On the Photochemistry of Aqueous Solutions of Chloride, Bromide, and Iodide Ions

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The photochemistry of aqueous solutions of Cl^-, Br^-, I^- and OH^- was investigated at 2537, 2288, and 1849 Å., in the temperature range 5–37°. The excited halide ions dissociate into a halogen atom and a solvated electron. Scavengers for solvated electrons, such as H_3O^+, N_2O, or acetone compete with the secondary diffusive recombination of these but do not interact with the spectroscopic excited state. Cl atoms dehydrogenate ethanol and methanol, while I atoms appear to be unable to do so at all wave lengths. For Br atoms, however, the results indicate that at 2288 Å., formed in their lower energy $^2P_{3/2}$ state, they do not dehydrogenate the scavengers but may be able to do so when formed in the higher energy $^2P_{1/2}$ state at 1849 Å. The effects of temperature, wave length, added salt, and type of halide ion indicate that the atom–electron pair is formed from the excited ion in a distinct step. This process, essentially one of charge asymmetrization, competes with the deactivation of the excited ion. The value of the limiting constant quantum yield, Γ, obtained at high scavenger concentrations depends on this competition.

Introduction

In previous work,[1-5] the photochemistry of the iodide ion was investigated at 2537 Å. in aqueous solutions at 25°. The effect of different scavengers on the quantum yields of the products indicated that there was no interaction between the scavenger and the spectroscopic excited state of the ion. The experimental results could be explained, however, in terms of a dissociation of the excited ion into an iodine atom and a solvated electron produced in close proximity. This nonhomogeneous initial distribution of radicals is often referred to using the colorful expression of radicals formed in a solvent cage. The radical formation process competes with the decay of the excited state, back to the ground state ion

$$I^-_{aq} \overset{h\nu}{\rightleftarrows} I^-_{aq}{}^* \longrightarrow (I_{aq} + e^-_{aq})$$

where the parentheses stress the fact that I_{aq} and e^-_{aq} are formed in pairs. Various scavengers were shown to capture e^-_{aq}, thus preventing the recombination

$$(I_{aq} + e^-_{aq}) \longrightarrow I^-_{aq}$$

Such a recombination of original partners is known as "secondary (diffusive) recombination." The term "primary recombination," describing recombination between radicals not yet separated by a solvent molecule, is somewhat misleading, as primary recombination is the kinetic equivalent to the deactivation of the excited state. Radicals which escape secondary recombination achieve a homogeneous distribution and, if no scavenger is present, will ultimately undergo a "bulk recombination" process.

A quantitative kinetic analysis, based on Noyes' approach for the treatment of scavenging competing with secondary recombination of radicals,[6,7] relating the quantum yield of the products to the scavenger concentration, was carried out,[1-5] and found to agree

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(1) J. Jortner, M. Ottolenghi, R. Levine, and G. Stein, *J. Phys. Chem.*, **65**, 1232 (1961).

(2) J Jortner, M. Ottolenghi, and G. Stein, *ibid.*, **66**, 2029 (1962).

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

(4) J. Jortner, M. Ottolenghi, and G. Stein, *ibid.*, **66**, 2042 (1962).

(5) J. Jortner, M. Ottolenghi, J. Rabani, and G. Stein, *J. Chem. Phys.*, **37**, 2488 (1962).

(6) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

(7) R. M. Noyes, *ibid.*, **78**, 5486 (1956); *cf.* J. C. Roy, R. R. Williams, and W. H. Hamill, *ibid.*, **76**, 3274 (1954).

with the experimental results. Similar mechanisms, resulting in the formation of solvated electrons, appear to operate in the photochemistry of I^- in D_2O, methanol, ethanol, 1-propanol, and methyl cyanide as solvents.[8]

The purpose of the present work was to investigate whether the above conclusions are specific to the I^- ion or if the formation of solvated electrons is also common to other ions, characterized by charge transfer to the solvent (c.t.t.s.) bands. A second object was to get a closer insight of the detailed mechanism of the transition from the spectroscopic excited state to the reactive radical pair. We therefore investigated the effects of ultraviolet radiation on aqueous solutions of Cl^-, Br^-, and I^-, with special attention to the effects of changing wave length, temperature, and added salts on the photochemistry of the three halide ions, as well as some experiments on solutions of the OH^- ion.

Experimental

Light Sources and Actinometry: 2537 Å. A low pressure mercury arc lamp was used. Details of the irradiation technique, filtration of light at other wave lengths, and actinometry were as described previously.[1,2] The light intensity was 1.5×10^{-6} einstein $l.^{-1}$ $sec.^{-1}$.

2288 Å. An Osram-Cd/1 cadmium arc lamp was used operated at 12 v. (through a choke from the 220 v. mains) and 1.5 amp. a.c. There is no emission below 2000 Å. The light intensity at 2144 Å. was found to be less than 5% of that at 2288 Å. and is included with the latter. Our solutions did not absorb any of the lines emitted above 2650 Å. Actinometry was carried out by means of uranyl oxalate solution, using for the quantum yield of the actinometer the value[9] of 0.55 for 2288 Å. In a first experiment the actinometric solution in the reaction vessel was irradiated directly. In a second experiment a 1-cm. path length 4 *N* acetic acid solution filter,[10] absorbing all the light below 2400 Å., was inserted between the reaction vessel and the lamp. The chemical change on illumination was determined in both cases by titration with 0.01 *N* $KMnO_4$ solution. From the difference between the two values, the light intensity at 2288 Å. was determined as 3.4×10^{-7} einstein $l.^{-1}$ $sec.^{-1}$.

