when diffusion can be neglected, the corresponding equations are

$$-\partial[\mathrm{H}]/\partial X = k_{\mathrm{S}_1}[\mathrm{S}_1][\mathrm{H}] + k_\mathrm{r}[\mathrm{H}]^2 - k_{-\mathrm{S}_1}[\mathrm{HS}_1]$$
$$-\partial[\mathrm{HS}_1]/\partial X = -k_{\mathrm{S}_1}[\mathrm{H}][\mathrm{S}_1] + k_{-\mathrm{S}_1}[\mathrm{HS}_1] + k_{\mathrm{S}_2}[\mathrm{S}_2][\mathrm{HS}_1] \quad (53)$$

and by applying equation 47 the yield is

$$Y = \{(k_{\mathrm{S}_1}\varphi[\mathrm{S}_1]e_{\mathrm{S}_2})/k_\mathrm{r}\} \ln \{1 + (k_\mathrm{r}A/k_{\mathrm{S}_1}\varphi[\mathrm{S}_1]e_{\mathrm{S}_2})\} \quad (54)$$

In the case of homogeneous kinetics the reaction scheme of consecutive scavenging leads to the expression

$$Y = (\tau_1 e_{\mathrm{S}_2}{}^2[\mathrm{S}_1]^2/V)(\{1 + (2AV/\tau_1 e_{\mathrm{S}_2}{}^2[\mathrm{S}_1]^2)\}^{1/2} - 1) \quad (55)$$

where $\tau_1 = k_{\mathrm{S}_1}{}^2/2k_\mathrm{r}$.

Some general conclusions may now be derived regarding these results for homogeneous and heterogeneous kinetics. For high S_2 concentrations $e_{\mathrm{S}_2} \rightarrow 1$ and the equations reduce to those obtained for the case of a single scavenger. Therefore the rate-determining step in this case involves the formation of the HS_1 intermediate complex. At lower S_2 concentrations e_{S_2} is less than unity and for $\mathrm{S}_2 << k_{-\mathrm{S}_1}/k_{\mathrm{S}_2}$ the kinetic equations become equivalent to those obtained for the triple collision mechanism

$$\mathrm{H} + \mathrm{S}_1 + \mathrm{S}_2 \longrightarrow \text{products} \quad (56)$$

It is found then that in this approximation both heterogeneous and homogeneous treatments lead to the result that the yield is dependent on the concentration function $e_{\mathrm{S}_2}[\mathrm{S}_1]$ alone, when the consecutive scavenging mechanism is the actually operating one.

Conclusions

The impetus for the present investigation was given by one of the referees of the original draft of what forms now Part II of the present work. He requested detailed examination of those assumptions which were made in that and previous papers based on estimation of the experimental conditions, without a quantitative basis.

As the result of the present work we conclude regarding the absolute value of the rate constants, that under our conditions of vigorous stirring and bubbling the constants derived under the assumption of homogeneous kinetics are probably lower by not more than one order of magnitude than the true ones. As we cannot determine either u or φ accurately, no closer estimate is possible of the degree of agreement. However comparison of the values thus obtained by us with values derived from other experimental investigations support this conclusion. This point will be discussed in the following papers. Similarly, reaction mechanisms derived under these conditions under the assumption that homogeneous kinetics may be applied are the mechanisms arrived at also when heterogeneous kinetics are assumed.

In view of these conclusions homogeneous kinetics will be employed in some future papers, with due reference to the considerations now obtained.

THE MECHANISM OF OXIDATION BY HYDROGEN ATOMS IN AQUEOUS SOLUTION. PART II. REACTION MECHANISMS WITH DIFFERENT SCAVENGERS

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The mechanism of oxidation by hydrogen atoms of various acceptors is discussed. It is shown that two alternative pathways exist for the oxidation of ions dissolved in water. One involves the relatively slow reaction of H atoms with $\mathrm{H^+_{aq}}$ to form $\mathrm{H_2{}^+_{aq}}$, which oxidizes acceptors, *e.g.*, $\mathrm{I^-_{aq}}$. Alternatively other acceptors, *e.g.*, metal cations may directly form intermediate complexes with H, with faster rate constants. The intermediate hydride complex may react with $\mathrm{H^+_{aq}}$, yielding molecular hydrogen. When this faster, hydride complex, pathway is available, the slower $\mathrm{H_2{}^+}$ mechanism may not be of kinetic importance. The experimental results for the oxidation of $\mathrm{Fe^{2+}}$ ions by H atoms can be adequately explained by this mechanism. The results of radiation chemical and photochemical experiments are discussed.

