Hydrogen Evolving Systems. 1. The Formation of H_2 from Aqueous Suspensions of $Fe(OH)_2$ and Reactions with Reducible Substrates, Including Molecular Nitrogen[1]

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Abstract: The evolution of hydrogen from mildly alkaline suspensions of $Fe(OH)_2$ appears to involve elemental iron as the intermediate, which is generated by way of a base-induced disproportionation of $Fe(OH)_2$. The disproportionation reaction also occurs in strongly alkaline suspensions of $Fe(OH)_2$; under these conditions H_2 is not formed and elemental iron accumulates in the precipitates instead. Disordered modifications of $Fe(OH)_2$ seem to exist which undergo disproportionation preferentially. The reactive modifications of $Fe(OH)_2$ are formed in higher relative concentrations or are stabilized by weak complexing or dispersing agents such as sugars and polyhydric alcohols, as well as to some extent by $Mg(OH)_2$ or glycine. The disproportionation of $Fe(OH)_2$ is significantly stimulated by ultraviolet light, as evidenced by the increased yields of H_2 in uv-light exposed samples. The evolution of H_2 is also stimulated by coprecipitation of $Fe(OH)_2$ with $Ni(OH)_2$. A variety of reducible substrates, e.g., C_2H_2, C_2H_4, CO, and N_2, act as inhibitors of H_2 formation. Reduction of these substrates occurs in a manner typical of reactions with highly dispersed elemental iron. With molecular nitrogen, hydrazine and ammonia are formed; both products were identified by specific colorimetric tests as well as by using $^{30}N_2$-enriched nitrogen as the substrate and subsequent mass-spectrographic analysis.

In attempts to develop functional H_2-evolving systems that might qualify as models of hydrogenase action, we decided to reinvestigate a reaction which was first described by Schikorr[2], who showed that aqueous suspensions of $Fe(OH)_2$ decompose under certain conditions into H_2 and Fe_3O_4 according to the idealized stoichiometry in eq 1:

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \qquad (1)$$

Reaction eq 1 is thermodynamically favored ($\Delta G^{298°} = -9.9$ kcal)[3] but appears to be inhibited at room temperature and has numerous complicating features. Hydrogen is evolved only over a narrow pH range and/or in the presence of certain promoters such as metallic iron, added metal ions such as Ni^{2+} or Pt^{2+}, colloidal Pt, copper powder, or Na_2S.[3,4] Pure $Fe(OH)_2$ has been shown by several investigators to be stable from room temperature up to about 100 °C.[3-5] Between 100 and 300 °C, $Fe(OH)_2$ decomposes into Fe_3O_4 and H_2, but the magnetite produced under these conditions contains elemental iron,[3] which suggests the occurrence of a simultaneous disproportionation according to eq 2:

$$4Fe(OH)_2 \rightarrow Fe + Fe_3O_4 + 4H_2O \ (G^{298°} = -7.7 \text{ kcal}) \qquad (2)$$

During the thermolysis, $Fe(OH)_2$ is dehydrated to FeO or $Fe_{0.95}O$, respectively, whose disproportionation into magnetite and elemental iron has also been demonstrated[6] (eq 3):

$$4FeO \rightarrow Fe_3O_4 + Fe \qquad (3)$$

In aqueous suspensions at room temperature, only about 16% of the theoretical amount of H_2 according to eq 1 is generated from $Fe(OH)_2$.[3] The mechanism of H_2 evolution is unknown. It has recently been proposed that oligomeric aggregates of $Fe(OH)_2$ exist in which the Fe^{2+} ions are arranged in a structure favoring the formation of the Fe_3O_4 lattice. These aggregates of $Fe(OH)_2$ were considered to be sufficiently reactive to attack water to yield atomic hydrogen, whose recombination to H_2 requires the presence of an acceptor such as platinum or nickel.[7] Although we consider the latter suggestion as unlikely, the existence of reactive oligomers or of disordered aggregates in precipitated $Fe(OH)_2$ seems plausible. Since the evolution of H_2 from $Fe(OH)_2$ suspensions is slow, it occurred to us that the lifetime of the reactive-$Fe(OH)_2$ modifications might be short and that the simultaneous conversion of $Fe(OH)_2$ into the unreactive crystalline form competes with the H_2-producing reaction. In order to stabilize the reactive forms of $Fe(OH)_2$, we therefore precipitated $Fe(OH)_2$ from solutions of ferrous salts in the presence of sugars, polyhydric alcohols, and other complexing or dispersing agents. This provided us with systems which produce more H_2 than pure $Fe(OH)_2$. In addition, the rates of H_2 evolution became conveniently measurable at room temperature even in the absence of added metallic promoters or cocatalysts. In the following we describe the results of studies of reactive $Fe(OH)_2$ suspensions which led to the identification of the species responsible for H_2 evolution, and to other interesting observations in these systems.

