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Conversion of Solvated Electrons into Hydrogen Atoms in the Photo- and Radiation Chemistry of Aqueous Solutions

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Radiation chemical and photochemical experiments are reported which show that the conversion of solvated electrons to H atoms is not specific to the H_3O^+ ion. Proton donors in general may react in the conversion $e_{aq}^- \rightarrow H$. The relative reaction rates correlate with the *pK* values of these acids as implied by Brønsted general acid catalysis law. The implications of this result for the nature of the solvated electron in water are briefly considered.

INTRODUCTION

RECENTLY experimental evidence became available showing that two forms of reducing radicals are present in irradiated aqueous solutions. These two have widely different reactivities with specific scavengers.[1–5] One form is converted into the other by reaction with H_3O^+.[2–7] The possible pairs of the reducing species considered were the solvated electron e^-_{aq} and the H atom, or alternatively the H atom and the H_2^+ ion. Recently results were obtained supporting the first possibility.[3] Evidence was also obtained showing that H atoms externally generated and introduced into the aqueous solutions reacted with H_2O_2,[8] chloroacetic acid,[9] and formic acid[10] with the same specific rate constant as the acid form produced by radiolysis. Kinetic salt effects[11,12] gave evidence that the reducing radical produced in the radiolysis of neutral solutions has a unit negative charge and may be identified as the solvated electron.

Experiments in which aqueous solutions of I^-_{aq} were photolyzed with uv light of 2536 Å showed[13] that the mechanism of hydrogen evolution in the presence of specific scavengers involves the intermediate formation in these systems of solvated electrons e^-_{aq}. The conversion of e^-_{aq} to atomic H by reaction with H_3O^+ was observed.[13] The H atoms produced reacted with organic scavengers (e.g., aliphatic alcohols and formate) in a manner analogous to the reactivity of the "acid form" in the radiolysis of water, so that the two intermediates are likely to be identical.

Thus both radiation chemical[3,7] and photochemical data[13] indicate that the H_3O^+ ion is an efficient scavenger for e^-_{aq}, yielding H atoms according to $H_3O^+ + e^-_{aq} \rightarrow H + H_2O$. The detailed mechanism has not yet been established. Some recent observations in this laboratory are relevant concerning this point. Lifshitz[14] observed an increase of the hydrogen yield from formate solutions irradiated by x-rays at $pH \sim 7$ on the addition of KH_2PO_4. Isotopic labeling experiments[14] (using formic acid, HCOOD, in D_2O) indicated that the action of KH_2PO_4 was to convert e^-_{aq} to H atoms capable of dehydrogenating the substrate. Na_2HPO_4 had a negligible effect on the hydrogen yield.

The effect of KH_2PO_4 on the quantum yield of the photochemical evolution of hydrogen from neutral iodide solutions in the presence of $1M$ isopropanol was also observed.[13] We have now investigated the general mechanisms for the conversion of e^-_{aq} to H atoms.

EFFECT of HF, $H_2PO_4^-$ and NH_4^+ IN THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS

(a) Effect of the $H_2PO_4^-$ Anion in Solutions Containing Formate and Acetone

Irradiations were carried out with 200 kVp x-rays without filtration. The dose rate was ~1000 rad min^{-1} as determined by the ferrous sulfate dosimeter. The amount of hydrogen evolved was determined by a thermal conductivity gauge.[10]

Experiments were carried out in solutions containing formate, phosphate, and acetone at $pH = 6.25$. At this *p*H in solutions containing formate alone, i.e., in the absence of a good electron scavenger, the experimental hydrogen yield $G(H_2)$ was found to be somewhat erratic, yields[15] of $G(H_2) \sim 2.0$ being obtained.[2] Addition of $5\times10^{-5}M$ acetone which effectively scavenges e^-_{aq}, reduces this hydrogen yield to 1.1.[2]

Addition of $0.1M$ KH_2PO_4 to formate solutions in the absence of acetone resulted in $G^0(H_2) = 3.85$ at

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[15] In this paper we denote by $G(H_2)$ the experimentally measured hydrogen yield, while G_{H_2} and G_H denote the yields of "molecular" hydrogen and atomic hydrogen, respectively.

$pH=6.25$. This result is interpreted by assuming that in the presence of the $H_2PO_4^-$ ion e^-_{aq} reacts with it to yield hydrogen atoms

$$e^-_{aq}+H_2PO_4^- \rightarrow H+HPO_4^= \qquad (1)$$

followed by H_2 production by dehydrogenation of the organic scavenger (e.g., formate)

$$H+RH_2 \rightarrow H_2+RH. \qquad (2)$$

Thus $G^0(H_2)$ should equal $G_{H_2}+G_H+G_{e^-}$, where the yield of solvated electrons $G_{e^-}=2.65$,[2(b),7] of atomic hydrogen $G_H=0.5$[2,3] and the molecular hydrogen yield $G_{H_2}=0.5$. The present result is in fair agreement with the previously obtained value of 3.7 ± 0.1.[2(b)] Addition of acetone lowers $G(H_2)$ (Table I), due to

$$e^-_{aq}+CH_3COCH_3 \rightarrow (CH_3COCH_3)^-. \qquad (3)$$

The reduction of acetone by H atoms is slow and may be neglected.[2(b)] In the presence of acetone the experimental hydrogen yield $G(H_2)$ is given by

$$G(H_2)=G_{H_2}+G_H+\frac{G_{e^-}}{1+(k_3/k_1)([CH_3COCH_3]/k_1[H_2PO_4^-])}. \qquad (4)$$

Hence we get

$$\frac{k_3}{k_1}\frac{[CH_3COCH_3]}{[H_2PO_4^-]}=\frac{G^0(H_2)-G(H_2)}{G(H_2)-(G_{H_2}+G_H)}. \qquad (5)$$

From Fig. 1 we thus obtained $k_{e^-+\text{acetone}}/k_{e^-+H_2PO_4^-}=570$. These results are consistent with competition for e^-_{aq} by the $H_2PO_4^-$ ion and acetone.