Investigations of the radiation chemistry[1,2] of aqueous solutions of ferrous ions led to the assumption that H atoms may act as oxidizing agents in acid solutions. Evidence from the photochemistry of ferrous[3,4] and of iodide[5,6] ions was adduced to support this view. Recently using hydrogen atoms generated externally and introduced as such into the aqueous solutions it was shown that hydrogen atoms are indeed capable of oxidizing ferrous to ferric ions[7-9] and iodide to iodine.[10] The reaction was shown to be pH dependent.[9,10] However the actual mechanism was not finally established. Namely it was proposed[1,2] that the oxidation involves the formation of $\mathrm{H_2{}^+_{aq}}$ ion according to

$$\mathrm{H} + \mathrm{H^+_{aq}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{H_2{}^+_{aq}} \quad (1)$$

which acts as the actual oxidizing species

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(1) J. Weiss, *Nature*, **165**, 728 (1950).

(2) T. Rigg, G. Stein and J. Weiss, *Proc. Roy. Soc.*, **211A**, 375 (1952).

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(10) G. Czapski, J. Jortner and G. Stein, *ibid.*, **63**, 1769 (1959).

$$H_2{}^+_{aq} + M^{n+} \xrightarrow{k_2} H_2 + M^{(n+1)+} \qquad (2)$$

This mechanism was investigated in detail[10] and it was found that it was in agreement with the results obtained in the oxidation of iodide ions by atomic hydrogen. It was also compared with alternative mechanisms: the *p*H independent mechanism[11] of H abstraction from the hydration layer; the mechanism involving[12,8] triple collision between H,H^+_{aq} and the ion to be oxidized; and a mechanism in which H^+_{aq} was assumed to form a complex with the ion. None other than the mechanism involving $H_2{}^+_{aq}$ agreed with the results. The value obtained for k_1, the velocity constant of the formation of $H_2{}^+$ according to reaction 1 was found to be 10^2–10^3 mole liter^{-1} sec.$^{-1}$ by applying homogeneous kinetics. However the mechanism of the oxidation of the ferrous ion by H atoms could not be decided and consideration of the available evidence led to the conclusion[13] that in this case another mechanism may be operating. It was suggested[13] that in this alternative mechanism the hydride forming properties of the H atom may be of importance. The mechanism involving intermediate hydride complex formation was shown[14] to be consistent with the mechanism of homogeneous activation of H_2 by solutions of metal ions and[15] with the results of radiation chemical experiments.[16] In the present paper our detailed results of the reinvestigation of the oxidation of ferrous ions by atomic hydrogen are reported and the mechanism operating discussed in detail.

Experimental

Procedure.—The production of atomic hydrogen by electrodeless discharge at 30 Mc. was as described previously.[9,10] Atomic hydrogen was passed for 10 minutes through 25 ml. of the evacuated solution maintained at ~4°. The pumping velocity in the present series of experiments was 150 liter min.$^{-1}$. In order to improve reproducibility, no air was admitted after completing the run and full hydrogen atmosphere was maintained during the opening of the reaction vessel for analysis. With these precautions reproducibility was better than in our previously reported experiments. Each experiment was repeated at least three times and reproducibility was ±15% or better.

Determination of the dose of H atoms was carried out using the reduction of 10^{-3} *M* ferricyanide solutions.[17] During the runs the constancy of the dose was checked by the oxidation of 0.05 *M* Fe^{2+} solutions in 0.8 *N* H_2SO_4. The dose in the present series of experiments was 1.2 × 10^{-6} mole liter^{-1} sec.$^{-1}$.

Analysis.—The ferric ion concentration was determined by absorption measurements at 305 mμ in 1 cm. cells using a Beckman DU Spectrophotometer. The dependence of the molar absorption coefficient on the concentration of the sulfate ion and sulfuric acid concentration was determined in H_2SO_4 solutions in the *p*H region 0.4–3.0, containing 0.01–0.2 *M* Na_2SO_4. Identical results were obtained by replacing Na_2SO_4 by $FeSO_4$. The experimental results were duly corrected for the effect of sulfate ion concentration.