Results

Hydrogen Evolution from $Fe(OH)_2$ and the Effect of Additives. Hydrogen evolution from $Fe(OH)_2$ in aqueous suspensions was observed within the pH range 8-10 only, reaching a maximum at 8.6 (Figure 1), if NaOH is used to adjust the pH; no H_2 was evolved from borate-buffered solutions. If the $Fe(OH)_2$ is precipitated in the presence of glucose, fructose, sucrose, or glycerol, an up to sixfold stimulation of H_2 evolution was observed. Ethylene glycol and glycine had weaker stimulatory effects. None of the additives changed the pH dependence of H_2 evolution substantially. Coprecipitation of $Fe(OH)_2$ with $Mg(OH)_2$ also caused some stimulation, but $Al(OH)_3$, $Be(OH)_2$, and $Mn(OH)_2$ did not, or proved inhibitory. The results of typical experiments under near optimal conditions are summarized in Table I. It may be seen that the H_2 evolution is also temperature dependent: In the presence of glucose as the complexing or dispersing agent, maximum amounts of hydrogen are generated at 50°, only traces at 86°, and none at 100°. The stimulation of H_2 production by the complexing or dispersing agents is observed only if they are present during the precipitation of $Fe(OH)_2$. If $Fe(OH)_2$ is precipitated from aqueous solutions of $FeSO_4$ prior to the addition of glucose or glycerol, for example, the evolution of H_2 is not markedly accelerated. The formation of H_2 from $Fe(OH)_2$ at room temperature requires approximately 12 h for completion. The yields of H_2 cannot be increased further if the temperature is later raised to 50°. During the reaction in the optimal pH range the originally white suspensions of $Fe(OH)_2$ turn dark green due to the simultaneous conversion of ferrous hydroxide into mixed Fe^{2+}, Fe^{3+} hydroxides or

Table I. Temperature Dependence and Effect of Additives on H_2 Evolution from $Fe(OH)_2$

No.	Additives/conditions[a]	Temp, °C	Max yields of H_2 (μmol/100 μmol of Fe)[b]
1	None	26	1.6
2	None	50	1.8
3	None	68	1.6
4	Glucose, 10%	0	6.0
5	Glucose, 10%	10	7.5
6	Glucose, 10%	25	9.0
7	Glucose, 10%	50	10.0
8	Glucose, 10%	68	7.2
9	Glucose, 10%	86	1.0
10	Glucose, 10%	100	0.2
11	Glycerol, 20%	26	10.5
12	Sucrose, 5%	26	8.7
13	Fructose, 10%	26	9.0
14	Ethylene glycol, 20%	26	2.0
15	Glycine, 2%	26	1.9
16	$Mg(OH)_2$ (Fe:Mg = 1:2)	26	2.6
17	$Al(OH)_3$ (Fe:Al = 1:2)	26	0.4
18	$Be(OH)_2$ (Fe:Be = 1:2)	26	0.2
19	$Ni(OH)_2$ (Fe:Ni = 2:1)	26	14.5
20	$Ni(OH)_2$ (Fe:Ni = 2.1), glucose, 10%	26	25.0
21	$Mn(OH)_2$ (Fe:Mn = 2:1)	26	0

[a] All reaction solutions contained 100 μmol of $Fe(OH)_2$ in a total volume of 5.0 ml. Experiments were carried out in glass bottles of 38 ml total volume. The concentrations of the additives were varied to determine the optimal concentrations, the initial pH of the reaction suspensions was 8.6, differences between initial and final pH were small. [b] After 18 h of reaction under 1 atm of pure argon. Yields of H_2 were determined by gas-chromatographic analysis of the gas phase; measurement accuracy was ±5%.

aquated oxides. The same precipitates are formed immediately if base is added to mixed solutions of Fe^{2+} and Fe^{3+} salts, under these conditions no H_2 is evolved.