TABLE I. Hydrogen yields in solutions containing acetone, formate and phosphate irradiated by 200-kV x rays. All solutions contain 0.094 *M* KH_2PO_4+0.016 *M* Na_2HPO_4, 0.094 *M* formate. $pH=6.25$.

[Acetone]	Dose (rad)	$G(H_2)$
0	1000	3.85
1.8×10^{-5}	1300	3.45
7.3×10^{-5}	2000	2.85
1.4×10^{-4}	2000	2.50
2.7×10^{-4}	2300	2.20
8.2×10^{-4}	3000	1.60

(b) Solutions Containing Phosphate, Formate, and Ferricyanide

The aim of these experiments was to use ferricyanide[2,10] to capture e^-_{aq} in competition with phosphate. The reaction

$$Fe(CN)_6^{-3}+e^-_{aq} \rightarrow Fe(CN)_6^{-4} \qquad (6)$$

eliminates electrons without the formation of H atoms. Those electrons which in the competition between reactions 1 and 6 react with phosphate, form H atoms. These may yield H_2 through reaction (2) with formate, or react with ferricyanide

$$Fe(CN)_6^{-3}+H \rightarrow Fe(CN)_6^{-4}+H^+. \qquad (7)$$

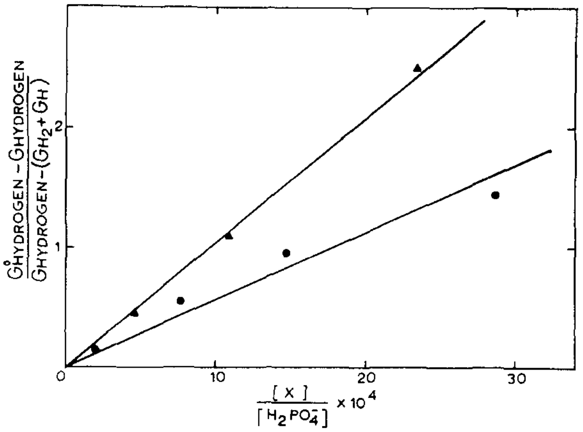

FIG. 1. The effect of varying X=acetone ● and ferricyanide ▲ concentration on $G(H_2)$ in the radiolysis of 0.1*M* KH_2PO_4–Na_2HPO_4 solutions at $pH=6.25$ in the presence of 0.1*M* formate.

TABLE II. Hydrogen yields in solutions containing ferricyanide and formate irradiated by 200-kV x rays. $pH=6.25$. All solutions contain 0.094*M* KH_2PO_4+0.016*M* Na_2HPO_4. (b) Same as (a) but with 0.94*M* KH_2PO_4 and 0.16*M* Na_2HPO_4 added. The last column shows the calculated $G(H_2)$ values corrected for increased absorption.

[formate] *M*	[ferricyanide] *M*	Dose (rad)	$G(H_2)$
	(a)		
9.4×10^{-2}	0	1000	3.85
9.4×10^{-2}	5.4×10^{-5}	1500	2.95
9.4×10^{-2}	1.1×10^{-4}	1500	2.40
9.4×10^{-2}	2.2×10^{-4}	1500	1.83
9.4×10^{-2}	4.4×10^{-4}	3000	1.57
9.4×10^{-2}	5.9×10^{-3}	2000	0.83
5.5×10^{-4}	0	1000	3.55
5.5×10^{-4}	3.2×10^{-5}	2000	1.80

(b)

[formate] *M*	[ferri-cyanide] *M*	Dose rad	$G(H_2)$ uncorrected	$G(H_2)$ corrected for absorption
9.2×10^{-2}	0	1000	5.9	3.9
9.2×10^{-2}	1.0×10^{-4}	1000	5.4	3.6
9.2×10^{-2}	9.4×10^{-4}	1000	3.4	2.3
9.4×10^{-4}	0	1000	5.3	3.5
9.4×10^{-4}	5.0×10^{-5}	1500	2.95	1.95

TABLE III. (a) Solutions containing $HCOO^- = 9.4\times10^{-4}$ M and 2×10^{-4} M Na_2HPO_4+KOH, $pH = 7.9$, dose 1000 rad.

(a)

$[(NH_4)_2SO_4]$ M	[acetone] $10^{-5}M$	$G(H_2)$
0.4	0	2.8
0.1	0	2.8
0.08	0	2.6
0.1	1.8	2.1
0.1	3.6	1.7
0.1	7.2	1.5

(b)

(b) Solutions of NH_4^+. Dose 1000 rad. pH adjusted by adding KOH.