1849 Å. A low pressure Hg vapor lamp was used. In the case of Cl^- and Br^- solutions, there was no need to filter out radiation at higher wave lengths since these were not absorbed. For I^- solutions an X-ray irradiated LiF crystal filter was used as recommended by Weeks, Gordon, and Meaburn.[11]

At this wave length 10^{-2} *M* methanol dissolved in water[12] was used as an actinometer, measuring the hydrogen yield. The light intensity calculated was 8×10^{-8} einstein $l.^{-1}$ $sec.^{-1}$, assuming a quantum yield of 0.65 for the actinometer.[12b]

Reaction Vessels and Thermostatic Arrangements. The reaction vessels were adapted from 1-cm. optical path length spectrophotometer cells, since effectively total absorption in these could be obtained in all cases. The reaction cells were seated inside square copper blocks through which thermostated water was circulated. The temperature was constant inside the reaction cells to within ±0.5° of the stated values.

Gas Analysis. Reaction yields were determined from the amounts of gaseous products: H_2 and N_2 formed. H_2 was determined using a McLeod gage and separately using a Pirani gage. Agreement between the two methods indicated the purity of the gaseous product. N_2 from H_2O containing solutions was determined after freezing out H_2O in a CO_2-acetone-cooled trap and only then N_2O in a liquid air-cooled trap. Agreement between readings on the McLeod and Pirani gages indicated the purity of the product. To check our results control combustion experiments were carried out showing the absence of O_2 in all experiments. Experiments were designed so that simultaneous evolution of N_2 and H_2 should not take place. Iodine liberated was determined as I_3^- by spectrophotometry.[1]

Materials used were Analar grade. Distilled water was redistilled from alkaline permanganate followed by distillation from dilute phosphoric acid.

Results

Comparison of the Photochemistry of I^- Solutions at 2537, 2288, and 1849 Å. The results of experiments in which aqueous I^- solutions at 25° were irradiated with light of 2537 Å., in the presence of various scavengers, were described previously.[1-5] In all scavenger systems the limiting quantum yield of the final products, Γ, reached at high scavenger concentrations, was found to be $\Gamma = 0.29$. Thus the yield of formation of the pair ($I_{aq} + e^-_{aq}$) from the excited state is 0.29.

In the present experiments at 2288 Å. and 25°, two systems were investigated. (a) H_3O^+ is used as the

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(8) J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **67**, 1271 (1963).

(9) C. R. Masson, V. Boekelheide, and W. A. Noyes, Jr., in A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1956, p. 295.

(10) E. J. Bowen, "The Chemical Action of Light," Oxford University Press, London, 1946, p. 283.

(11) J. L. Weeks, S. Gordon, and G. M. A. C. Meaburn, *Nature*, **191**, 1186 (1961).

(12) (a) L. Farkas and Y. Hirschberg, *J. Am. Chem. Soc.*, **59**, 2450 (1937); (b) J. H. Baxendale, *Trans. Faraday Soc.*, **56**, 37 (1960).

scavenger,[3,5] $e^-_{aq} + H_3O^+ \rightarrow H + H_2O$, converting the solvated electron into an H atom, and 1 *M* methanol as the H atom scavenger converting it to molecular hydrogen.[3] Experiments were carried out at pH 0.82 and 1.65, using H_2SO_4 to set the pH. In both experiments, where $[I^-] = 0.01$ *M*, the value for the quantum yield of H_2, $\gamma(H_2)$, was 0.25 ± 0.01. Thus the yield is independent of $[H^+]$ in this range, and $\Gamma = \gamma(H_2)$ so that $\Gamma = 0.25 \pm 0.01$. (b) Here N_2O is used as the scavenger of e^-_{aq},[3] according to $e^-_{aq} + N_2O \rightarrow O^- + N_2$. Solutions containing $(I^-) = 0.1$ *M* were irradiated in the presence of 2.10^{-2} *M* N_2O. The quantum yield of I_2, $\gamma(I_2)$, was 0.23 ± 0.01, and the quantum yield of N_2, $\gamma(N_2) = 0.24 \pm 0.01$. As $[N_2O]$ is sufficient for total electron scavenging, we may again assume $\gamma(N_2) = \Gamma$. The values of Γ determined in the two independent scavenging systems are thus in fair agreement. We conclude, in view of the uncertainty of ±10% in the actinometry at 2288 Å., that the values of Γ do not differ significantly from those at 2537 Å.

At 1849 Å. control experiments were first carried out to show the efficiency of the X-irradiated LiF filters in removing light at 2537 Å. Solutions of 0.15 *M* I^- were irradiated at pH 2 in the presence of 1 *M* methanol through 5-mm. path length of 0.1 *N* NaCl solution (to remove light at 1849 Å.) and through the LiF filter. At twice the usual dose of irradiation, H_2 was not evolved. Without the NaCl filter $\gamma(H_2) = \Gamma = 0.97$ was obtained at pH 2. In order to determine the value of the "experimental residual yield,"[2] γ_r^{ex}, (*i.e.*, the yield at high pH values when practically any efficient scavenger for the radicals, except the solvent itself, is absent) experiments were carried out in 0.15 *N* I^- and 1 *M* ethanol solutions at pH 11.9, using NaOH (OH^- does not contribute significantly to the absorption in this case). $\gamma_r^{ex}(H_2) = 0.04$ was found.

