*H dependence of the initial quantum yield in the region below *p*H 3.5 may be due to either of the causes: (a) Interaction of the H^+ ion with the excited state of the iodide or with one of the species participating in the secondary recombination in the photochemical cage. These possible mechanisms will lead to a *p*H dependent rate of introduction of radicals into the bulk. (b) It was proposed by Rigg and Weiss[3] that a scavenging reaction of H atoms occurs

$$H + H^+ \rightleftarrows H_2^+$$

followed by

$$H_2^+ + I^- \longrightarrow H_2 + I \qquad (10)$$

These reactions are assumed to compete with the back reactions 7 and 8.

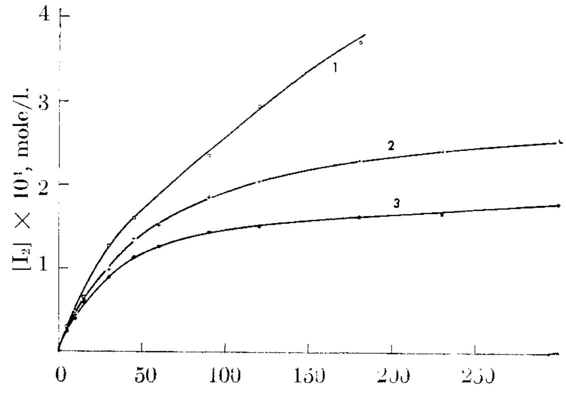

Fig. 4.—Photo-oxidation curves at various I^- concentrations at *p*H 5.5, $J = 9.7 \times 10^{-7}$ einstein liter^{-1} sec.$^{-1}$ (1) $I^- = 0.6$ *M*, (2) $I^- = 0.3$ *M*, (3) $I^- = 0.15$ *M*.

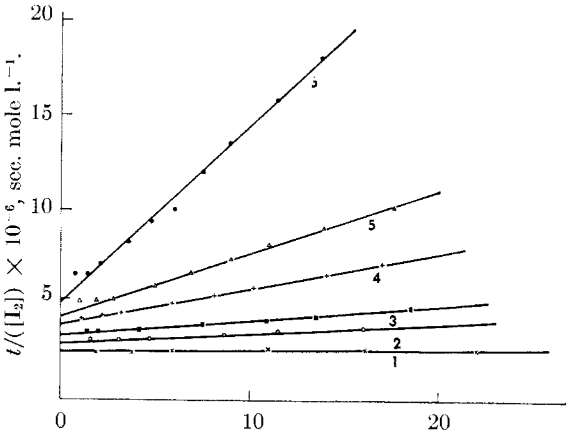

Fig. 5.—Graphical determination of initial yields at different *p*H values: $I^- = 0.15$ *M*; curve numbers the same as in Fig. 1.

In this mechanism[8] no clear cut distinction between secondary cage recombination and bulk recombination was presented. However, the treatment is based on conventional steady-state kinetics[8] leading to the dependence of the initial photo-oxidation rate on $J^{2/3}$. These results for bulk scavenging are inconsistent with the independence of the quantum yield of light intensity. Thus the *p*H dependence is attributed to mechanism (a) which, however, is not unique. Farkas and Farkas[25] postulated the direct interaction of the excited electron with the H^+ ion. This idea was supported by Franck and Platzman[10] who reported a linear dependence of γ_i on H^+ which is in variance with our experimental results. The independence of γ_i of light intensity is consistent either with Farkas' mechanism or with a model of radical scavenging by H^+ from a photochemical cage, this scavenging reaction competing efficiently with secondary recombination. By investigating the *p*H dependence of γ_i we intended to distinguish between these possibilities.

Our experimental results can be represented by the equation

$$\gamma_i = \eta + W[H^+]^{1/2} \qquad \text{(IV)}$$

where at 25°

$\eta = 0.092 \pm 0.005$
$W = 0.33 \pm 0.02$

This equation is satisfactorily fulfilled in the *p*H

[25] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1113 (1938).