Materials.—A.R. ferrous ammonium sulfate and sulfuric acid were used. Solutions were prepared in triply distilled water. Matheson's electrolytic hydrogen was further purified by passing through palladized asbestos.

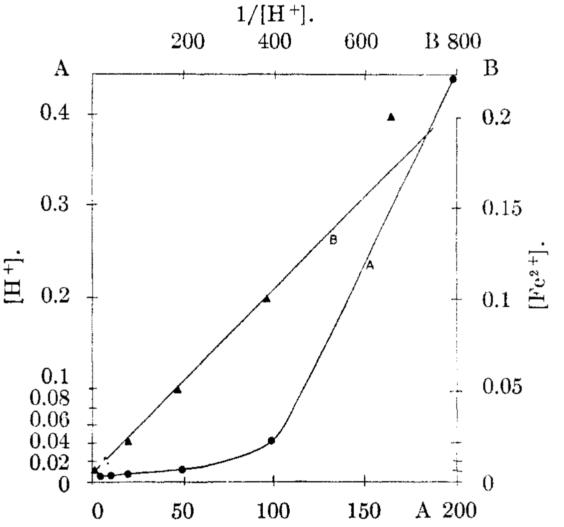

Fig. 1A.—Plot of the experimental results for the oxidation of Fe^{2+} according to the $H_2{}^+$ mechanism. *Y* = 0.34*A*. B.—Plot of the experimental results for the oxidation of Fe^{2+} according to the hydride mechanism.

Results

The oxidation of Fe^{2+} ions in acid solution by H atoms was investigated in the *p*H range of 0.4–3.0 and ferrous ion concentration of 0.001 to 0.2 *M*. The experimental results are presented in Table I. The reaction is found to be *p*H dependent in agreement with previous results.[9] The known ratio of the rate constants[18,9] of the reduction of Fe^{3+} and oxidation of Fe^{2+} by H atoms indicates that the decrease in the oxidation yield cannot be assigned to the back reaction between Fe^{3+} ions formed and H atoms. The dependence of the yield on Fe^{2+} concentration and the concentration of H^+ ions is attributed to the competition with the recombination reaction

$$2H \xrightarrow{k_r} H_2 \qquad (r)$$

Our experimental results cannot be reconciled with the oxidation mechanism involving the hydrogen molecule ion as an intermediate. In the preceding paper the problem of analyzing the results obtained by the method of H atom production and introduction into aqueous solutions was discussed. It was shown that both the homogeneous and the heterogeneous kinetic approach to the treatment of the experimental results leads to the conclusion that for the consecutive scavenging reaction scheme the yield is a function of $e_{S_2}[S_1]$, where $e_{S_2} = [S_2]/\{(k_{-S_1}/k_{S_2}) + [S_2]\}$, as defined in the preceding paper.

By applying these conclusions to the oxidation mechanism involving $H_2{}^+$ we see that the oxidation yield should be dependent on $[H^+][Fe^{2+}]/\{(k_{-1}/k_2) + [Fe^{2+}]\}$. When for different Fe^{2+} and H^+ concentrations the same yield is obtained, this function should remain constant. In other words for different scavenger concentrations which give the same oxidation yield, the plot of $[H^+]$ *vs.* $1/[Fe^{2+}]$ should result in a straight line. Such results for *Y* = 0.34*A* are presented in Fig. 1A.

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[16] F. S. Dainton and D. B. Peterson, *ibid.*, **186**, 878 (1960).

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[18] W. G. Rothschild and A. O. Allen, *Rad. Res.* **8**, 101 (1958).

The plot is not linear and thus we have to conclude that the experimental results are in disagreement with the oxidation mechanism involving H_2^+.

