

mediates, and may be related to the nature of the H atom equivalent present in irradiated solutions. Thus the special case of O<sub>2</sub> remains to be fully explained and deserves more detailed investigation in the future.

The nature of the FeH<sup>2+</sup> complex should be briefly considered. This may in all probability be a *ferric hydride* possibly consisting of a Fe<sup>3+</sup>H<sup>-</sup> "charge transfer" complex in which a labile ion pair is formed. Similar intermediates were recently postulated in the homogeneous activation of H<sub>2</sub> in solution by some transition and post-transition cations.<sup>22</sup> 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<sup>23</sup> in the enzymatic activation of molecular hydrogen by the enzyme hydrogenase of *Proteus vulgaris*, and recently reinvestigated in the case of *Desulfovibrio*.<sup>24</sup> The enzyme is considered to contain iron.

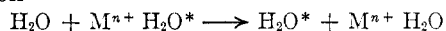
The rate of exchange of solvent molecules from the hydration layer of some transition cations with

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the medium was shown from n.m.r. measurements<sup>25</sup> to be of the order of 10<sup>5</sup> liter mole<sup>-1</sup> sec.<sup>-1</sup> for the reaction



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<sub>2</sub><sup>+</sup> mechanism, in agreement with our previous results.<sup>17</sup>

Combining the value now obtained of  $k_3 \sim 10^5$  liter mole<sup>-1</sup> sec.<sup>-1</sup> for the rate of reaction of Fe<sup>2+</sup> with H atoms, with the value of the ratio of the rate constants between H atoms and Fe<sup>2+</sup> or O<sub>2</sub>, respectively, gives an approximate value of  $k_{\text{H}+\text{O}_2} \cong 10^3 - 10^9$  liter mole<sup>-1</sup> sec.<sup>-1</sup>, in reasonable agreement with the results of Riesz and Hart.<sup>26</sup> However in this respect one has to bear in mind the reservations regarding the possible specific reactions of O<sub>2</sub> 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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(26) P. Riesz and E. J. Hart, *J. Phys. Chem.*, **63**, 859 (1959).

## 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<sub>2</sub> gas and introduced into aqueous solutions reacts with 10<sup>-4</sup>–10<sup>-5</sup> M H<sub>2</sub>O<sub>2</sub> with a velocity constant of  $k \cong 10^6$  liter mole<sup>-1</sup> sec.<sup>-1</sup>, unaffected by changing the pH from 1 to 13. The reactions involved are discussed and compared with those postulated for the radiolysis of aqueous H<sub>2</sub>O<sub>2</sub> 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<sub>aq</sub><sup>+</sup> or with H<sub>2</sub>O<sup>+</sup>. H atoms themselves may also result directly from, *e.g.*, the dissociation of excited water molecules or by dissociative electron capture by H<sub>2</sub>O. The ratio e<sub>aq</sub>/H may depend on the pH.

Once formed, H atoms may react with H<sub>aq</sub><sup>+</sup> to form H<sub>2aq</sub><sup>+</sup> ions. The ratio H/H<sub>2aq</sub><sup>+</sup> will depend on the pH.

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<sup>1</sup> have recently obtained evidence that the two forms show very

different velocity constants with H<sub>2</sub>O<sub>2</sub>. The possible pairs considered were e<sub>aq</sub> and H or alternatively H and H<sub>2</sub><sup>+</sup>. No decision was made between the two alternatives.

Allan and Scholes<sup>2</sup> 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<sup>3</sup> 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<sub>2</sub>O<sub>2</sub> in dilute aqueous solution.

### Experimental

Atomic hydrogen was produced as described before,<sup>4</sup> by an electrodeless high frequency discharge at 30 Mc. in

(1) J. T. 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**, 80 (1958); *J. Weiss, Nature*, **186**, 751 (1960).

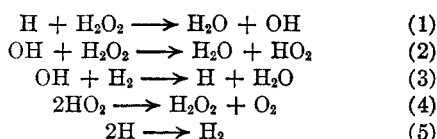
(2) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

(3) G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959).

H<sub>2</sub> gas at 30 mm. pressure. The dose rate in the present series of experiments was  $A = 2 \times 10^{-7}$  mole liter<sup>-1</sup>sec.<sup>-1</sup> determined by the ferricyanide dosimeter.<sup>5</sup> The gas was pumped through the solution at a velocity of 150 liter min.<sup>-1</sup>, producing a very vigorous bubbling and stirring. Experiments were carried out at about 4°. Blank experiments were carried out by passing H<sub>2</sub> through the solution without discharge. In the absence of H atoms no decomposition was observed. Initial and final H<sub>2</sub>O<sub>2</sub> concentrations were determined iodometrically at the higher concentrations, and below [H<sub>2</sub>O<sub>2</sub>] = 10<sup>-5</sup> M by the oxidation of FeSO<sub>4</sub>. Water was triply distilled. H<sub>2</sub>O<sub>2</sub> was Hopkin and Williams' Analar.