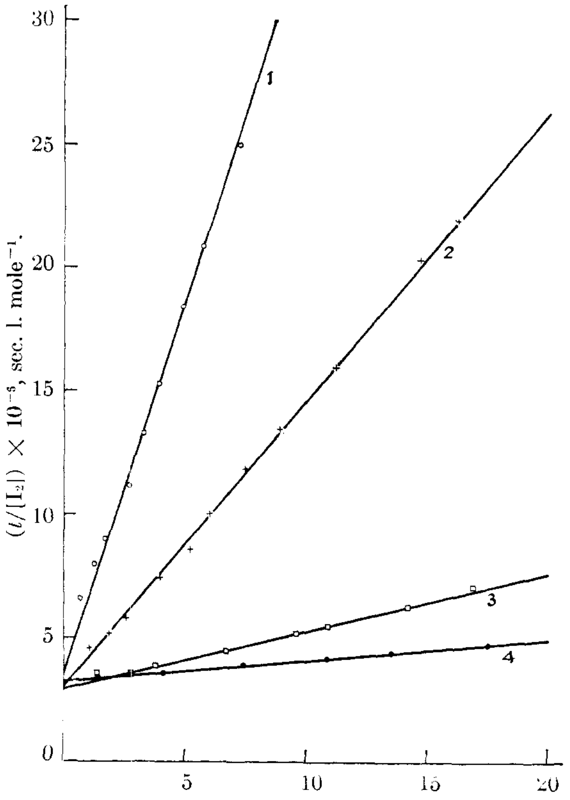

Fig. 6.—Graphical determination of initial yields at various I^- concentrations: (1) pH 0.87, $I^- = 5 \times 10^{-3}$ *M;* (2) pH 0.87, $I^- = 1.5 \times 10^{-2}$ *M;* (3) pH 0.87, $I^- = 5 \times 10^{-2}$ *M;* (4) pH 0.90, $I^- = 1.5 \times 10^{-1}$ *M.*

region up to pH 2.0 and I^- concentrations under investigation. The square root law is presented in Fig. 7. In this plot we have used the initial quantum yields obtained by the extrapolation method. The intercept of the line in Fig. 7 yields the value of 0.092 ± 0.005 which is equal to $3\gamma_i^r$ in good agreement with the prediction of equation I.

At $p\text{H} > 2$ deviations from linearity in the linear plot of Fig. 7 occur due to the change in reaction mechanism. At low pH below 0.7 the deviations are predicted by the theory of diffusion controlled scavenging. Theoretical predictions for efficient scavenging reactions competing with secondary recombinations predict such a functional dependence on scavenger concentrations.[26]

Application of the Theory of Diffusion Controlled Scavenging.—The square root law was derived by application of two models: a continuous model[27] and random walk in three dimensions.[28] The approach developed by Noyes[26,28] will be applied here.

Denoting by β' the total probability of two original partners to react and by $h(t)\text{d}t$ the probability of these radicals to react between the time t and $t + \text{d}t$, then

$$\beta' = \int_0^\infty h(t)\text{d}t \qquad \text{(V)}$$

The residual yield for the introduction of the radicals into the bulk is

$$\alpha^r = \Gamma(1 - \beta') \qquad \text{(VI)}$$

where Γ is the cross-section for primary photodissociation followed by the formation of radical pair in a solvent cage.

In the presence of a scavenger the probability of a radical to escape geminate recombination is[26,28]

$$\int h(t)\,(1 - e^{-k[\text{S}]t})\,\text{d}t = \beta' - \int h(t)\,e^{-k[\text{S}]t}\,\text{d}t =$$
$$\beta' - \int_{4a^2/\beta'^2}^{\infty} at^{-3/2}\,e^{-k[\text{S}]t}\,\text{d}t =$$
$$2a\,(\pi k\,[\text{S}])^{1/2} - \frac{8a^2k}{\beta'}\,[\text{S}] \qquad \text{(VII)}$$

where k is the long time bulk rate constant for the scavenging reaction,[28] [S] the scavenger concentration, and a is a parameter defined by Noyes.[26]

The integration of $h(t)$ is valid according to this approximation only after a certain period corresponding to the formation of distinct chemical species and subsequent few diffusive displacements. This period is selected as the relaxation time of the solvent molecules 10^{-11} sec. Thus we set $4a^2/\beta'^2 = 10^{-11}$ sec. and as $\beta' \sim 1$ hence $4a^2 \sim 10^{-11}$ sec. The theoretical expression for relatively low scavenger concentrations is thus given by

$$\alpha = \alpha_r + 2a\Gamma(\pi k[\text{S}])^{1/2} \qquad \text{(VIII)}$$

Fitting our experimental results into this scheme using the value of $W = 0.33$ obtained from Fig. 3 we obtain $k = 3 \times 10^8$ M^{-1} sec.$^{-1}$ as an upper limit, assuming $\Gamma = 1$.