Oxidation Mechanism Involving Hydride Formation.—These discrepancies can be reconciled by assuming that the detailed mechanism of oxidation by H atoms is different in the case of I^- and Fe^{2+}.[13] We shall consider the possibility of a mechanism of oxidation in which initially H atoms interact with Fe^{2+} with the formation of a complex.[14,15]

$$Fe^{2+}_{aq} + H \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} FeH^{2+}_{aq} \quad (3)$$

Followed by the interaction of H^+ ions with the complex

$$FeH^{2+}_{aq} + H^+_{aq} \xrightarrow{k_4} Fe^{3+}_{aq} + H_2 \quad (4)$$

This kinetic scheme is equivalent to the consecutive scavenging mechanism investigated in Part I, and it will be shown that the dependence of the oxidation yield on the concentrations of Fe^{2+} and H^+ can now be satisfactorily accounted for on the basis of this mechanism. Using the expressions derived in Part I, the diffusion model is applied to the experimental results. The oxidation yield was obtained from the expression

$$Y = A\Delta_1/W_1 \quad (I)$$

where Δ_1 is obtained from the solution of the cubic equation

$$2\Delta_1^3 + 3\Delta_1^2 + \Delta_1 = W_1 \quad (II)$$

$$W_1 = k_rA/6(k_3[Fe^{2+}])^{3/2}\varphi D^{1/2} e_{H^+}{}^{3/2} \quad (III)$$

$$e_{H^+} = [H^+]/(k_{-3}/k_4) + [H^+]$$

using the values $A = 3 \times 10^{-8}$ mole sec.$^{-1}$, $D = 4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, $k_r = 10^{13}$ mole^{-1} cm.^{3} sec.$^{-1}$. The best parameters were chosen in the following way: at *p*H 0.4 it was assumed that $e_{H^+} \rightarrow 1$, and thus the equations reduce to those obtained for the single scavenger model. Hence $k_3\varphi^{2/3}$ could be evaluated. Then we selected the value of k_{-3}/k_4 which yields best agreement with the *p*H dependence. Satisfactory agreement was obtained by setting $k_3\varphi^{2/3} = 7.5 \times 10^6$ mole^{-1} liter sec.$^{-1}$ cm.$^{4/3}$ and $k_{-3}/k_4 = 0.05$ mole liter^{-1}. Next we analyzed the results according to the forced convection mechanism

$$Y = (k_3\varphi u e_{H^+}[Fe^{2+}]/k_r) \ln \{1 + (k_rA/k_3\varphi u e_{H^+}[Fe^{2+}])\} \quad (IV)$$

Best agreement was obtained by setting $k_3\varphi u = 1.5 \times 10^7$ mole^{-1} liter sec.$^{-1}$ cm.^{3} sec.$^{-1}$ and $k_{-3}/k_4 = 0.05$ mole liter^{-1}. Applying the homogeneous kinetic treatment

$$Y = (\tau e_{H^+}[Fe^{2+}]^2/V) \{\{1 + (2A/V\tau e_{H^+}[Fe^{2+}]^2)\}^{1/2} - 1\} \quad (V)$$

where $\tau = k^2_3/2k_r$. The experimental results could best be fitted with this equation by assuming $\tau = 0.005$ (*i.e.*, $k_3 \approx 10^4$ liter mole^{-1} sec.$^{-1}$) and $k_{-3}/k_4 = 0.05$.

The comparison of the calculated data with the experimental results is given in Table I. The agreement with the heterogeneous kinetic treatments is better than with the homogeneous kinetics. It is seen from these results and from Fig. 1B that the results are satisfactorily accounted for by

Table I

Oxidation Yield of Fe^{2+} Solutions at 4°

Dose of H atoms, 1.2×10^{-6} mole liter^{-1} sec.$^{-1}$; duration of run, 600 sec.; yields express the final Fe^{3+} concn. in units of 10^{-4} mole l.$^{-1}$; calculated yields, H = homogeneous, D = diffusion, C = forced convection kinetics assumed.