### Results and Discussion

In neutral solutions, at pH~6, the decomposition was investigated at several concentrations of H<sub>2</sub>O<sub>2</sub>. The results are shown in Table I. We assume the mechanism



Our solutions were saturated with H<sub>2</sub> gas at 30 mm. pressure. Assuming that the solubility of H<sub>2</sub> is  $0.8 \times 10^{-3}$  M per atmosphere, the H<sub>2</sub> concentration in the solution is  $3 \times 10^{-5}$  M. The rate constants  $k_2$  and  $k_3$  are about equal.<sup>1</sup> We shall neglect reaction 2 compared with reaction 3 for H<sub>2</sub>O<sub>2</sub> concentrations of 10<sup>-5</sup> M or lower. We shall also disregard the radical recombinations H + OH and OH + OH. Under these simplifying conditions, assuming homogeneous kinetics (the justification for which was discussed separately<sup>6</sup> and is considered again in the Appendix) steady-state treatment gives

$$-d[\text{H}_2\text{O}_2]/dt = [\text{H}_2\text{O}_2]k_1A^{1/2}/k_5^{1/2} \quad (6)$$

Setting<sup>7</sup>  $k_5 = 10^{10}$  liter mole<sup>-1</sup>sec.<sup>-1</sup>, the values of  $k_1$  shown in Table I are obtained. Of the significance of these values it may be said that as the concentration of H<sub>2</sub>O<sub>2</sub> increases to 10<sup>-4</sup> M or higher, reaction 2 may no longer be neglected; as the concentration increases further, the chain decomposition of H<sub>2</sub>O<sub>2</sub>, negligible below  $5 \times 10^{-5}$  M becomes of increasing importance. On the other hand at concentrations of 10<sup>-5</sup> M and lower, the determination of H<sub>2</sub>O<sub>2</sub> becomes less accurate. We thus conclude that from these experiments  $k_1 = 1 \times 10^6$  liter mole<sup>-1</sup>sec.<sup>-1</sup>. This value should be compared with that of  $k_1$  in the gas phase, which is of the order of 10<sup>6</sup> liter mole<sup>-1</sup>sec.<sup>-1</sup>.<sup>8</sup>

To investigate the pH dependence of  $k_1$  the experiments shown in Table II were carried out in approximately 10<sup>-4</sup> M H<sub>2</sub>O<sub>2</sub>, where analytical accuracy is good. The results show that from pH~1 to ~13 the decomposition yield is approximately independent of pH. As to the absolute value of  $k_1$  these experiments at about 10<sup>-4</sup> M H<sub>2</sub>O<sub>2</sub> probably give a slightly too low value for the reasons discussed above.

The rate constant for the reaction of H atoms with O<sub>2</sub> was recently found<sup>9</sup> to be 10<sup>8</sup> to 10<sup>9</sup> liter

TABLE I  
DECOMPOSITION OF UNBUFFERED H<sub>2</sub>O<sub>2</sub> SOLUTIONS BY ATOMIC HYDROGEN AT 4°

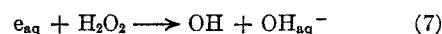
[H <sub>2</sub> O <sub>2</sub> ]initial, mole l. <sup>-1</sup>	[H <sub>2</sub> O <sub>2</sub> ]final, mole l. <sup>-1</sup>	ΔC, mole l. <sup>-1</sup>	ΔC/ [H <sub>2</sub> O <sub>2</sub> ] mean	k <sub>1</sub> , 10 <sup>4</sup> l. mole <sup>-1</sup> sec. <sup>-1</sup>
	6.15 × 10 <sup>-6</sup>			
7.02 × 10 <sup>-6</sup>	5.85 × 10 <sup>-6</sup>	1.02 × 10 <sup>-6</sup>	0.16	6.0
	0.78 × 10 <sup>-5</sup>			
1.01 × 10 <sup>-5</sup>	0.67 × 10 <sup>-5</sup>	0.26 × 10 <sup>-5</sup>	.29	10.5
	0.78 × 10 <sup>-5</sup>			
	3.30 × 10 <sup>-5</sup>			
4.04 × 10 <sup>-5</sup>	3.26 × 10 <sup>-5</sup>	0.81 × 10 <sup>-5</sup>	.23	8.4
	3.21 × 10 <sup>-5</sup>			
	0.815 × 10 <sup>-4</sup>			
1.00 × 10 <sup>-4</sup>	0.860 × 10 <sup>-4</sup>	0.15 × 10 <sup>-4</sup>	.16	6.0
	0.865 × 10 <sup>-4</sup>			