The nature of the scavenging reaction will now be considered. A plausible mechanism for hydrogen atom scavenging by H^+ is that of H_2^+ formation according to reaction 9.[8] However independent experimental work[15] indicates that the rate constant of H_2^+ formation is relatively low, $k_9 \sim 10^3$ M^{-1} sec.$^{-1}$, a result which is much lower than the scavenging rate constant. Thus we are forced to conclude that H_2^+ formation is not involved in the scavenging reaction. The magnitude of the rate constant k shows that the scavenging process involves electron transfer. However at present we cannot decide whether it is an H atom or an electron which undergoes the random walk process in the photochemical cage and which interacts with H^+.

Thus the scavenging mechanisms may involve the charge transfer process

$$(\text{I} + \text{H}) + \text{H}^+ \longrightarrow \text{I} + \text{H}^+ + \text{H}$$

Theoretical estimates[29] indicate the efficiency of this reaction at relatively large separations.

Alternatively the scavenging reaction may involve thermal electron capture by the hydroxonium ion, which may be an efficient process. The

$$(\text{I} + e) + \text{H}^+ \longrightarrow \text{I} + \text{H}$$

possibility of specific reactions of thermalized electrons was considered in detail in radiation chemistry.[30,31] Recently the question of the distinction between hydrogen atoms and related species was raised. Thus Barr and Allen[32] postu-

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[26] R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

[27] L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

[28] R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 5486 (1956).

[29] W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

[30] H. Frohlich and R. L. Platzman, *Phys. Rev.*, **92**, 1152 (1953).

[31] D. Armstrong, E. Collinson, F. S. Dainton, D. M. Donaldson, E. Hayon, N. Miller and J. Weiss, *Proc. 2nd Int. Conf. Peaceful Uses of Atomic Energy, Geneva*, **29**, 80 (1958).

lated the existence of two forms of H atoms in aqueous solutions. One of these probably is the thermalized electron.[33,34]

Dependence of γ_i on I^- Concentration.—The experimental results presented in Fig. 6 indicate that the initial quantum yield is independent of initial iodide concentration in the concentration region 5×10^{-3} to 0.15 M at low pH. These results were obtained under conditions of total light absorption which hold up to the lower I^- concentration employed. These results are in variance with previously reported experimental data[8] and indicate that contrary to previous suggestions[8,11] the iodide ion concentration does not affect the rate of introduction of radicals into the bulk.

Radical Reactions in the Bulk.—As a result of the scavenging reaction, or by diffusion away from original partners, hydrogen and iodide atoms are introduced into the bulk. At relatively low pH below 2.0 hydrogen atoms act as oxidizing agents for the iodide ion. Recently this fact was demonstrated by oxidation of the iodide ion by H atoms externally generated, and it was shown that the results are consistent with an oxidation mechanism involving H_2^+ as the actual oxidizing species.[15] In this low pH region the initial rate of introduction of H atoms into the bulk is equal to the initial photo-oxidation rate.

The nature of the oxidation reaction of I^- by atomic hydrogen in the photochemical system was investigated by considering the compound rate constants ratio k_r/k_{ox}. This value was obtained from the ratio of slope to intercept from Figs. 5 and 6. The accuracy of the rate constants obtained is about 5%. These data are presented in Table II.

TABLE II

THE DEPENDENCE OF k_r/k_{ox} ON pH AND IODIDE ION CONCENTRATIONS

pH	I^-, M	$1/H^+$, M^{-1}	$10^{-4}\,\frac{k_r}{k_{ox}}$
0.65	1.5×10^{-1}	4.15	0.58
.87	5×10^{-3}	. . .	0.89
.87	1.5×10^{-2}	. . .	1.0
.87	5×10^{-2}	. . .	0.76
.9	1.5×10^{-1}	7.7	0.71
1.1	1.5×10^{-1}	11.9	1.46
1.36	1.5×10^{-1}	23.3	2.25
1.78	1.5×10^{-1}	57.0	5.20

The ratio of the rate constants is found to be pH dependent. A plot of this ratio as a function of $1/[H^+]$ is a straight line, with a positive intercept. (Fig. 8). The experimental results can be fitted by the expression

$$\frac{k_r}{k_{ox}} = 1.5 \times 10^3 + \frac{900}{[H^+]} \qquad \text{(IX)}$$

No dependence of k_r/k_{ox} on I^- could be detected up to 1.5×10^{-1} M. For higher iodide concentrations the results were not accurate enough to establish this point.