Scavenger added M	ammonium salt used M	pH	[acetone] M	$G(H_2)$
$HCOO^-$, 9.2×10^{-2}	NH_2HCOO^-, 9.2×10^{-2}	8.3	...	3.0
$HCOO^-$, 9.2×10^{-2}	NH_2HCOO^-, 9.2×10^{-2}	8.3	1.3×10^{-5}	2.1
$HCOO^-$, 9.2×10^{-4}	NH_4Cl, 0.11	6.3	...	2.8
Methanol 5×10^{-2}	NH_4Cl, 0.11	8.0	...	3.0
$HCOO^-$, 9.2×10^{-4}	NH_4F, $1M$	7.6	...	2.5
$HCOO^-$, 9.2×10^{-4}	NH_4F, $1M$	7.6	1.4×10^{-4}	1.8

The experimental hydrogen yield $G(H_2)$ is given by

$$G(H_2) = G_{H_2} + \frac{G_H}{1+\dfrac{k_7[Fe(CN)_6^{-3}]}{k_2[HCOO^-]}} + \frac{G_{e^-}}{\left(1+\dfrac{k_6[Fe(CN)_6^{-3}]}{k_1[H_2PO_4^-]}\right)\left(1+\dfrac{k_7[Fe(CN)_6^{-3}]}{k_2[HCOO^-]}\right)} \quad (8)$$

where[10,16] $k_7/k_2 = 15$; $G_{e^-} = 2.65$, $G_H = 0.5$, and $G_{H_2} = 0.5$. The results are shown in Table II. In the presence of $10^{-1}M$ formate, ferricyanide does not compete with it appreciably for H atoms at concentrations $<4\times10^{-4}M$. From the hydrogen yields thus obtained, and the hydrogen yield in the absence of ferricyanide $G^0(H_2) = G_{H_2}+G_H+G_{e^-} = 3.85$, $k_6/k_1 = 1050$ is obtained (Fig. 1). Correction was made for the amount of ferricyanide reduced during irradiation. The two results at [ferricyanide]$>4\times10^{-4}M$, and the results at low formate show the effect of scavenging by ferricyanide of H atoms as well. The results agree well with the previously obtained values[2,16] of $k_6/k_1 = 1050$ and $k_7/k_2 = 15$. The results thus support the identification of the product of reaction (1) as H atoms, since they give the established value of k_7/k_2. To confirm this point experiments were carried out at higher phosphate concentrations. The results are shown in Table III(b). The hydrogen yields corrected for increased absorption are by a factor of 1.5 lower than the uncorrected experimental yields.[17] The corrected $G(H_2)$ yields agree with the values previously obtained, giving $k_6/k_1 = 1000\pm100$ and $k_7/k_2 = 20$.

With the results of the preceding section we obtain $k_{e^-+Fe(CN)_6^{-3}}/k_{e^-+CH_3COCH_3} = 1.8$ in good agreement with the value 1.9 previously obtained.[2(b)]

(c) Phosphate Ion and Other Scavengers

In some experiments NO_2^- was used as the e^-_{aq} scavenger. In solutions containing $0.1M$ formate, $0.11M$ phosphate [as in Table II(a)], and $1\times10^{-4}M$ $NaNO_2$ $G(H_2) = 2.45$ was obtained. Since[2] $k_{H+NO_2^-}/k_{H+HCOO^-} = 4$, NO_2^- cannot in these experiments compete with formate for H atoms. It reacts with e^-_{aq}[2] without the formation of H atoms, and accordingly $G(H_2)$ reduces in the presence of NO_2^-. Calculations similar to Eq. (5) yield $k_{e^-+NO_2^-}/k_{e^-+H_2PO_4^-} = 770$. Another system used by us contained RH_2 = methanol = $5\times10^{-2}M$ (instead of formate) to scavenge H atoms, and nitrate ions $1.1\times10^{-4}M$ (KNO_3) to scavenge e^-_{aq} in competition with phosphate ($0.094M$ KH_2PO_4+

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

[17] The following procedure was used: In solutions containing $4\times10^{-4}M\,Fe(CN)_6^{-3}$ and $0.1M$ formate at $pH = 6$, $G_r = G_{Fe(CN)_6^{-4}} = 5.8 = G_H + G_{OH} + G_{e^-}$ [J. Rabani and G. Stein, Trans. Faraday Soc. (to be published)]. Addition of $1M$ KH_2 PO_4 and $0.1M$ NaH_2 PO_4 results in $G_r = 8.8$. Hence the correction factor = 1.5.

$0.016M$ Na_2HPO_4). At the concentration employed NO_3^- does not compete with methanol for the H atoms[18] but competes with $H_2PO_4^-$ for e^-_{aq}. In this system $G(H_2)=2.05$ was obtained, compared with $G(H_2)=3.55$ in the absence of NO_3^-. Hence $k_{e^-+NO_3^-}/k_{e^-+H_2PO_4^-}=1300$ was calculated.

The value thus obtained $k_{e^-+NO_3^-}/k_{e^-+NO_2^-}=1.8$ is in fair agreement with the values of 3.6 and 2 that can be obtained from the previous work of Salzman and Schwarz.[19] We consider that in their case the competition is for e^-_{aq}.

(d) Effect of the NH_4^+ Ion on the Radiolysis of Neutral Formate Solution

The results of experiments using ammonium salt solutions at $pH=7.6$ are shown in Table III. In the absence of added acetone the hydrogen yield is increased by addition of $(NH_4)_2SO_4$ reaching a value of $G(H_2)=2.8$ compared to $G(H_2)\sim 2$ in the absence of the ammonium salt. This effect is attributed to H atom formation by

$$NH_4^+ + e^-_{aq} \rightarrow NH_3 + H \qquad (9)$$

followed by reaction (2).

However, unlike phosphate, NH_4^+ even at higher concentrations does not raise $G(H_2)$ above the value 2.8–3.0. Added acetone reduces the hydrogen yield and from these results $k_{e^-+\text{acetone}}/k_{e^-+NH_4^+}$ may be estimated as follows.