The Photochemistry of Br^- at 2288 and at 1849 Å. At 2288 Å., 0.5 *M* KBr solutions containing 1 *M* methanol were irradiated. The pH values were set using H_2SO_4, 2.5×10^{-3} *M* acetate or phosphate buffers, or NaOH. The absorption of all these solutions without added KBr was negligible compared with their absorption when KBr was added. The quantum yield of H_2 evolution remained constant during irradiation, up to hydrogen concentrations of 10^{-4} *M*. The dependence of $\gamma(H_2)$ on the pH is shown in Fig. 1 and indicates that at 25° $\Gamma = 0.50 \pm 0.01$, while the constant experimental residual yield obtained at pH > 7 is $\gamma_r^{ex} = 0.025$ (an additional experimental point at pH 11 giving the same value is not shown in the graph). In Fig. 2, $1 + \log[1 - (\gamma(H_2)/\Gamma)]$ is plotted as a function of $\sqrt{[H^+]}$. This plot is according to the general scavenging equation[2]

$$\ln\left(1 - \frac{\gamma(H_2)}{\Gamma}\right) = \ln\beta' - \frac{2a}{\beta'}\sqrt{\pi k_{H^+ + e^-_{aq}}[H^+]} \qquad (1)$$

which describes the competition between the scavenging process $H^+ + e^-_{aq} \rightarrow H$ and the secondary recombination $Br_{aq} + e^-_{aq} \rightarrow Br^-_{aq}$. *a* is a parameter defined by Noyes,[6,7] and $\beta' = 1 - \gamma_r/\Gamma$. γ_r is the total yield of solvated electrons and halogen atoms which escape secondary recombination, and diffuse into the bulk, when no external scavenger is present. The intercept of the straight line gives $\beta' = 0.58 \pm 0.05$ and hence $\gamma_r = 0.21 \pm 0.03$. It can be seen that γ_r^{ex} is much smaller than γ_r. This is due to the

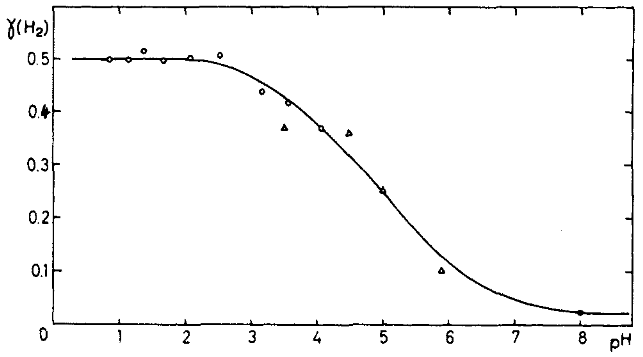

Figure 1. The pH dependence of the quantum yield of H_2 in the photochemistry of KBr (0.5 *M*) at 2288 Å. in the presence of 1 *M* methanol: ○, pH adjusted with H_2SO_4; ●, pH adjusted with 2.5×10^{-3} *M* K_2HPO_4/NaH_2PO_4 buffer; △, pH adjusted with 2.5×10^{-3} *M* CH_3COOH/CH_3COONa buffer.

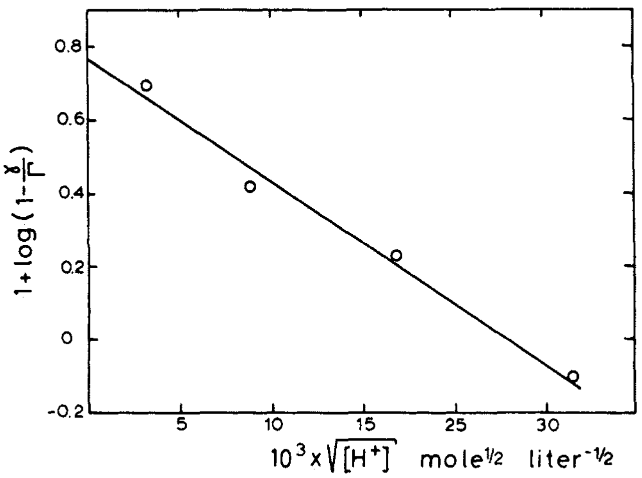

Figure 2. The plot of the experimental results of Fig. 1 according to the cage scavenging eq. 1.

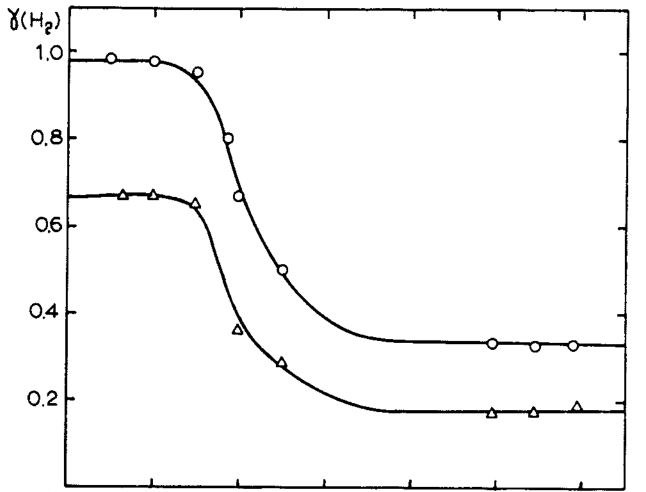

Figure 3. Hydrogen quantum yields in the photochemistry of 0.5 M KBr (△) and 0.5 M KCl (○) at various pH values, in the presence of 1 M CH_3OH.

bulk recombination Br (or Br_2^-) + $e^-_{aq} \rightarrow Br^-$ which competes with the processes by which, in this pH range, e^-_{aq} is converted to hydrogen with the participation of the solvent. From the slope and from this value of β', we obtain $2a\sqrt{\pi k_{H^+ + e^-_{aq}}} = 44$ l.$^{1/2}$ mole$^{-1/2}$.