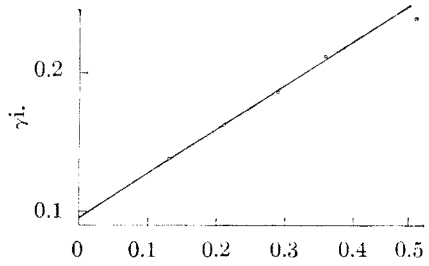

Fig. 7.—The dependence of initial quantum yields on the square root of H^+ ion concentration.

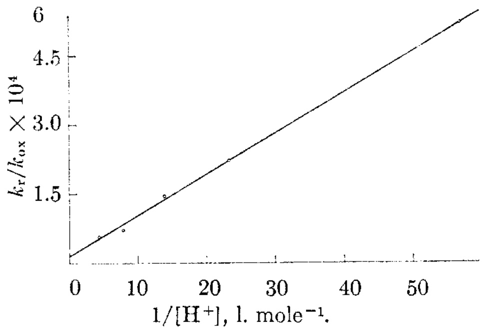

Fig. 8.—The dependence of the compound rate constants ratio k_r/k_{OH} on $1/H^+$ for 0.15 M I^-.

We wish to show that these results are consistent with the oxidation mechanism involving H_2^+. We assume that oxidation of the I^- ion proceeds by reactions 9 and 10. The possible reaction

$$H_2^+ + I_2^- \longrightarrow H_2 + I_2$$

is not introduced because of the low steady state concentrations I_2^- compared with that of I^-. The reduction reaction of iodine and I^- may proceed by

$$I_2 + H_2^+ \longrightarrow I^- + 2H^+ + I \qquad \text{(11a)}$$
$$I_3^- + H_2^+ \longrightarrow 2I^- + 2H^+ + I \qquad \text{(11b)}$$
$$I_2 + H \longrightarrow I^- + H^+ + I \qquad \text{(12a)}$$
$$I_3^- + H \longrightarrow 2I^- + H^+ + I \qquad \text{(12b)}$$

Under our experimental conditions iodine is present mainly as I_3^-. However the pronounced dependence of the reduction yield of iodine on I^- concentration at pH 5.5 (Fig. 4) indicates that triiodide ions are more stable toward reduction compared with free I_2.

The concentration of free I_2 can be obtained from the expression

$$[I_2] = \frac{K_e[I_2]_t}{K_e + [I^-]} \cong \frac{K_e[I_2]_t}{[I^-]}$$

where $K_e = 1.4 \times 10^{-3}$ at 25° is the equilibrium constant for the reaction

$$I_3^- \rightleftarrows I_2 + I^-$$

and $[I_2]_t$ is the total iodine concentration. Application of steady state treatment to the bulk reactions 9, 10, 11 and 12 leads to the result

$$\frac{d[I_2]_t}{dt} = \frac{\alpha J}{2}\left(1 + \frac{X[I^-] - Y[I]_2}{X[I^-] + Y[I_2]}\right) \qquad \text{(X)}$$

where $X = k_9k_{10}[H^+]$.

$$Y = k_9k_{11}[H^+] + k_{-9}k_{12} + k_{10}k_{12}[I^-] + k_{11}k_{12}[I_2]$$

$$k_{11} = k_{11}{}^a + \frac{k_{11}{}^b K_e}{[I^-]}$$

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$$k_{12} = k_{12}{}^{a} + \frac{k_{12}{}^{b}K_e}{[I^-]}$$

Thus we obtain

$$\frac{k_r}{k_{ox}} = \frac{k_{11}}{k_{10}} + \frac{k_{12}(k_{-9}/k_{10} + [I^-])}{k_9[H^+]} + \frac{k_{11}k_{12}}{k_9k_{10}}[I_2] \quad (XI)$$

For relatively low I_2 concentrations the linear term in I_2 can be neglected. This is indicated from Figs. 5 and 6 where no deviations from linearity were observed.