mole<sup>-1</sup> sec.<sup>-1</sup>. By an independent method we reached<sup>6</sup> a similar result. Barr and Allen<sup>1</sup> have shown that one of the species in which the hydrogen atom equivalent appears in irradiated solutions reacts with H<sub>2</sub>O<sub>2</sub> at a rate comparable to that with which it reacts with O<sub>2</sub>. The other form, obtainable also by the reaction of OH radicals with molecular H<sub>2</sub>, reacts with O<sub>2</sub> so much faster than with H<sub>2</sub>O<sub>2</sub>, that added H<sub>2</sub>O<sub>2</sub> is not an efficient scavenger for it in the presence of O<sub>2</sub>.

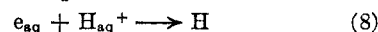
Our results are entirely consistent with the assumption that this species, reacting relatively slowly with H<sub>2</sub>O<sub>2</sub>, is the H atom, as  $k_1$  is found to be some 10<sup>8</sup> times lower than  $k_{\text{H} + \text{O}_2}$ .

This conclusion agrees also with the finding of Bunn, *et al.*,<sup>10</sup> that reaction 3 leads to the formation of atomic hydrogen and does not proceed by charge transfer.

We conclude therefore that the pair of reactive entities under the conditions of irradiation discussed by Barr and Allen<sup>1</sup> is e<sub>aq</sub> and atomic H. We thus agree with the conclusions of Allan and Scholes.<sup>2</sup> We consider that the fast radiation-induced decomposition process of H<sub>2</sub>O<sub>2</sub> in neutral solutions is



In acid solution the process



will proceed efficiently. On the other hand the formation of H<sub>2aq</sub><sup>+</sup> from H and H<sub>aq</sub><sup>+</sup> is a relatively slow process<sup>11</sup> with  $k_{\text{H} + \text{H}^+} \sim 10^3$  liter mole<sup>-1</sup>sec.<sup>-1</sup>. We thus conclude that the acid form of the primary radiation product, electron in water, is the H atom as such. These results are consistent with the sequence  $e_{\text{aq}} \xrightarrow{\text{H}^+} \text{H} \xrightarrow{\text{H}^+} \text{H}_{2\text{aq}}^+$ , as the pH decreases. H<sub>2aq</sub><sup>+</sup> will become kinetically important at low pH values only in systems where no other acceptor can directly and rapidly react with e<sub>aq</sub> or H atoms by other pathways. Recently additional experimental evidence has been accumulating regarding specific reactions of electrons with suitable acceptors in the radiolysis of water.

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TABLE II  
THE pH DEPENDENCE OF THE DECOMPOSITION OF H<sub>2</sub>O<sub>2</sub> SOLUTIONS

Soln.	pH approx.	[H <sub>2</sub> O <sub>2</sub> ]initial, mole l. <sup>-1</sup>	[H <sub>2</sub> O <sub>2</sub> ]final, mole l. <sup>-1</sup>	$\frac{\Delta C}{\text{mole l.}^{-1}}$	$\frac{\Delta C}{[\text{H}_2\text{O}_2]_{\text{mean}}}$
H <sub>2</sub> SO <sub>4</sub> 0.16 N	1	1.12 × 10 <sup>-4</sup>	0.950 × 10 <sup>-4</sup>	0.18 × 10 <sup>-4</sup>	0.18
No addition	6	1.00 × 10 <sup>-4</sup>	.934 × 10 <sup>-4</sup>	.15 × 10 <sup>-4</sup>	.16
NaOH 4 × 10 <sup>-4</sup> N	10	0.99 × 10 <sup>-4</sup>	.85 × 10 <sup>-4</sup>	.135 × 10 <sup>-4</sup>	.15
			.52 × 10 <sup>-4</sup>		
NaOH 0.1 N	13	0.63 × 10 <sup>-4</sup>	.57 × 10 <sup>-4</sup>	.85 × 10 <sup>-6</sup>	.14

These data include the increased hydrogen yields in aqueous monochloroacetic acid<sup>3</sup> and aqueous methanol<sup>12</sup> at low pH, the pH dependence of the ratio of the reduction of Cu<sup>2+</sup> and formic acid,<sup>12,13</sup> and the relative stability of H<sub>2</sub>O<sub>2</sub> in acid solution under irradiation.<sup>14</sup> Similar to the case of H<sub>2</sub>O<sub>2</sub> in acid solution is that of N<sub>2</sub>O<sup>15</sup> where Dainton and Peterson attributed the sharp drop in decomposition at lower pH values to the formation of the acid form of H atoms. The analysis of their results<sup>16</sup> shows that the reaction of H atoms as such with N<sub>2</sub>O is a relatively slow process, with a rate constant of the order of 10<sup>3</sup>-10<sup>4</sup> liter mole<sup>-1</sup> sec.<sup>-1</sup>. It may be concluded accordingly that the precursor of atomic hydrogen in irradiated neutral solutions is the electron in water, while the acid form is the H atom as such.