Table I also contains the results of experiments in which $Fe(OH)_2$ was coprecipitated with $Ni(OH)_2$, both in the presence and absence of glucose. In the presence of glucose, up to 25 μmol of H_2 is generated per 100 μmol of $Fe(OH)_2$ in the Ni–Fe systems and the rate of H_2 evolution is significantly higher than in the absence of nickel. Only about half as much H_2 is generated from suspensions of Ni^{2+}–Fe^{2+} hydroxides in the absence of added glucose. The coprecipitation of $Fe(OH)_2$ with the hydroxides of Mg^{2+}, Al^{3+}, Be^{2+}, and Mn^{2+} caused a significant drop of H_2 evolution. These results are in qualitative accord with those of previous investigators[3] who, in addition, also observed an inhibitory effect of silica. The inhibitory effect of borate buffer may be related to that of silica and is attributed to the formation of colloidal isopolybases. We also confirmed that no H_2 is formed in the supernatant solutions of precipitated $Fe(OH)_2$. The yields of H_2 are somewhat dependent on the Fe^{2+} salt from which $Fe(OH)_2$ is generated. With ferrous sulfate, $FeSO_4 \cdot 7H_2O$, as the source of $Fe(OH)_2$ somewhat less H_2 is formed than if ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, is employed. Commercial samples of the latter are as a rule less contaminated by ferric iron than the former, a fact which is considered to be mainly responsible for the differences in H_2 yields. Contaminations by other metals were low and thus could not have influenced our observations.

Stimulation of H_2 Production by Ultraviolet Light. The rate of H_2 production from $Fe(OH)_2$ is substantially accelerated on irradiation with uv light emitted from a mercury vapor lamp. Light of wavelength between 330 and 300 nm is the most effective and acts primarily during the initial phases of the reaction. The accelerating effect of uv light is observed in both the absence and the presence of the dispersing or complexing agents. In the $Fe(OH)_2$–$Ni(OH)_2$ systems light stimulation was also observed, but the effect was small and the overall yield of H_2 generated was the same as in the dark reaction (Figure 2). Additional data on the light effect in these and other systems are given in Table II.

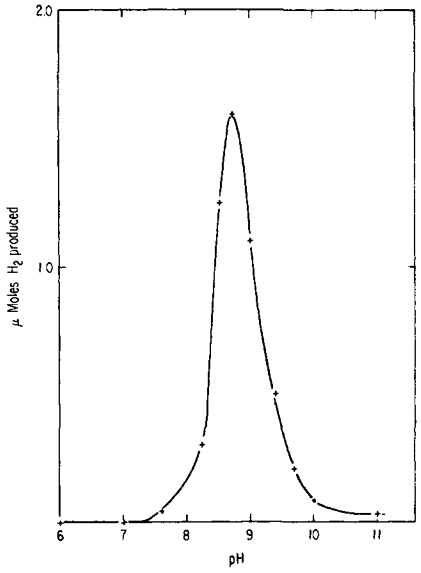


Figure 1. Evolution of H_2 from $Fe(OH)_2$ at 26° as a function of initial pH. Reactions were performed with 100 μmol of $Fe(OH)_2$ generated from $Fe(NH_4)_2SO_4$ by addition of NaOH. Yield measurements were after 18 h of reaction. Experimental conditions are given in footnote *a* in Table I.

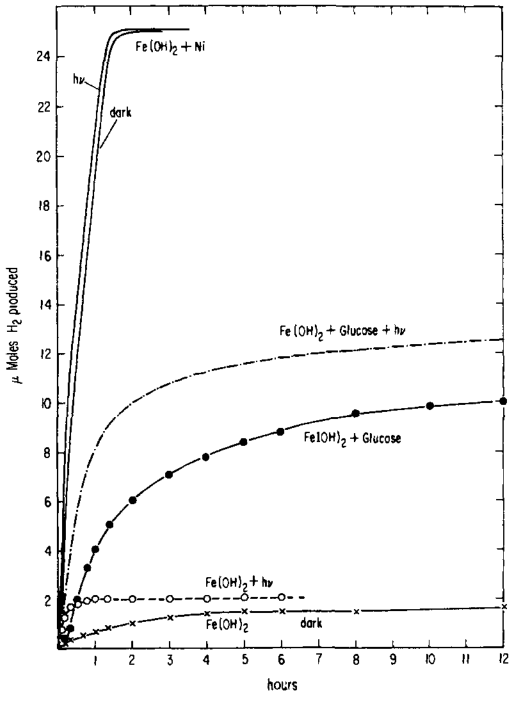


Figure 2. Time dependence of H_2 evolution from $Fe(OH)_2$ under various conditions. Initial concentration of $Fe(OH)_2$ = 100 μmol in a total reaction volume of 5.0 ml; pH of supernatant solution was 8.6 (adjusted by addition of NaOH), reaction temperature, 29°.