The *p*H dependence of the ratio of the rate constants is consistent with the oxidation mechanism involving $H_2{}^+$. The oxidation mechanism involving abstraction of H atoms from the hydration layer[35] requires that the ratio of the rate constants should not be dependent on *p*H, while the triple collision mechanism[36] requires that the intercept in Fig. 8 should be zero. Neither of these conditions is fulfilled.

It should be pointed out however that while the photochemical data indicate a *p*H dependent mechanism for the oxidation of I^- by H atoms, these results by themselves do not yield absolute evidence for the oxidation mechanism involving $H_2{}^+$. The main effect of H^+ ion on the photochemistry is due to the *p*H dependence of the rate of introduction of radicals into the bulk. The difficulties of the detection of the dependence of k_{ox}/k_r on I^- ion concentration which probably cancels out due to opposite effects remain to be elucidated.

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THE NATURE OF THE CHROMIUM(VI)-1,5-DIPHENYLCARBOHYDRAZIDE REACTION. II. THE CHROMIUM(II)-DIPHENYLCARBAZONE REACTION[1,2]

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Chromium(II) reacts with diphenylcarbazone in aqueous solution to give an intense magenta color. A molar absorbancy index of 3.6 × 10^4 (based on chromium(II) concentration) has been obtained at 546 mμ. The absorption spectrum is very similar to that of the magenta product of the aqueous chromium (VI)-1,5-diphenylcarbohydrazide reaction. It is concluded that the same colored substance, a chromium complex, is formed in both reactions.

Introduction

In several previous investigations[3-5] it has been found that chromium(II) reacts with diphenylcarbazone (phenylazoformic acid-2-phenylhydrazide) in aqueous media to give an intense magenta color, similar to that arising from the aqueous chromium(VI)-1,5-diphenylcarbohydrazide reaction. Very recently, however, Babko and Get'man[6] have reported that chromium(II) does not react with diphenylcarbazone. They attribute the results of previous investigators to the use of chromous acetate. Since they have found that diphenylcarbazone in acetic acid has the same color whether chromium(II) is present or not, Babko and Get'man conclude that the color observed by previous workers must have resulted from the side reaction of diphenylcarbazone with acetic acid.

Because of the doubt thrown on the existence of the chromium(II)-diphenylcarbazone reaction, which had seemed to be closely related to the chromium(VI)-1,5-diphenylcarbohydrazide reaction, we have made a detailed investigation of this and related systems.

Experimental

Materials.—Pure diphenylcarbazone was obtained from its double compound with 1,5-diphenylcarbohydrazide by the method of Krumholz and Krumholz.[7] The diphenylcarbazone was recrystallized from 1:2 EtOH-H_2O, m.p. 123-126°; lit.[7] 125°. *Anal.* Calcd. for $C_{13}H_{12}N_4O$: C, 64.97; H, 5.03; N, 23.32. Found: C, 64.80; H, 4.91; N, 23.49. The double compound was recrystallized from 1:1 EtOH-H_2O, m.p. 154-157°; lit.[7] 156-158°. Eastman 1,5-diphenylcarbohydrazide, lot 42, m.p. 173-174°, was used directly. Acetone was Eastman Spectro grade. Matheson prepurified nitrogen and "bone-dry" CO_2 were used. Other substances were reagent grade.

Solutions.—A 1 *M* chromium(II) solution, used in the qualitative expts., was prepared by reduction of a chromic chloride solution with zinc amalgam. The deep blue solution was stored under CO_2. For the quantitative expts. a more dilute chromous solution was prepared by the method of Stone[8] and stored under nitrogen. The all-glass apparatus used to store and dispense the solution was similar to the gravity type of apparatus described by Stone.[8] Chromium(II) was determined both iodimetrically[9] and potentiometrically.[10] The average of four such determinations was 1.17(±0.02) × 10^{-3} *M*. This solution also contained significant amounts of chromium(III). The presence of chromium(III) should not interfere with a study of the chromium(II)-diphenylcarbazone reaction, as chromium(III) does not react with diphenylcarbazone or 1,5-diphenylcarbohydrazide under the conditions of these expts.[3] Nevertheless, blanks containing appropriate amounts of chromium(III) were used. The chromium(III) stock solution contained 0.018 *M* $CrCl_3$ and 0.2 *M* HCl. Zinc(II) also was added to the blanks, since the chromous solution contained this species owing to its manner of preparation. The zinc(II) stock solution contained 0.5 *M* $ZnCl_2$ and 0.1 *M* HCl.

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