The limiting value $G^0(H_2)=G_H+G_{e^-}+G_{H_2}=3.6$ is reached when all e^-_{aq} is converted to H, and these are fully utilized in dehydrogenating RH_2. This value is not reached in the presence of NH_4^+ and we assume that this is due to incomplete conversion of e^-_{aq} to H. As is seen later NH_4^+ is a relatively inefficient converter of e^-_{aq} to H atoms. Thus a $0.1M$ solution of NH_4^+ is equivalent in this respect to only $3\times10^{-6}M$ H^+_{aq}. At the corresponding $pH\sim5$ or higher, in the presence of organic scavengers for H atoms hydrogen yields $G<3$ were also observed[2(b)] due to side reactions of e^-_{aq}. Assuming that e^-_{aq} reacts by a pseudo-first-order reaction (e.g., with impurities), denoting by $r[e^-_{aq}]$ the rate of the reaction leading to disappearance of e^-_{aq} without H atom formation we get

$$\frac{k_9[NH_4^+]}{r}=\frac{G^0(H_2)-(G_H+G_{H_2})}{G_H+G_{e^-}+G_{H_2}-G^0(H_2)}, \qquad (10)$$

where $(G_H+G_{e^-_{aq}}+G_{H_2})=3.6$ and $G^0(H_2)$ is the experimental hydrogen yield in the absence of added acetone Then in the same solution with added acetone

$$\frac{G_H+G_{e^-}+G_{H_2}-G(H_2)}{G(H_2)-(G_H+G_{H_2})}=\frac{k_{e^-+\text{acetone}}[\text{acetone}]+r}{k_9[NH_4^+]}. \qquad (11)$$

Table IV. Hydrogen yields in solutions containing acetone, isopropanol, and hydrofluoric acid irradiated by 200 kV x rays. Total dose 1000–3000 rad. All solutions contain $[HF]=0.0096$ M, $[HF_2^-]=0.016M$, $[(CH_3)_2CHOH]=0.01M$, $pH=5.02$.

[Acetone]	Dose (rad)	$G(H_2)$
0	1000	3.77
1.3×10^{-4}	1200	3.20
2.6×10^{-4}	2000	2.50
5.2×10^{-4}	2500	2.02

From the results in Table III(a) $k_{e^-+\text{acetone}}/k_{e^-+NH_4^+}=1\times10^4$.

Further experiments were carried out using NH_4Cl, NH_4F, and NH_4HCOO as the ammonium salts employed. The results are shown in Table III(b).

From these results $k_{e^-+\text{acetone}}/k_{e^-+NH_4^+}=1\times10^4$ confirming the previous value.

(e) Effect of Added HF on the Radiolysis of Aqueous Solutions

To investigate the possible conversion of e^-_{aq} to H atoms according to

$$HF+e^-_{aq}\rightarrow F^-+H \qquad (12)$$

solutions containing acetone as scavenger of e^-_{aq}, isopropanol[2(b)] as scavenger of H atoms, and hydrofluoric acid were employed. Since the dissociation constant of hydrofluoric acid is relatively low $(pK=3.2)$[20] the pH and F^- concentration have to be fairly high, to eliminate competition by the reaction $e^-_{aq}+H^+_{aq}\rightarrow H$. In this system the effect of the HF_2^- has to be taken into account,[20] according to the possible reaction

$$HF_2^-+e^-_{aq}\rightarrow H+2F^-. \qquad (13)$$

The solutions used contained $0.46M$ KF and $0.026M$ hydrofluoric acid, as used by Bell and McCoubrey,[20] so that the solutions contained $HF=0.0096M$, $F^-=0.44M$; and $HF_2^-=0.16M$, the pH being 5.03. The results are shown in Table IV.

$G^0(H_2)=3.75$ in the absence of acetone, is in agreement with the value of $G_{e^-}+G_H+G_{H_2}$. Assuming[20] that HF_2^- is approximately as effective as HF in converting e^-_{aq} to H, the relative rate constants $k_{e^-+\text{acetone}}/k_{e^-+HF}$ were obtained from

$$\frac{k_{e^-+CH_3COCH_3}[CH_3COCH_3]}{k_{e^-+HF}([HF]+[HF_2^-])}=\frac{G^0(H_2)-G(H_2)}{G(H_2)-(G_{H_2}+G_H)}. \qquad (14)$$

Hence $k_{e^-+\text{acetone}}/k_{e^-+HF}=80\pm20$.