At 1849 Å., 0.5 M solutions of KBr were irradiated in the presence of 1 M methanol. At this wave length pH values were set using H_2SO_4 (pH < 4), 2.5×10^{-3} M acetate buffer (pH 5.0), and KOH (pH > 9) The dependence of $\gamma(H_2)$ on pH is shown in Fig. 3. Since $\epsilon^{1849}{}_{Br^-} = 1 \times 10^4$ cm.$^{-1}$ mole^{-1} l., the absorption of light by components other than Br^- may be neglected. Even that of acetate,[13] with $\epsilon^{1849} = 1 \times 10^3$, may be neglected at the concentration employed, as[13] can be OH^- From the values of $\gamma(H_2)$ at low pH one gets $\Gamma = 0.69 \pm 0.01$. Experiments were also carried out using N_2O as the scavenger for e^-_{aq}. In the presence of N_2O at a partial pressure of 360 mm., from solutions of 0.5 M KBr, at 25° $\gamma(H_2) = \Gamma = 0.68 \pm 0.04$ was obtained. Since[14] $\epsilon^{1849}{}_{N_2O} = 40$, the absorption due to N_2O may be neglected.

Photochemistry of Cl^- Solutions at 1849 Å. Solutions of 0.5 M KCl were irradiated at this wave length in the presence of 1 M methanol as H atom scavenger, at varying pH values. The results are shown in Fig. 3, pH values being set as in the Br^- system. Since[13] $\epsilon^{1849}{}_{Cl^-} = 3800$ cm.$^{-1}$ mole^{-1} l., the absorption of light due to the added sulfate, acetate, and hydroxyl ions may be neglected. Additional experiments at pH 12 using 0.25 M KCl gave $\gamma(H_2) = 0.366$, as in the case of 0.5 M KCl solutions.

Using 0.5 M KCl solutions at pH 11.9 in the presence of 360 mm. pressure of N_2O we get $\Gamma = \gamma(N_2) = 0.99 \pm 0.04$ for this scavenger of solvated electrons.

Experiments were also carried out at pH 11.9 in 0.5 M KCl solutions containing 1 M methanol with the addition of 1.10^{-3} M acetone, which[15,16] captures e^-_{aq} without yielding H_2, but reacts more slowly with H atoms.[16] Irradiations at 1849 Å. were in the presence of the X-irradiated LiF crystal filter, to eliminate light at 2537 Å. which might cause photolysis of the acetone, while at 1849 Å. at the concentrations employed the absorption by acetone itself may be neglected. The results in the presence of acetone showed the reduction of $\gamma(H_2)$, the experimental residual yield of H_2, from ~0.33 to less than 0.03, demonstrating that the residual yield involves solvated electrons.

Photochemistry of OH^- at 1849 Å. The absorption spectrum of aqueous solutions of OH^- shows great similarity to that of the halogens (*e.g.*, it is affected similarly by changes in temperature[17]) and is attributed to a c.t.t.s.-type transition. At 1849 Å. in solutions of 0.1 M KOH containing N_2O at 520 mm. pressure, $\gamma(N_2)$ was found to be 0.5.

The Effect of Alcohol Concentration Some experiments have been carried out in order to clarify the role of the added ethyl alcohol on the experimental residual yield, *i.e.*, on the constant, pH independent yield of H_2 observed at pH > 8. The solutions employed contained varying amounts of ethanol and 5×10^{-2} M NH_4Cl at pH 7.8. It has been shown[5] that NH_4^+ acts as a scavenger for solvated electrons, converting them to H atoms. The low concentration of NH_4^+ employed by us was not sufficient for competing with secondary recombination of electrons but sufficient to prevent electron capture by impurities in the bulk. The results for solutions of I^-, Br^-, and Cl^- at various wave lengths are reported in Table I.

The Effect of Temperature on the Quantum Yield at 2537, 2288, and 1849 Å. (a) Iodide at 2537 Å. 1. In the Presence of N_2O. In the region of complete scavenging of e^-_{aq}, *i.e.*, solutions of 0.15 N KI at a partial pressure of $P_{N_2O} = 400$ mm. in unbuffered, nearly neutral solutions, the results shown in Fig. 4 were obtained between 5 and 37°. The solubility of N_2O changes with temperature in this range.[18] Plot-

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(13) G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1941.

(14) M. Zelikoff, K. Watanabe, and E. C. Y. Inn, *J. Chem. Phys.*, **21**, 1643 (1953).

(15) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

(16) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).

(17) J. Jortner, B. Raz, and G Stein, *ibid.*, **34**, 1455 (1961).

Table I: The Effect of Ethanol Concentration on the H_2-Quantum Yield in the Photochemistry of KBr (0.5 *M*), KCl (0.5 *M*), and KI (0.15 *M*) in Solutions Containing 5 × 10^{-2} *M* NH_4^+ at pH 7.8

	$\gamma(H_2)$			
C_2H_5OH, mole l.$^{-1}$	Br^- (1849 Å.)	Br^- (2288 Å.)	I^- (2537 Å.)	Cl^- (1849 Å.)
0.1	0.096	0.080	0.060	0.170
0.3	0.112	0.081	...	...
0.6	...	...	0.061	...
1.0	0.150	0.078	...	0.390
3.3	0.199	0.088	0.069	...

ting Seidell's data for our conditions we found that within this range, even at the highest temperature, $[N_2O]$ did not decrease below the concentration required for complete scavenging.

2. In the Presence of H_2SO_4. In Fig. 5 the complete scavenging curves are given for the H^+ concentration range from 2 to 10^{-4} *N* H_2SO_4, between 5 and 37°. In Table II values of Γ, the limiting quantum yields for the two cases, are compared.