Identification of Metallic Iron as the Reactive Species. If $Fe(OH)_2$ is precipitated with excess NaOH under strictly anaerobic conditions under argon, the originally white gels also turn blue-green on standing and more rapidly on exposure to

Table II. Effect of Ultraviolet Light on the Yield of H_2 Produced from $Fe(OH)_2$ under Various Conditions at 29°, after 18 h[a]

No.	Additives/conditions	H_2 (max), μmol/ 100 μmol of $Fe(OH)_2$ Dark	Light
1	None	1.6	2.0
2	Glucose, 10%	10.2	13.5
3	Sucrose, 5%	9.0	11.6
4	Glycerol, 20%	10.5	15.0
5	Ethylene glycol, 20%	2.0	3.1
6	$Mg(OH)_2$ (Fe:Mg = 1:2)	2.6	5.7
7	Glycine, 2%	1.9	2.8
8	$Ni(OH)_2$ (Fe:Ni = 2:1)	25.0	25.1

[a] In the light-experiments, reaction flasks were irradiated with a Blak-Ray Model 100A long-wave uv light source (225 W), at a distance of 20 cm. The dark-experiments were performed as simultaneous controls at the same temperature.

Table III. Hydrogen Evolution from Precipitates of $Fe(OH)_2$ at pH 8.6, in the Dark or on Uv Irradiation, before and after Acidification. Experimental Conditions as in Experiment No. 6, Table I

		H_2 (μmol) before (after) acidification		Total	
No.	Time before acidification, min	Dark	Light	Dark	Light
1	0	0 (0)	0 (0)	0	0
2	10	0.50 (0.55)	0.75 (0.59)	1.05	1.34
3	20	0.72 (1.25)	1.19 (1.35)	1.97	2.54
4	30	1.45 (1.50)	2.00 (2.10)	2.95	4.10
5	40	1.94 (1.80)	2.96 (2.95)	3.94	5.91
6	60	2.85 (1.50)	7.00 (1.50)	4.35	8.50
7	180	6.20 (0.50)	12.50 (0.50)	6.70	13.00
8	1080	9.20 (0.10)	13.50 (0.00)	9.30	13.50

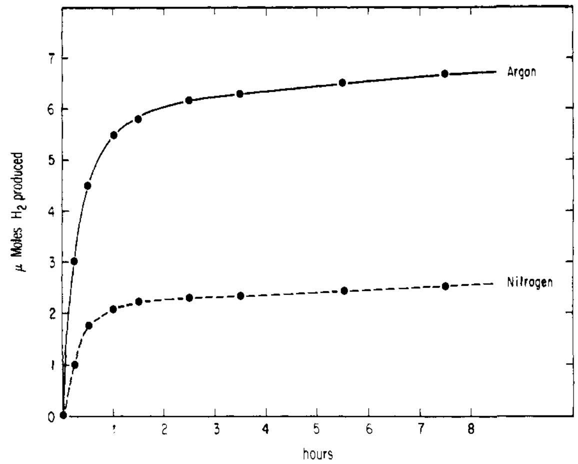


Figure 3. Inhibition of H_2 evolution from $Fe(OH)_2$ suspensions in 10% aqueous glucose by N_2 at 1 atm: reaction temperature, 26°; initial concentration of $Fe(OH)_2$, 100 μmol. The $Fe(OH)_2$ was generated from $FeSO_4$.

uv light than in the dark, *but virtually no H_2 is formed* under these conditions. These precipitates yield the expected amount of H_2 (10-12 μmol per 100 μmol of $Fe(OH)_2$) upon acidification, however. This important result suggests that $Fe(OH)_2$ disproportionates into *elemental iron* and mixed Fe^{2+}-Fe^{3+} hydroxides, since neither white $Fe(OH)_2$ nor Fe_3O_4 or other mixed Fe^{2+}-Fe^{3+} hydroxides or aquated iron oxides yield H_2 on acidification. Evidently, 5-6 μmol of Fe^0 are formed per 100 μmol of $Fe(OH)_2$ during the base-induced disproportionation. The results in Table III indicate that elemental iron (or a species with the reactivity of elemental iron) accumulates in the iron hydroxide precipitates even at pH 8.6 and that the base-induced disproportionation of $Fe(OH)_2$ and not the subsequent H_2 evolution is accelerated by uv light.