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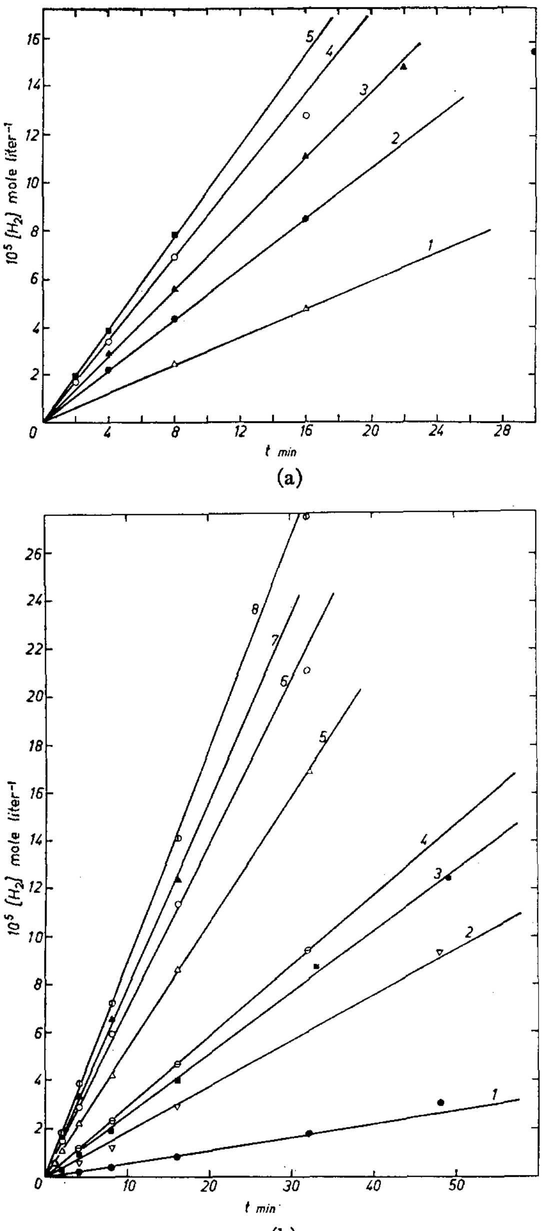

(a)

(b)

FIG. 2. The photochemical evolution of H_2 from $0.15M$ I^- solutions at 2536 Å and 25°C in the presence of $1M$ methanol. Light intensity 3.5×10^{-5} Einstein liter^{-1} min^{-1}.

(a) The effect of $H_2PO_4^-$ at $pH=6.25$.

Curve	1	2	3	4	5
$H_2PO_4^-$ M	3.85×10^{-3}	7.7×10^{-3}	1.9×10^{-2}	3.85×10^{-2}	1.54×10^{-1}

(b) The effect of NH_4^+ at $pH=7.8$.

Curve	1	2	3	4
NH_4^+ M	5×10^{-3}	2.5×10^{-2}	7.7×10^{-2}	7.7×10^{-2}
Curve	5	6	7	8
NH_4^+ M	2.3×10^{-1}	6.15×10^{-1}	1.0	4.0

For curve 4(b) we used $8\times10^{-3}M$ HCOOK instead of methanol.

EFFECT OF $H_2PO_4^-$, NH_4^+, AND HF ON THE PHOTOCHEMICAL EVOLUTION OF H_2 FROM SOLUTIONS OF I^-_{aq}

Light absorption in the charge transfer bands of halide ions in solution results in electron transfer to a bound state determined by the solvent. Experimental and theoretical work[21] shows that the first excited level involves a centrosymmetric-bound s-type state. Recently the scavenging mechanisms and the nature of the intermediates in the photochemistry of the iodide ion, were investigated.[13] Our photochemical results were interpreted by assuming the consecutive production of two forms of reducing radicals in the photochemical system. The reaction scheme in the presence of organic scavengers, which react with H atoms to form H_2 is given in the form[13]

$$I^- \xrightarrow{h\nu} I^-_{aq}{}^* \rightarrow (I+e^-) \xrightarrow{H^+} (I+H) \xrightarrow{RH_2} RH+H_2,$$

where ( ) represents a solvent cage. This mechanism was confirmed using a series of specific scavengers of e^-_{aq} and of H atoms, respectively. The experimental data were treated using extended diffusion equations to account for the competition between secondary recombination and scavenging.

(a) Experimental Results

Photochemical experiments were carried out at 25°C using a 2536 Å light source. The experimental technique was previously described.[22] Experiments in the presence of KH_2PO_4 were conducted at $pH=6.25$ (where $[H_2PO_4^-]/[HPO_4^=]=8$). At this pH the effect of H_3O^+ on the conversion of e^-_{aq} to H is negligible. No effect of the $HPO_4^=$ ion on the quantum yield for the production of hydrogen $\gamma(H_2)$ was observed, as experiments carried out at $pH=8.1$ (where $[H_2PO_4^-]/[HPO_4^=]=10^{-2}$) showed that $\gamma(H_2)$ is independent of Na_2HPO_4 concentration between $10^{-3}-10^{-1}M$. No

TABLE V. Quantum yields for H_2 formation at 2536 Å and 25°C in the presence of $H_2PO_4^-$ at $pH=6.25$ in iodide solutions. $[I^-]=0.15\,M$ $[CH_3OH]=1\,M$

$[H_2PO_4^-]$ M	$\gamma(H_2)$
0	0.033
3.85×10^{-3}	0.075
7.7×10^{-3}	0.135
1.9×10^{-2}	0.172
3.85×10^{-2}	0.205
1.54×10^{-1}	0.246

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effect of added 1*M* KCl, NaCl, and NaBr on $\gamma(H_2)$ at $p\mathrm{H}\approx 6$ was detected. Light absorption by the monophosphate ion is negligible ($\epsilon = 1.5M^{-1}$ cm^{-1} at 2536 Å). In the presence of the organic scavenger, free I_2 is not formed[13] and the hydrogen yields $\gamma(H_2)$ are independent of total dose (Fig. 2). Table V shows the effect of added KH_2PO_4 on $\gamma(H_2)$ obtained from I^- solutions in the presence of an efficient scavenger RH_2 for H atoms. These results show an enhancement of H_2 formation by the $H_2PO_4^-$ ion. A similar effect was observed on addition of NH_4^+ (Table VI).