Fe^{2+} concn., *M*	H_2SO_4 0.8 *N*, *p*H 0.4				H_2SO_4 0.1 *N*					H_2SO_4 0.05 *N*					H_2SO_4 0.01 *N*					H_2SO_4 0.005 *N*				
	Yield					Yield					Yield					Yield					Yield			
	Exp.	H	D	C	*p*H	Exp.	H	D	C	*p*H	Exp.	H	D	C	*p*H	Exp.	H	D	C	*p*H	Exp.	H	D	C
0.2	6.7	7.00	6.95	7.00	1.64	6.40	6.75	6.50	6.50	1.96	5.50	6.40	6.05	5.95	2.70	2.70	3.65	3.25	3.40	2.96	1.90	2.10	2.25	2.5
.1	6.85	6.95	6.80	6.70	1.52	6.20	6.50	6.10	6.00	1.87	5.40	5.75	5.40	5.35	2.61	2.75	2.65	2.50	2.90	2.84	1.60	1.65	1.65	2.1
.05	6.30	6.70	6.15	6.15	1.47	6.03	5.80	5.25	5.15	1.75	3.75	4.85	4.40	4.40	2.47	2.24	1.80	1.90	2.35					
.02	5.0	5.35	4.90	5.00	1.40	4.8	3.80	3.70	3.85	1.65	3.20	2.85	2.95	3.30	2.35	2.40	1.05	1.25	1.65					
.01	3.8	3.70	3.85	3.70	1.35	3.3	2.55	2.65	2.95	1.60	2.55	1.95	2.05	2.45	2.25	1.90	0.60	0.75	1.05					
.005	2.55	2.20	2.45	2.65	1.34	2.3	1.55	1.65	2.00															
.001	1.04	0.60	0.70	1.05																				

the ferrous–hydride mechanism. The rate constant for reaction 3 can be estimated. The results of the homogeneous kinetics yield the value of k_3 10^4 mole^{-1} liter sec.$^{-1}$ which is a lower limit. Estimating the effective surface area as $\varphi \sim 10$ cm.^{2} the heterogeneous treatment leads to $k_3 \sim 10^5$ mole^{-1} liter sec.$^{-1}$. Considering the value of the ratio k_{-3}/k_4 obtained it should be pointed out that some dependence of this ratio on Fe^{2+} concentration was observed, the ratio decreasing with decreasing Fe^{2+}. Thus at 0.01 and 0.02 *M* Fe^{2+} the experimental results for the diffusion treatment were in better agreement with the value of $k_{-3}/k_4 = 0.02$. This may be due for example to the diffusion of intermediates which is neglected in our treatment. However our experimental results do not enable us to establish the value with greater accuracy.

Discussion

The oxidation mechanism of the Fe^{2+} ion proceeds by hydride formation. However when we attempt to analyze the results previously obtained[19] for the oxidation of iodide ions by H atoms according to this mechanism a satisfactory agreement cannot be obtained. Figure 2 indicates that at a constant oxidation yield the function $[I^-][H^+]/(\gamma + [H^+])$ is not constant while as it was previously demonstrated[11] the oxidation yield is a function of $[H^+][I^-]/(0.1 + [I^-])$. Thus it agrees with the oxidation mechanism involving H_2^+ as an intermediate. The oxidation mechanism proposed for the ferrous ion is in agreement with the *p*H dependence of the yield in radiation chemical and photochemical experiments. The region in which *p*H dependence is observed due to competition with recombination, will depend on the rate of introduction of H atoms. A reinvestigation of the photochemical oxidation of ferrous ions in evacuated acid solution showed[4] that up to *p*H 2.4 the *p*H dependence of the initial quantum yield was due to the *p*H dependence of the primary photochemical H atom formation only, in 0.02 *M* Fe^{2+} and rate of formation of H atoms = 3×10^{-7} mole liter^{-1} sec.$^{-1}$. In radiation chemical experiments[18,20] at 10^{-3} *M* Fe^{2+} and rate of formation of H atoms = 3×10^{-8} mole liter^{-1} sec.$^{-1}$ no *p*H dependence was observed up to *p*H 2.1. Treating these systems according to the steady-state approach of eq. V, it appears that the condition for the independence of *Y* of *p*H and $[Fe^{2+}]$ will prevail when

$$A/V \ll k_3{}^2 e_{H^+}{}^2 [Fe^{2+}]^2 / 4k_r \qquad (VI)$$

Setting $k_3 \cong 10^5$ mole^{-1} liter sec.$^{-1}$ and $k_{-3}/k_4 = 0.05$ the inequality VI is fulfilled both for the photochemical and radiation chemical experiments. This comparison is qualitative only, as it is not clear whether the assumption of initial homogeneous distribution of the radicals in radiation chemistry is adequate when competition between first- and second-order reactions occur.