Table II: The Temperature Dependence of Γ in the Photochemistry of I^-, Br^-, and Cl^-

	Γ				
	I^- at 2537 Å.				
Temp., °C.	N_2O as scavenger for e^-_{aq}	H_3O^+ as scavenger for e^-_{aq}	Br^- at 2288 Å. H_3O^+ as scavenger for e^-_{aq} (pH 1.8)	Br^- at 1849 Å.	Cl^- at 1849 Å.
5	0.190	0.205	0.37	0.48	0.90
15	0.230	0.245	0.41	0.56	0.94
25	0.290	0.293	0.50	0.67	0.98
35	...	...	0.55	0.72	0.98
37	0.362	0.350	..	..	..

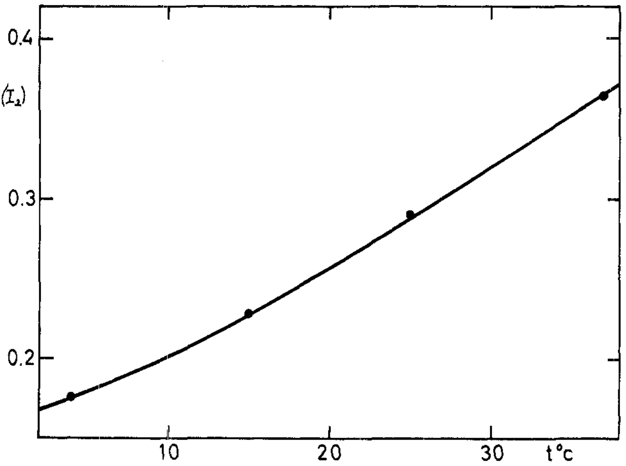

Figure 4. Temperature dependence of I_2 quantum yields in the photochemistry of I^- at 2537 Å. P_{N_2O} = 600 mm.; total scavenging is assumed so that $\gamma(I_2)$ = Γ.

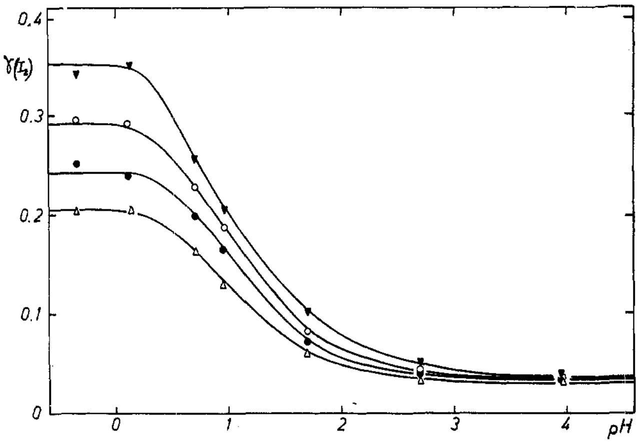

Figure 5. Scavenging of H atoms by H_3O^+ (see ref. 1) at various temperatures: △, 5°; ●, 15°; ○, 25°; ▼, 37°.

(*b*) *Bromide at 2288 and 1849 Å.* Solutions of 0.5 *M* Br^- were irradiated in the presence of 1 *M* methanol at pH 1.8, in the temperature range 5 to 35°. The results are shown in Table II.

(*c*) *Chloride at 1849 Å.* Solutions of 0.5 *M* Cl^- were irradiated in the presence of 1 *M* methanol at pH 1.8 in the temperature range 5 to 35°. The results are shown in Table II.

Effects of Added Salts on the Quantum Yield. We investigated the effect of large amounts of added salts on the limiting quantum yield Γ in view of the investigation of the effect of such additions on the spectrum[19] of I^-

When 0.15 *M* KI solutions were irradiated at 2537 Å. and 25°, in the presence of 5 *M* HCl and 9 *M* LiCl, and 2.5 *M* HCl and 9 *M* LiCl, $\gamma(H_2)$ remained constant at 0.298 ± 0.002. Similarly, when up to 1 *M* KBr was added, $\gamma(H_2) = 0.293 \pm 0.003$ was obtained using 1.78 *M* H_2SO_4 as the scavenger, and $\gamma(I_2) = 0.293 \pm 0.003$ using 590 mm. pressure of N_2O.

Discussion

1. The Reactivity of the Halogen Atoms in the Photochemistry of the Halides. The photochemical results for Br^- at 2288 Å. show a close similarity to those of I^- at 2537 Å.[1-4] Thus we may assume again the formation of the pair ($X + e^-_{aq}$) with e^-_{aq} scavenged by H_3O^+ or N_2O. The scavenging by H_3O^+ is shown by the dependence of $\gamma(H_2)$ on pH in Fig. 1. Figure 2 shows that Noyes' scavenging kinetics are obeyed.

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(18) A. Seidell, "Solubilities of Inorganic and Organic Compounds," Supplement to Third Ed., D. Van Nostrand, New York, N. Y., 1955.

(19) G. Stein and A. Treinin, *Trans. Faraday Soc.*, 56, 1393 (1960).

Table III: Values of the Experimental Parameters γ_r^{ex}, Γ, and γ_r^{ex}/Γ in the Photochemistry of I^-, Br^-, and Cl^- at Various Wave Lengths

	System				
Parameter	I^-, 2537 Å.	Br^-, 2288 Å.	I^-, 1849 Å.	Br^-, 1849 Å.	Cl^-, 1849 Å.
Γ	0.29	0.5	0.97	0.67	0.98
γ_r^{ex}	0.015	0.025	0.039	0.175	0.34
γ_r^{ex}/Γ	0.05	0.05	0.04	0.26	0.35