In the presence of fluoride, experiments were carried out in solutions containing[20] $HF = 0.0096M$, $F^- = 0.44M$, and $HF_2^- = 0.016M$, at $p\mathrm{H} = 5.03$. The I^- concentration was 0.15*M*. At 25°C using 2536 Å, the quantum yield $\gamma(H_2) = 0.19$ was found, compared to $\gamma(H_2) = 0.07$ in the absence of fluoride at this *p*H.

TABLE VI. The dependence of the quantum yield for H_2 evolution at 2536 Å and 25°C on NH_4Cl concentration in iodide solutions. $p\mathrm{H} = 7.8$ (adjusted with NH_4OH) $[I^-] = 0.15M$.

$[NH_4^+]$ *M*	Organic scavenger	$\gamma(H_2)$
10^{-3}	1*M* CH_3OH	0.013
5×10^{-3}	1*M* CH_3OH	0.013
2.5×10^{-2}	1*M* CH_3OH	0.047
7.7×10^{-2}	8×10^{-3} KHCOO	0.064
7.7×10^{-2}	1*M* CH_3OH	0.073
2.3×10^{-1}	1*M* CH_3OH	0.133
6.15×10^{-1}	1*M* CH_3OH	0.182
1.0	1*M* CH_3OH	0.204
1.0	0.7*M* C_2H_5OH	0.202
4.0	1*M* CH_3OH	0.230
4.0	0	10^{-3}

These results are interpreted by assuming that $H_2PO_4^-$ and NH_4^+ and HF (or HF_2^-) convert the solvated electron into an H atom by

$$(I+e)+H_2PO_4^- \rightarrow (I+H)+HPO_4^{=},$$

$$(I+e)+NH_4^+ \rightarrow (I+H)+NH_3,$$

$$(I+e)+HF(\text{or } HF_2^-) \rightarrow (I+H)+F^-(\text{or } 2F^-). \quad (15)$$

The H atoms thus formed react with the organic scavenger. The low value of $\gamma(H_2)$ in NH_4Cl solutions in the absence of an organic scavenger (Table VI) exclude any mechanism involving direct molecular hydrogen formation.

(b) Kinetic Analysis of the Photochemical Data

In Fig. 3 we present a general scavenging plot for electron scavenging by H_3O^+, HPO_4^-, NH_4^+, and HF (or HF_2^-) (assuming as before that HF and HF_2^- are of equal effectiveness). One unified curve is obtained for the dependence of the quantum yield on the normalized scavenger concentration $R[S]$, i.e., the solute concentration $[S]$ multiplied by a normalization constant R chosen for each scavenger to give best agreement with the previous results[13] for H_3O^+. The correlation of the quantum yields is good and supports the conclusions that the three scavengers lead to H atom formation by a similar process. As the scavenging yield is determined by $k_s[S]$[13] (where k_s is the rate constant for scavenging) the normalization constants should have the same ratios as the rate constants for the reaction of e^-_{aq} with the scavenger. These results are presented in Table VII.

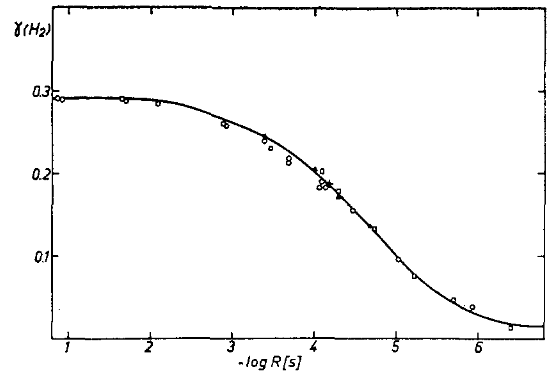

FIG. 3. The effect of H_3O^+, $H_2PO_4^-$, NH_4^+, and HF on the quantum yields for the photochemical evolution of hydrogen from I^- solution at 2536 Å and 25°C in the presence of 1*M* methanol: ○, H_3O^+, $R=1$; +, $HF+HF_2^-$, $R=4.10^{-3}$; ▲, $H_2PO_4^-$, $R=2.5\times10^{-3}$; □, NH_4^+, $R=8\times10^{-5}$.

The experimental scavenging data are analyzed using Noyes[23] treatment for scavenging competing with geminate recombination. For relatively low scavenger concentrations the concentration dependence of the quantum yield is

$$\gamma = \gamma_r + 2a\Gamma(\pi k_s[S])^{\frac{1}{2}}, \quad (16)$$

where γ_r is the residual yield in the presence of a scavenger at a concentration sufficient to prevent radical recombination in the bulk, but too low to compete with secondary recombination. Γ is the quantum yield for radical pairs escaping primary re-

TABLE VII. Photochemical kinetic data for electron scavenging by acids in the presence of 1*M* methanol.

scavenger *S*	$2a(\pi k)^{\frac{1}{2}}$ $M^{-\frac{1}{2}}$	$k_{H_3O^++e}/k_{S+e}$ (from Fig. 2)	$(1/R)$ (from Fig. 1)
H_3O^+	32	1	1
$HF+HF_2^-$	...	...	250
$H_2PO_4^-$	2.0	250	400
NH_4^+	0.43	6000	12000