The largest amounts of Fe^0 accumulate in the precipitates during the first 40 min of reaction. After 18 h, almost all of the Fe^0 is consumed, although magnetic measurements in such precipitates still revealed the presence of traces of ferromagnetic species, corresponding to about 0.5 mol % Fe^0. Even though this result is not necessarily conclusive in view of the possible presence of other ferromagnetic species (Fe_3O_4), the Fe^0 containing precipitates were invariably noted to be far more oxygen sensitive than Fe^{2+}-Fe^{3+} hydroxides prepared by the addition of base to solutions of ferrous and ferric salts, a fact which is best attributed to the presence of elemental iron.

Reactions with Reducible Substrates. The elemental iron generated by the base-induced disproportionation of $Fe(OH)_2$ should be highly dispersed if not atomic and hence was expected to react with a variety of reducible substrates. Whereas freshly precipitated, white $Fe(OH)_2$ does not react with acetylene, the subsequent evolution of H_2 is suppressed and C_2H_4, C_2H_6, and traces of CH_4 are produced in the ratio of 1:0.085:0.018. Ethylene also inhibits H_2 evolution and is reduced to C_2H_6 and CH_4. A slow reduction of CO to CH_4 was observed as well (Table IV). The addition of methyl iodide to freshly precipitated $Fe(OH)_2$ also inhibits H_2 evolution and gives rise to the formation of a mixture of CH_4 and C_2H_6; with ethyl iodide, C_2H_6 and traces of C_2H_4 and C_4H_{10} are formed. Oxygen, nitrous oxide, and other oxides of nitrogen also inhibit H_2 production and are reduced, but the reactions with these substrates are not unexpected and were not studied in detail.

Reduction of Molecular Nitrogen. The evolution of H_2 from suspensions of $Fe(OH)_2$ is significantly inhibited by N_2 (Figure 3). Employing $^{30}N_2$-enriched nitrogen as the substrate, evidence for the reduction of molecular nitrogen to N_2H_4 and NH_3 was obtained. In a typical experiment, 100 μmol of $Fe(OH)_2$ was allowed to react with $^{30}N_2$-enriched N_2 under the conditions of optimal hydrogen evolution. Subsequent analysis of the carefully degassed reaction mixture by measurement of the yields of $^{30}N_2$ and $^{29}N_2$ in the N_2 released on hypobromite oxidation indicated that both N_2H_4 and NH_3 derived from gaseous N_2 were formed in amounts corresponding to 0.2-0.3, and 0.9-1.4 μmol, respectively. In subsequent experiments with normal N_2 as the substrate, the formation of both N_2H_4 and NH_3 in similar yields was confirmed by colorimetric assays. The results are summarized in Table IV. Since coprecipitation of $Fe(OH)_2$ with $Ni(OH)_2$ increases the yields and rate of H_2 production, nitrogen fixation experiments were also performed in nickel-containing systems. Nitrogen at 1 atm inhibited H_2 evolution by 10% relative to runs under argon (i.e., 22 μmol of H_2 were produced under N_2, relative to 25 μmol of H_2 under argon), but the yields of NH_3 and of N_2H_4 were similar to those observed in the nickel-free systems. This suggests that nitrogen is reduced predominantly by Fe rather than Ni. As expected, the reduction of N_2 is significantly inhibited by CO (see Table V).

Discussion

H_2 Evolution from $Fe(OH)_2$ Gels. The evolution of H_2 from suspensions of $Fe(OH)_2$ in mildly alkaline aqueous media was traced back to the disproportionation of $Fe(OH)_2$ into elemental iron and Fe_3O_4 or aquated precursors thereof. The elemental iron generated under these conditions subsequently reacts with H_2O to yield H_2. With pure $Fe(OH)_2$, the rate of H_2 evolution is slow. However, a substantial increase of the rate

Table IV. Effects of Reducible Substrates on H_2 Evolution from $Fe(OH)_2$-Glucose Suspensions and Yields of Reduction Products after 18 h of Reaction at 26° [a]