The present work provides also good support for the considerations<sup>5</sup> regarding the absolute value of the rate constants obtained by the present method. The value of  $k_1 = 10^6$  liter mole<sup>-1</sup> sec.<sup>-1</sup> was obtained by the application of homogeneous kinetics. It was shown<sup>6</sup> by comparison with heterogeneous kinetics that under our experimental conditions rate constants derived from homogeneous kinetics are lower by probably not more than one order of magnitude than the true one, and may possibly closely correspond to it. We see that in the present case not only does the value of  $k_1$  thus obtained agree well with the results of radiation chemistry, but is consistent with the value of  $k_1$  obtained from gas phase experiments.

### Appendix

In this paper homogeneous steady-state kinetics were applied. It is interesting to compare the results with those obtained by applying mass transport controlled kinetic processes. This problem was discussed in detail.<sup>6</sup> In the present case for

purely diffusion controlled conditions the homogeneous steady-state equations should be replaced by

$$D_H \partial^2 [\text{H}] / \partial X^2 = k_1 [\text{H}] [\text{H}_2\text{O}_2] - k_2 [\text{OH}] [\text{H}_2] + \frac{k_5 [\text{H}]^2}{k_6 [\text{H}]^2} \quad (1a)$$

$$D_{OH} \partial^2 [\text{OH}] / \partial X^2 = k_2 [\text{OH}] [\text{H}_2] - k_1 [\text{H}] [\text{H}_2\text{O}_2] \quad (2a)$$

where  $D_H$  and  $D_{OH}$  are the diffusion coefficients of H and of OH. As  $D_H > D_{OH}$  and  $[\text{H}] > [\text{OH}]$ , the diffusion of the OH radical is neglected and we set  $D_{OH} \partial^2 [\text{OH}] / \partial X^2 = 0$ . Hence we obtain

$$D_H \partial^2 [\text{H}] / \partial X^2 = k_5 [\text{H}]^2 \quad (3a)$$

The solution of this equation is subject to the boundary conditions  $[\text{H}] \rightarrow 0$  and  $\partial [\text{H}] / \partial X \rightarrow 0$  when  $X \rightarrow \infty$ , and to the relation

$$D_H \int \partial^2 [\text{H}] / \partial X^2 dV = A^* \quad (4a)$$

where  $V$  is the total volume of the system and  $A^*$  is the total dose rate in mole sec.<sup>-1</sup>. The decomposition yield of H<sub>2</sub>O<sub>2</sub> is obtained in the form

$$d[\text{H}_2\text{O}_2] / dt = k_1 [\text{H}_2\text{O}_2] / V \int [\text{H}] dV \quad (5a)$$

The solution of equation 3a is given by<sup>6</sup>

$$H = 1 / \{ \varphi^{2/3} (2k_r D_H / 3A^*)^{1/3} + (k_r / D_H)^{1/2} X \}^2 \quad (6a)$$

where  $\varphi$  is the effective mean surface for the diffusion process estimated<sup>6</sup> as of the order of 10 cm.<sup>2</sup>. The decomposition yield is

$$d[\text{H}_2\text{O}_2] / dt = (k_1 [\text{H}_2\text{O}_2] \varphi^{2/3} / V) (18 D_H A^* / k_r^2)^{1/3} \quad (7a)$$

Setting  $D_H = 4 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>,  $A^* = 5 \times 10^{-9}$  mole sec.<sup>-1</sup>,  $V = 25$  cm.<sup>3</sup>,  $k_r = 10^{13}$  cm.<sup>3</sup> mole<sup>-1</sup> sec.<sup>-1</sup> and by using the data of Table I we get  $k_1 \varphi^{2/3} = 2 \times 10^7$  liter mole<sup>-1</sup> sec.<sup>-1</sup> cm.<sup>4/3</sup> and thus  $k_1$  is of the order of 10<sup>6</sup> liter mole<sup>-1</sup> sec.<sup>-1</sup>.

We thus see that the homogeneous kinetic treatment gave a lower limit of  $k_1$ , while as discussed previously, the purely diffusion controlled treatment leads to an upper value for  $k_1$ . In the actual forced convection situation of our experiments the employment of homogeneous kinetic will probably yield a value for the rate constant which is in agreement with the true value to better than one order of magnitude.

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