Table III summarizes the values of Γ, γ_r^{ex} (the experimental, constant, residual yield at high pH values), and those of the parameter γ_r^{ex}/Γ. This parameter represents the fraction of radicals which ultimately escape secondary recombination. It should be noted that the value of the ratio γ_r^{ex}/Γ is exceptionally high for Cl^- and Br^- at 1849 Å., compared with those for I^- at 2537 and 1849 Å. and for Br^- at 2288 Å. Our explanation of this phenomenon is as follows. In the case of Cl^-, not only H atoms but Cl atoms also dehydrogenate the alcohol as shown by Berces and Trotman-Dickenson.[20] In our system the scavenging of Cl atoms competes with the recombination $Cl + e^-_{aq} \rightarrow Cl^-$. Assuming that the radicals formed in the dehydrogenation process are relatively poor scavengers of e^-_{aq}, this will increase the efficiency of the processes by which e^-_{aq} is converted to molecular hydrogen at this pH. In the absence of an efficient scavenger, solvated electrons in aqueous solutions will react with the solvent yielding molecular hydrogen. Matheson and Rabani (private communication) studied this reaction by means of electron pulse techniques and found that a second-order reaction occurs with a rate constant $k_{e^-_{aq} + e^-_{aq}} \cong 10^{10}$ mole^{-1} sec.$^{-1}$. However, in our photochemical experiments the rate of formation of e^-_{aq} is lower by mean orders of magnitude, so that a first-order reaction: $e^-_{aq} + H_2O \rightarrow H + OH^-_{aq}$, may play a role. Such a process agrees with the results of Lifshitz and Stein (to be published), who studied deuterium isotope effects in the radiation chemistry of aqueous systems. Acetone, 10^{-3} M, practically eliminates any hydrogen evolution. This is consistent with e^-_{aq} being responsible, by reacting with the solvent water, for the formation of H_2 in this pH range. As previously stated, acetone acts as an efficient electron scavenger in a process that does not lead to gas evolution.

Unlike the case for Cl, energetic reasons prevent the dehydrogenation of the alcohol by I and ground state Br atoms (C–H = 97 kcal., H–I = 71 kcal., and H–Br = 87 kcal., while H–Cl = 102 kcal.). Considering the behavior of the Br^- system at 1849 Å. where the ratio γ_r^{ex}/Γ is similar to the one in the Cl^- system rather than to that of Br^- at 2288 Å., we suggest that Br atoms formed at 1849 Å. are capable of dehydrogenating the alcohol while those formed at 2288 Å. behave like I atoms and are incapable of reaction with the aliphatic scavenger. This assumption is supported by the spectroscopic studies which indicate that the Br atom formed at 2288 Å. is in the $^2P_{3/2}$ state while at 1849 Å. it appears in the $^2P_{1/2}$ atomic state. Since $E^{Br}{}_{^2P_{1/2}} - E^{Br}{}_{^2P_{3/2}} = 10$ kcal., the reaction between the alcohol and the $^2P_{1/2}$ Br atom can no more be excluded. In the case of I^-, even if I is formed in the $^2P_{1/2}$ state (at 1849 Å.), $E^{I}{}_{^2P_{1/2}} - E^{I}{}_{^2P_{3/2}} = 21$ kcal. and the dehydrogenation process does not occur.

These views are also supported by the experimental results presented in Table I. It can be seen that in the case of I^- at 2537 Å. and of Br^- at 2288 Å., the quantum yields are almost unaffected by the alcohol concentration (the small rise at 3.3 M C_2H_5OH may be due to an increase in Γ which markedly depends on the solvent[8]). However, when going over to Cl^- and Br^- at 1849 Å., $\gamma(H_2)$ increases significantly with the alcohol concentration. According to our previous arguments this is consistent with the existence of the scavenging process $X + C_2H_5OH \rightarrow X^- + H^+ + C_2H_4OH$ where X represents Cl or $^2P_{1/2}$ Br atoms. When X is an I ($^2P_{3/2}$ or $^2P_{1/2}$) or a $^2P_{3/2}$ Br atom the process does not take place and the alcohol concentration does not affect the results.

2 The Dissociation of the Excited State. The investigations of the spectra of I^-, Br^-, Cl^-, and OH^- in aqueous solution,[21,22] and the effects of changes in temperature,[23] solvent,[24] and added ions,[19] are consistent with the assumption that on the absorption of a light quantum the ground state ion, occupying a cavity defined by the surrounding oriented water molecules, goes over into an excited state in which according to the Frank–Condon principle the atomic nuclei have preserved their previous positions. This excited (c.t.t.s. state consists of an electron in a 2s orbital in the coulombic, spherically symmetrical, field of the oriented solvent medium.[22] The excited electron in this orbital is confined over the first layer of water molecules of hydration, its mean radius being $R_{ex} \cong 5.8$ Å. Previous work[2,3] showed that electron scavengers, H^+_{aq}

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[20] T. Berces and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4281 (1961).

[21] G. Stein and A. Treinin, *Trans. Faraday Soc.*, **55**, 1087 (1959).

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

[23] (a) M. Smith and M. C. R. Symons, *Discussions Faraday Soc.*, **24**, 206 (1957); (b) G. Stein and A. Treinin, *Trans. Faraday Soc.*, **55**, 1091 (1959).

[24] I. Burak and A. Treinin, *ibid.*, in press.

or N_2O, could not directly interact with this excited state to scavenge the excited electron from it. The reason for this is not likely to be an energetic one, since the reaction $e^- + H^+_{aq} \rightarrow H$ is exoergic by ~50 kcal. for an unbound electron. In the first excited state the energy of binding of the electron is[21] only ~35 kcal. It appears rather that the reason is one of time scale. The velocity of decay of the excited state to the ground state is too great for scavengers such as H^+_{aq} at concentrations of the order of 1–4 M to compete with it. The situation in the case of this "primary recombination" is similar to that for the so-called primary (nondiffusive) cage recombination in the photochemistry of, *e.g.*, diatomic molecules and others in solution[25] where scavengers able to compete with it could not be found.