In our treatment it was assumed that the recombination reaction r itself is *p*H independent. The possible reactions $FeH^{2+} + H$ and $H_2^+ + H$ are not included in the kinetic scheme. It is assumed[9] that since in these molecules the bond energies Fe^{2+}–H and H–H^+ have to be considered, these reactions will be activation controlled, and will be slower than the diffusion controlled reaction r.

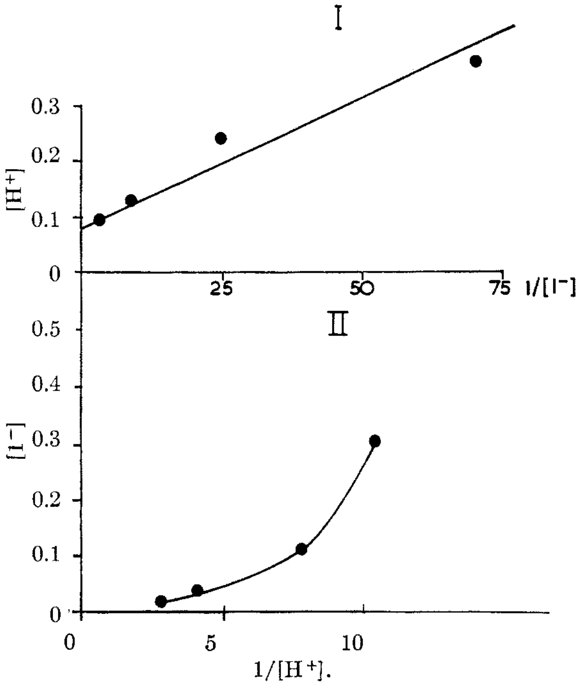

Fig. 2.—Plot of the experimental results of ref. 10 for the oxidation of I^- by H atoms: I, H_2^+ mechanism; II, hydride mechanism.

When the competitive reactions between Fe^{2+} ions on the one hand and other scavengers, *e.g.*, molecular O_2[18] or methanol[21] were investigated it was found that the ratio of the rate constants was nearly independent of *p*H within a rather wide *p*H range. Radiation chemical experiments[18] showed that $k_{H+O_2}/k_{H+Fe^{2+}}$ is 1200 at *p*H 0.35 and 1500 at *p*H 2.1. Photochemical experiments[4] gave for this ratio the value of 900 ± 300 at *p*H 0.35 and 1500 ± 400 at *p*H 2.4. According to the mechanism now proposed the competition is seen to be between the ferrous ion and the acceptor, O_2 or methanol, for H atoms, H^+ not being involved at this stage, since its reaction with H is slower. This will be the case as long as the dissociation reaction of the complex may be neglected in comparison with its reaction with H^+. The value of $k_{-3}/k_4 = 0.05$–0.02 mole liter^{-1} is consistent with the results of Baxendale and Hughes.[21] Similarly it can be shown[15] that the results of Dainton and Peterson[16] for the competition between Fe^{2+} and N_2O for H atoms leads to the value of $k_{-3}/k_4 = 0.05$, in excellent agreement with our experimental results. However in order to explain the results of Rothschild and Allen[18] k_{-3}/k_4 should be of the order of 0.01. Our photochemical experiments indicate that at *p*H values higher than 2.1 deviations already occur from constancy of the ratio of rate constants. These discrepancies may be due to specific reactions of the O_2 molecule with inter-

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(19) Correction of error. In ref. 10 the ordinate of Figs. 1, 2, 4, 5 and 6 has to be multiplied by a factor of 300.

(20) A. O. Allen and W. G. Rothschild, *Rad. Res.*, **7**, 591 (1957).

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mediates, and may be related to the nature of the H atom equivalent present in irradiated solutions. Thus the special case of O_2 remains to be fully explained and deserves more detailed investigation in the future.

The nature of the FeH^{2+} complex should be briefly considered. This may in all probability be a *ferric hydride* possibly consisting of a $Fe^{3+}H^-$ "charge transfer" complex in which a labile ion pair is formed. Similar intermediates were recently postulated in the homogeneous activation of H_2 in solution by some transition and post-transition cations.[22] For the negative iodide ion the formation of such an ion pair is unlikely.