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

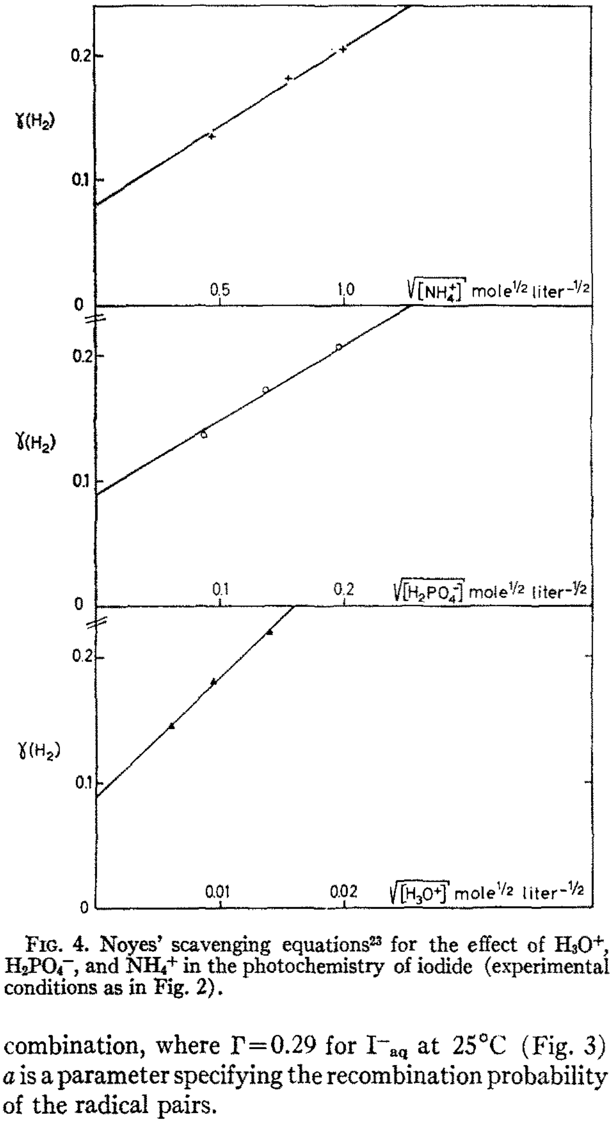

FIG. 4. Noyes' scavenging equations[23] for the effect of H_3O^+, $H_2PO_4^-$, and NH_4^+ in the photochemistry of iodide (experimental conditions as in Fig. 2).

combination, where $\Gamma=0.29$ for I^-_{aq} at 25°C (Fig. 3) a is a parameter specifying the recombination probability of the radical pairs.

The square-root plots for H_3O^+, $H_2PO_4^-$, and NH_4^+ (Fig. 4) lead to the values of $2a\Gamma(\pi k_s)^{1/2}$. It was shown[24] that Γ is unaffected by addition of inert salts (e.g., NaBr and LiCl) within the concentration range employed by us. Therefore in our calculations we used the value $\Gamma=0.29$ independent of salt concentration. From the parameters $2a(\pi k_s)^{1/2}$ thus obtained the rate constants ratios for relative efficiencies for scavenging of e^-_{aq} are obtained. The slight differences between these and the $1/R$ values are due to the fact that the square-root plots are based on data at relatively low concentrations, and the dependence of the rate constants on the "age" of the radical pair was not taken into account.[25]

TABLE VIII. Relative rate constants for the conversion $e_{aq}^-\to$H

	$\frac{k_{H_3O^++e^-}}{k_{BH^++e^-}}$ (radiation chemistry)	$\frac{k_{H_3O^++e^-}}{k_{BH^++e^-}}$ (photochemistry)
H_3O^+	1	1
$HF+HF_2^-$	180	250
$H_2PO_4^-$	1300	400
NH_4^+	23000	12000

The three intercepts in Fig. 3 are equal, i.e., $\gamma_r=0.08\pm0.01$. The residual yield[22] is independent of the nature of the scavenger as implied by the theory of geminate recombination.

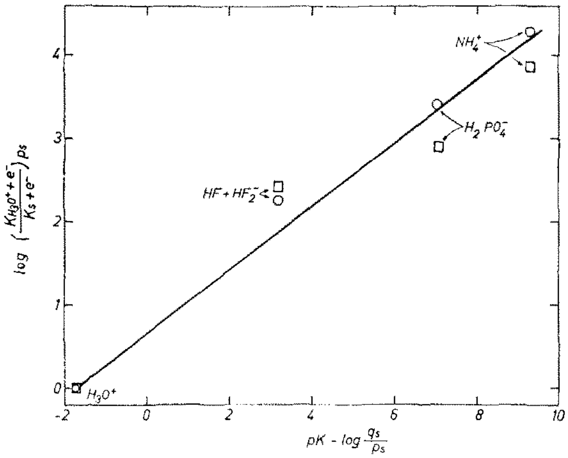

FIG. 5. The Brønsted law for general acid catalysis in the conversion $e^-_{aq}\to$H. The dependence of $k_{H_3O^++e^-}/k_{BH^++e^-}$ on the pK values of the acids BH^+. (For $H_2PO_4^-$ $p=2$ and $q=3$, while for H_3O^+, HF, HF_2^-, and NH_4^+ $p=q=1$). □ photochemical data; ○ radiation chemical data.