The results in the present and previous[2,5] work indicate however that there is a process able to compete with the decay of the excited state. This process leads to the formation of a halogen atom and a solvated electron, e^-_{aq}, in close proximity.

$$X^-_{aq}{}^* \longrightarrow (X_{aq} + e^-_{aq})$$

The two fragments now begin a random walk diffusion process; the distribution of radicals tending to become homogeneous. In previous papers[1-5] we considered the possibility of a direct interaction of the scavenger with the excited state of the ion (preventing "primary recombination") or, alternatively, homogeneous scavenging in the bulk of the solution, occurring after a presumably fast diffusion of the radical partners from each other, so that secondary recombination would be of low probability. Neither of these possibilities accounts for the experimental results obtained in the previous or in the present work. The results, however, are in good agreement with a mechanism of scavenging processes, competing with secondary recombination of the parent atom and the solvated electron. Three regions of changing quantum yield may be observed. At high scavenger concentrations secondary recombination is effectively prevented and a plateau of limiting quantum yield, Γ, is reached. The situation is of total scavenging and the value of Γ corresponds to the yield of formation of the atom-electron pairs. At lower scavenger concentrations the quantum yield decreases with the decrease in the scavenger concentration, in quantitative agreement with the theoretical predictions on the effect of scavengers on secondary recombination.[2-4,6,7] Finally, at very low scavenger concentrations, one should expect to reach a region in which scavenging competes with bulk recombination and homogeneous kinetics applies. However, our experimental results in this region are not accurate enough to confirm such an assumption. The pH-independent residual yield obtained above pH 7 is due to the fact that the water solvent itself acts as a scavenger to solvated electrons and a condition of zero scavenger concentration cannot be achieved.

The formation of e^-_{aq} from the primary excited state occurs in competition with the decay to the ground state which is rapid enough to prevent direct scavenging from the spectroscopic excited state. It involves a process of asymmetrization, in which the electronic charge is no more spherically symmetrical around the halogen atom (a 2s electron bound in the polarization field of the original ion) but a solvated, self-trapped electron in its lowest (1s) energy level. It should be noted[24] that in both cases the same effective charge $Z_{eff} = [(1/D_{op}) - (1/D_s)] = 0.5$ (where D_{op} and D_s represent the optical and static dielectric constants of water) determines the field in which the electron is bound. The main difference between the states is the type of electronic orbital, 2s in the excited state of the ion, with the neutral atom at the center, and in the case of the solvated electron, which has been displaced relative to the atom.

The Effect of Temperature on Γ. Considering the formation of the pair $(X + e^-_{aq})$ as a process resulting from the competition between a thermal deactivation and a thermal asymmetrization, we allocate an activation energy E_1 to the first process and E_2 to the second. Thus denoting the rate of decay to the ground state by

$$A = k_1 \exp(-E_1/RT)$$

and the rate of asymmetrization by

$$B = k_2 \exp(-E_2/RT)$$

(where k_1 and k_2 contain transmission coefficients and entropy factors), the limiting quantum yield, Γ, will be given by

$$\Gamma = \frac{B}{A + B} = \frac{1}{1 + (A/B)} = \frac{1}{1 + \dfrac{k_1}{k_2} \exp \dfrac{(E_2 - E_1)}{RT}}$$

Denoting $\Delta E = (E_2 - E_1)$ and $k_1/k_2 = C$

$$\ln \{(1/\Gamma) - 1\} = \ln C + (\Delta E/R)1/T \quad (2)$$

Figure 6 shows the plots of log $\{(1/\Gamma) - 1\}$ *vs.* $1/T$ for I^-_{aq} at 2537 Å. and for Br^-_{aq} at 2288 Å. The slopes give ΔE = 4.9 kcal. mole^{-1} for I^-_{aq} and ΔE = 4.0 kcal. mole^{-1} for Br^-_{aq}. For Cl^-_{aq} at 1849 Å. the quantum yield approaches 1, and the change with

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(25) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

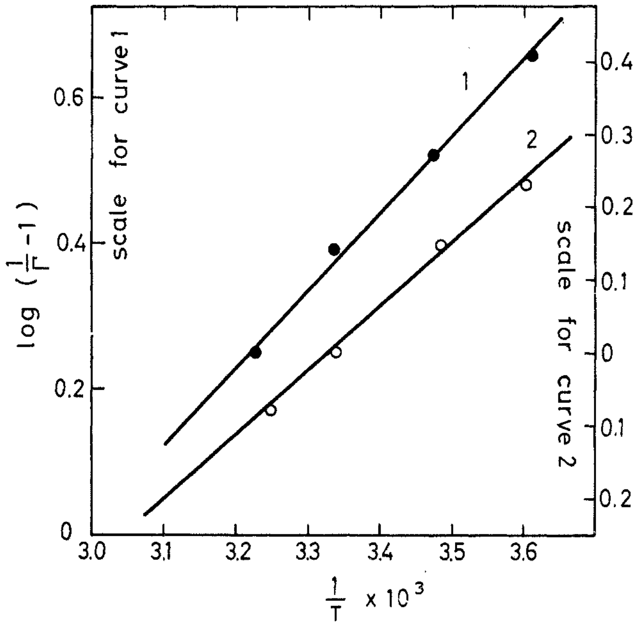

Figure 6. Test of eq. 2 for the temperature dependence of Γ in the photochemistry of I^- at 2537 Å. and Br^- at 2288 Å.

temperature is too small for the derivation of a reliable value of ΔE.