The possibility of such hydride complex intermediates was also postulated by Krasna and Rittenberg[23] in the enzymatic activation of molecular hydrogen by the enzyme hydrogenase of *Proteus vulgaris*, and recently reinvestigated in the case of Desulfovibrio.[24] The enzyme is considered to contain iron.

The rate of exchange of solvent molecules from the hydration layer of some transition cations with the medium was shown from n.m.r. measurements[25] to be of the order of 10^5 liter mole^{-1} sec.$^{-1}$ for the reaction

$$H_2O + M^{n+} H_2O^* \longrightarrow H_2O^* + M^{n+} H_2O$$

which is of the same order of magnitude as the upper value for the rate of formation of the ferrous complex with H atoms derived in the present work.

According to the mechanism now proposed the oxidation of non-labile ferrous complexes, *e.g.*, ferrocyanide, will not occur by the hydride mechanism, but by the H_2^+ mechanism, in agreement with our previous results.[17]

Combining the value now obtained of $k_3 \sim 10^5$ liter mole^{-1} sec.$^{-1}$ for the rate of reaction of Fe^{2+} with H atoms, with the value of the ratio of the rate constants between H atoms and Fe^{2+} or O_2, respectively, gives an approximate value of $k_{H+O_2} \cong 10^8 - 10^9$ liter mole^{-1} sec.$^{-1}$, in reasonable agreement with the results of Riesz and Hart.[26] However in this respect one has to bear in mind the reservations regarding the possible specific reactions of O_2 with intermediates in irradiated solutions.

We thank Prof. J. Halpern for valuable comments. This investigation was supported by the Israel Atomic Energy Commission.

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THE ROLE OF HYDROGEN ATOMS IN THE DECOMPOSITION OF HYDROGEN PEROXIDE AND IN THE RADIATION CHEMISTRY OF WATER

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Atomic hydrogen generated by an electrodeless high frequency discharge in H_2 gas and introduced into aqueous solutions reacts with 10^{-4}–10^{-5} *M* H_2O_2 with a velocity constant of $k \cong 10^5$ liter mole^{-1} sec.$^{-1}$, unaffected by changing the *p*H from 1 to 13. The reactions involved are discussed and compared with those postulated for the radiolysis of aqueous H_2O_2 solutions.

In the radiolysis of dilute aqueous solutions electrons are one of the primary products. Electrons may react directly with suitable acceptors, or may form H atoms through reacting with water, with H_{aq}^+ or with H_2O^+.H atoms themselves may also result directly from, *e.g.*, the dissociation of excited water molecules or by dissociative electron capture by H_2O. The ratio e_{aq}/H may depend on the *p*H.

Once formed, H atoms may react with H_{aq}^+ to form H_{2aq}^+ ions. The ratio H/H_{2aq}^+ will depend on the *p*H.

In addition to these general considerations recently experimental evidence became available showing that two different forms of H atom equivalent are present in irradiated solutions, these two exhibiting widely different reactivity with specific acceptors. Thus Barr and Allen[1] have recently obtained evidence that the two forms show very different velocity constants with H_2O_2. The possible pairs considered were e_{aq} and H or alternatively H and H_2^+. No decision was made between the two alternatives.

Allan and Scholes[2] investigating the reactions in irradiated aqueous solutions of some organic acceptors, came to similar conclusions, but identified the pair of reactants as the electron in water and H atoms. The considerations of Weiss[3] point in the same direction.

To differentiate between the two possibilities and provide evidence for the identification of the species involved in the radiolysis of water, we investigated the rate of reaction of atomic hydrogen with H_2O_2 in dilute aqueous solution.

Experimental

Atomic hydrogen was produced as described before,[4] by an electrodeless high frequency discharge at 30 Mc. in

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[1] N. F. Barr and A. O. Allen, *J. Phys. Chem.*, **63**, 928 (1959). See also A. O. Allen and H. A. Schwarz, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, **29**, 30 (1958).

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[3] E. Hayon and J. Weiss, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, **29**, 80 (1958); J. Weiss, *Nature*, **186**, 751 (1960).

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