EVIDENCE FOR GENERAL ACID CATALYSIS IN THE CONVERSION OF e^-_{aq} TO H

The radiation chemical and photochemical data now reported yield evidence for the conversion of e^-_{aq} to H atom by a number of acids

$$H_3O^++e^-_{aq}\to H+H_2O,$$

$$HF(\text{and } HF_2^-)+e^-_{aq}\to H+F^-(\text{or } 2F^-),$$

$$H_2PO_4^-+e^-_{aq}\to H+H_2PO_4^{=},$$

$$NH_4^++e^-_{aq}\to H+NH_3.$$

In order to compare the radiation chemical with the photochemical data the rate constant ratio $k_{H_3O^++e^-}/k_{CH_3COCH_3+e^-}$ has to be estimated. This rate constant ratio depends on the ionic strength μ of the solution.[11,12] This dependence can be represented in the form[2(b)] $k_{H_3O^++e^-}/k_{CH_3COCH_3+e^-}=5\times10^{-(\mu^{1/2}/1+\mu^{1/2})}$ in agreement with the results of Czapski and Schwarz.[11] Between $\mu=0.15$–0.5 used in the radiation chemical experiments in the present work this rate constant ratio is 2.7–2.0.

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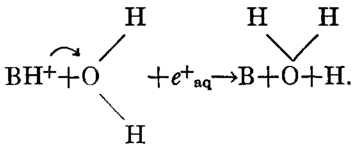
[24] J. Jortner, M. Ottolenghi, and G. Stein (to be published).

[25] R. M. Noyes, J. Phys. Chem. **65**, 763 (1961).

Considering the uncertainty in applying the Debye–Hückel kinetic salt effect at these high ionic strengths we used the mean value $k_{\mathrm{H_3O^+}+e^-}/k_{\mathrm{CH_3COCH_3}+e^-}=2.3$ for the calculation of the rate constant ratios. The relative rate constants obtained from photo and radiation chemistry are presented in Table VIII. The differences between the radiation chemical and photochemical data are probably due to the approximations involved in the photochemical scavenging mechanism.

These results show that the conversion of e^-_{aq} to H atom is not specific for the H_3O^+ ion which is just a member of a class of proton donors. The correlation between the relative reaction rates and the pK values of the acids (Fig. 5) is attributed to a mechanism involving general acid catalysis.[26,27] The mechanism for H atom formation seems to involve a proton transfer from the acid BH^+ to a water molecule located in the vicinity of the solvated electron.



$$\mathrm{BH^+ + OH_2 + e^+_{aq} \rightarrow B + OH_2 + H}. \tag{17}$$

The experimental results fit quite well the Brønsted general acid catalysis law,[26,27] which relates the effectiveness of an acid catalyst with its acid–base strength. Our data can be fitted to the Brønsted equation[26]

$$k/p=G_A(qK/p)^\alpha, \tag{18}$$

where k is the rate constant for the acid catalyzed reaction, K the dissociation constant of the acid, p the number of dissociable protons bound equally to different atoms in the acid, and q the number of equivalent points at which a proton can be attached to different atoms in the conjugated base. For $H_2PO_4^-$ $p=2$ and $q=3$, while for the others $p=q=1$. G_A and α are the constants for a series of similar acid catalysts in the same reaction. Our experimental data yield (Fig. 5) $\alpha\approx0.4$ which is a reasonable value for general acid catalysis.

In view of the seemingly more general character of this catalysis the possibility of the conversion of e^-_{aq} to H by organic acids in their irradiated aqueous solution has to be considered. Recent data by Hart[28] indicate that at relatively high concentration of formic acid $G(H_2)$ is independent of the solute concentration. This may be due to catalysis of the conversion $e^-_{\mathrm{aq}}\rightarrow$H by the formic acid, competing with electron capture by the acid without hydrogen formation. Similar effects were observed in the radiation chemistry of aqueous solutions of acetic and glycolic acids.[29] However, in these cases additional specific factors appear to affect the results.

Another relevant point involves radiation chemical studies in buffered solutions, where the effects considered in this work have to be taken into account.

Considering the role of water as a Brønsted catalyst, recent studies indicate that the conversion of e^-_{aq} to H by H_2O, i.e., $e^-_{\mathrm{aq}}+H_2O\rightarrow H+OH^-$ is a slow process.[2(b),11,30] As pointed out[2(b),11] 10^{-5}–$10^{-6}M$ of an efficient scavenger (e.g., O_2, acetone, or H^+) suppresses this reaction so that $k_{e^-+\mathrm{H_2O}}[H_2O]/k_{e^-+\mathrm{H^+}}<10^{-5}$, hence $k_{e^-+\mathrm{H_2O}}/k_{e^-+\mathrm{H^+}}<2\times10^{-7}$. A possible reaction path for the reaction of e^-_{aq} with H_2O involves general acid catalysis by H_2O. This reaction is slow due to the high pK value of water. Using the pK values for H_3O^+ and H_2O[27] and $\alpha=0.4$ we obtain from the Brønsted relation $k_{\mathrm{H_2O}+e^-}/k_{\mathrm{H_3O^+}+e^-}\geq10^{-7}$ which is a lower limit for this ratio of the rate constants. Hence the efficiency of the scavenging of e^-_{aq} by H_2O can now be estimated within a narrow range.

Regarding the nature of proton transfer reactions involving the $e^-_{\mathrm{aq}}\rightarrow$H conversion, proton transfer reactions obeying the Brønsted catalytic law are activation controlled and not diffusion-controlled reactions. These proton transfer reactions involve an activated state and the free energy of activation is about half of the free energy of dissociation of the acid catalyst. Thus even the most efficient conversion reaction involving H_3O^+ should be activation controlled with a rate constant not higher than 10^9M^{-1} sec^{-1}.

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[27] J. M. Brønsted and K. J. Pedersen, Z. physik. Chem. (Leipzig) **108**, 185 (1924).

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[29] E. Hayon and J. Weiss, J. Chem. Soc. **1960**, 5091.

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