These results therefore prove that at least one of the competing processes involves an activation energy. However, only the difference ΔE may be calculated and the separate values E_1 and E_2 cannot be evaluated from our experimental results. The exact nature of the two processes is still not completely clear. The radiationless deactivation may resemble that of excited centers in ionic crystals in which energy may be needed to reach a cross section point of the energy curve with that of the ground state. The configuration coordinate may be one depending on the relative distance between the first hydration layer and the central atom (or ion). The asymmetrization process is essentially one of relative diffusion of X and the expanded electronic orbital, whose efficiency will be determined by the diffusion rate of the less mobile species. It is difficult to say which of the two will be the more mobile, as the diffusion coefficient of solvated electrons is not known. It should also be noted that both diffusive displacements may be abnormal, that of X in the sense that the atom must diffuse out of a cavity around which solvent molecules were organized by the original field of the ion. In the case of the electronic charge the displacement must be accompanied by a transition to the ground, 1s, state of the solvated electron.

The Dependence of Γ on Wave Length, Type of Halide Ion, and Added Salts. Passing from 2537 to 2288 Å. the absorption, in the case of I^-_{aq}, is always in the same band, leading to the formation of a 2s electron and a $^2P_{3/2}$ iodine atom. Spectroscopic studies[21] showed that the main reason for the broadening of the absorption band is due to changes in the ground state of the ion. In solution the ions are situated in cavities bound by the solvent water; the broad absorption band is due to the distribution of the equivalent radii of such cavities. According to this theory, changes of equivalent radius affect mainly the energy of binding in the ground state. The excited state, and in particular the energy of binding of the excited electron, remains largely unaffected. The present results agree with this assumption and may be interpreted as showing that the increased energy of $h\nu$ at 2288 Å. compared with 2537 Å. is needed in the case of I^-_{aq} to raise the electron to about the same level from a deeper ground state in the potential well formed by the oriented solvent.

Proceeding to 1849 Å., Γ rises considerably, its ratio to γ_r^{ex} remaining the same as at 2537 and 2288 Å. At 1849 Å., the absorption is in a band which may pertain to another transition.[26] In this the excited electron may go to a higher, *e.g.*, 3s state in the potential well described by the Franck–Platzman theory. Two reasons may then contribute to the higher value of Γ: lower recombination probably to the ground state and higher efficiency of the reaction leading to the formation of the solvated electrons from the excited state.

As to the change of Γ in the series I^- at 2537 Å., Br^- at 2288 Å., and Cl^- at 1849 Å., all these transitions yield a 2s state of the excited electron and the $^2P_{3/2}$ state of the halogen atom. Nevertheless, the efficiency of the asymmetrization of the first excited state to yield a solvated electron and a halogen atom increases in the series $I^-_{aq} < Br^-_{aq} < Cl^-_{aq}$. Two causes may contribute to this. The process of asymmetrization may involve the movement of the halogen atom, which will be easier for the light Cl than for the heavier Br or I.

A second cause may be a different rate of deactivation, A, decreasing in the order I^-, Br^-, Cl^-. However the lack of values of k_1 and E_1 prevents a quantitative analysis of such an effect.

The complete lack of salt effects on Γ, even in highly concentrated solutions, is consistent with the spectroscopic studies[19] which claim that added salts may influence the ground state of the ion (*i.e.*, the effective cavity radius) but do not effect markedly the excited state, the changes in D_{op} and D_s with addition of salts being negligible. Our photochemical results show that both A and B may remain unaffected by foreign ions and are also consistent with the fact that the excited

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(26) G. Scheibe, *Z. physik. Chem.*, **35**, 355 (1929).

state is not affected by high concentrations of the salts now employed.

After the completion of this manuscript Hart and Boag's work[27] appeared, showing the absorption spectrum of the hydrated electron in water and in aqueous solutions irradiated with pulses of ionizing radiation. Subsequently, Matheson and Rabani[28] found spectroscopic evidence for the formation of solvated electrons in the flash photolysis of aqueous solutions, including those of halide ions. These results give strong support for the views expressed in the present and previous[1-5,8] papers.

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Heat Capacities and Thermodynamic Properties of Globular Molecules. X. Fusion of Pentaerythrityl Fluoride[1]

by John C. Trowbridge and Edgar F. Westrum, Jr.

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The heat capacity of crystalline and liquid $C(CH_2F)_4$ has been determined by adiabatic calorimetry from 295 to 385°K. The small entropy of fusion, 3.35 cal./(mole °K.), at the 367.43°K. triple point temperature confirms the plastically crystalline nature of this substance.

Introduction

Low temperature heat capacity studies on pentaerythritol[2] and the pentaerythrityl halides[3] revealed the presence of a transition at 249.40°K. to the plastically crystalline state in pentaerythrityl fluoride, $C(CH_2F)_4$, with 12.66 cal./(mole °K.) entropy of transition.[4] Study of the thermodynamics of the fusion process was undertaken to provide a basis for further correlation of the crystal II → crystal I transition in the fluoride with that in pentaerythritol and to give an added test of the proposed mechanism of transition in the former.

Experimental

Calorimetric Sample. The identical sample used previously[4] was loaded in the nitrogen atmosphere of the drybox. For these measurements 58.6279 g. (*in vacuo*) of pentaerythrityl fluoride were used. Further indication of purity is provided by the fractional fusion studies.

Calorimeter and Thermostat. The Mark IV intermediate temperature thermostat and silver calorimeter W-22[5] were used in these measurements with the quasi-adiabatic technique previously employed.[6] The calorimetric system had previously been calibrated[7] with the Calorimetry Conference Sample of synthetic sapphire.[8]

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(1) This work was supported in part by the United States Atomic Energy Commission.

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(3) D. H. Payne and E. F. Westrum, Jr., *ibid.*, **66**, 748 (1962).

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(8) G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, *J. Res. Natl. Bur. Std.*, **57**, 67 (1956).