No.	Substrate	Yield, H_2 μmol	% inhibition	Products and yields[b] of reduced substrates (μmol)
1	None (Ar)	7.00[c]	0	
2	C_2H_2 (1 atm)	1.95	72	C_2H_4 (6.5), C_2H_6 (0.55), CH_4 (0.12)
3	C_2H_4 (1 atm)	2.95	58	C_2H_6 (4.0), CH_4 (0.05)
4	CO (1 atm)	0.05	99	CH_4 (0.4)
5	CH_3I (0.64 mmol)	2.50	64	CH_4 (11.0), C_2H_6 (trace)
6	C_2H_5I (0.64 mmol)	2.45	62	C_2H_6 (12.5), C_4H_{10} (trace)
7	N_2O (0.2 atm)	0.70	90	N_2, H_2O
8	O_2 (1 atm)	0	100	H_2O

[a] Reaction solutions contained, in a total volume of 5.0 ml of 10% glucose at pH 8.6: $Fe(OH)_2$ (initial concentration, 100 μmol). [b] Yields quoted for experiments carried out with simultaneous uv irradiation; slightly lower yields were observed in dark experiments. [c] Yield is lower than in experiment no. 6 (Table I), because $Fe(OH)_2$ was prepared from $FeSO_4$ rather than from $Fe(NH_4)_2SO_4$.

Table V. Reduction of Molecular Nitrogen with Reacting $Fe(OH)_2$ under Various Conditions

No.	Components/conditions	Yields NH_3	(μmol) N_2H_4	μequiv of N reduced
1	$Fe(OH)_2$, 10% glucose (with $^{30}N_2$), uv light	1.35	0.33	2.01[a]
2	As in 1, but with normal N_2	1.20	0.20	1.6[b]
3	As in expt 2, in the dark	0.65	0.09	0.83
4	As in expt 2, with 5 cm^3 of CO	0.24	0.06	0.36
5	As in expt 3, with 5 cm^3 of CO	0.18	0.04	0.26
6	$Fe(OH)_2$, 20% glycerol	0.70	0.09	0.88
7	$Fe(OH)_2$, 10% glucose, uv light, reacted twice, after one regeneration[c]	2.30	0.38	3.06
8	$Fe(OH)_2$, $Ni(OH)_2$ (2:1), 10% glucose, uv light	0.63	0.32	1.25
9	$Fe(OH)_2$, H_2O suspension, uv light	0.53	0.05	0.63
10	As in expt 9, in the dark	0.18	0.02	0.22
11	As in expt 2, at $t = 0$ (background)	0.02	0	0.02
12	As in expt 9, at $t = 0$ (background)	0.01	0	0.01

[a] Yields determined by hypobromite oxidation of the reaction solution and mass-spectrographic analysis of the N_2 generated (see Experimental Section). [b] Yields determined by colorimetric assays for NH_3 and N_2H_4 (experiments 2-12); this necessitated the use of $FeSO_4$ as the source of $Fe(OH)_2$; in experiment 1, $Fe(NH_4)_2(SO_4)_2$ was employed. [c] Reduction of Fe^{3+} by H_2SO_3 followed by reprecipitation of $Fe(OH)_2$ with NaOH.

is observed if the $Fe(OH)_2$ is precipitated from aqueous solutions of ferrous salts in the presence of sugars, polyhydric alcohols, or other dispersing or weak complexing agents. This suggests the existence of oligomeric or disordered aggregates of $Fe(OH)_2$ in which the Fe^{2+} ions are arranged in a manner favoring the formation of structural entities of the Fe_3O_4 lattice, or of aquated precursors thereof; the reactive aggregates are evidently stabilized by weak complexing agents. Their composition and structure remains to be elucidated but this poses serious difficulties in view of their instability and the changes which could occur during attempts at isolation. In spite of these limitations, our work permits the conclusion that the hydrogen production is associated with the formation of elemental iron under the reaction conditions. The disproportionation of $Fe(OH)_2$ occurs preferentially in the presence of alkali, and if the pH of the medium is sufficiently high, elemental iron accumulates in the precipitates; hydrogen is produced from these precipitates only upon subsequent acidification. The aging process of freshly precipitated $Fe(OH)_2$ appears to be a competing side-reaction which is responsible for the lower-than-stoichiometric yields of H_2 as demanded by eq 1. Under optimal conditions in the presence of dispersing or weak complexing agents, the total yields of H_2 approach 20% of the theoretical amount. The rate of H_2 evolution is accelerated by uv light, but the results in Table III show that the disproportionation of $Fe(OH)_2$ rather than the subsequent reaction of Fe^0 with protons of the medium is light stimulated. Since the iron salts employed for the experiments were of high purity, it is unlikely that the effects observed are due to contaminations by traces of other metals. The overall reaction thus may be represented in terms of eq 4:

$$[Fe^{2+}\ldots Fe_{n-1}{}^{2+}(OH)_{2n}] \xrightarrow{h\nu} [Fe^{2+}\ldots Fe_{n-1}{}^{2+}(OH)_{2n}]^*$$
$$\rightarrow [Fe^0\ldots Fe_2{}^{3+}Fe_{n-3}{}^{2+}(OH)_{2n}] \xrightarrow[(H_2O)]{+2H^+} H_2$$
$$+ [Fe_2{}^{3+}Fe_{n-2}{}^{2+}(OH)_{2n+2}] \quad (4)$$

The coprecipitation of $Fe(OH)_2$ and $Ni(OH)_2$ has previously been found to increase the rate and yields of H_2 production.[3,4] Thermodynamic calculations show that the transfer of electrons from $[Fe(OH)_2]_n$ to Ni^{2+} according to eq 7 should occur spontaneously, i.e., that Ni^0 is formed; the reaction is estimated to have a $\Delta G^{298°}$ of −3.85 kcal:

$$[Ni^{2+}\cdots Fe_n(OH)_{2n+2}]$$
$$\rightarrow [Ni^0\cdots Fe_2{}^{3+}Fe_{n-2}{}^{2+}(OH)_{2n+2}] \quad (5)$$

The evolution of H_2 from Ni-containing $Fe(OH)_2$ is stimulated by uv light only weakly, presumably because most of the H_2 is generated from the elemental Ni^0 produced according to eq 5 and only a fraction is formed from Fe^0 as generated according to eq 4. The promotion of H_2 evolution by other metals could be due to other effects; colloidal Pt, for example, could accelerate H_2 evolution by acting as the cathode on interaction with $Fe(OH)_2$ or Fe^0. On the other hand, the observed[3] stimulation of H_2 production by S^{2-} indicates that other mechanisms exist by which the transfer of electrons according to eq 4 is facilitated. The H_2 evolution from $Fe(OH)_2$ suspensions follows a pseudo-first-order rate law rather closely for the dark experiments (Figure 4). In the uv-irradiated systems the rates of H_2 evolution are initially higher since the effect of light is significant only in the early phases of the re-

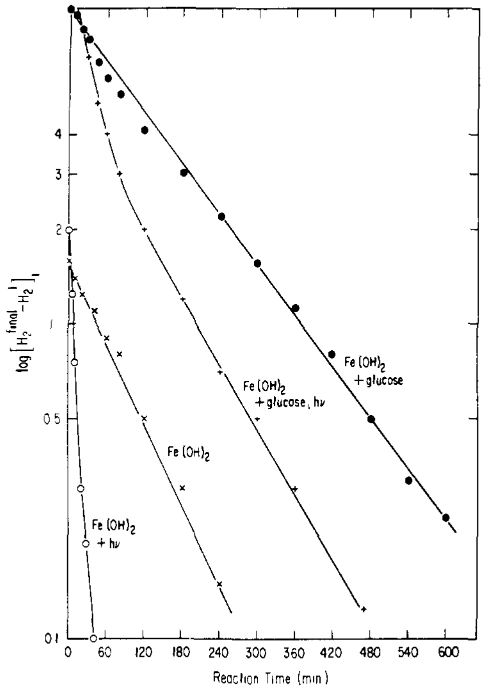
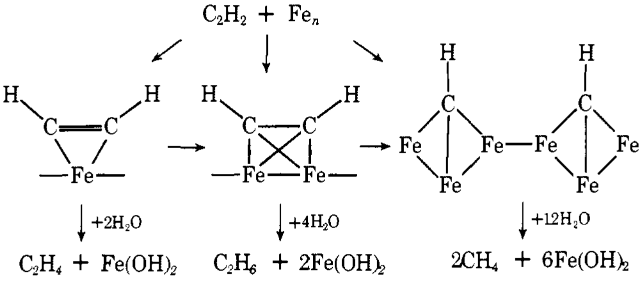
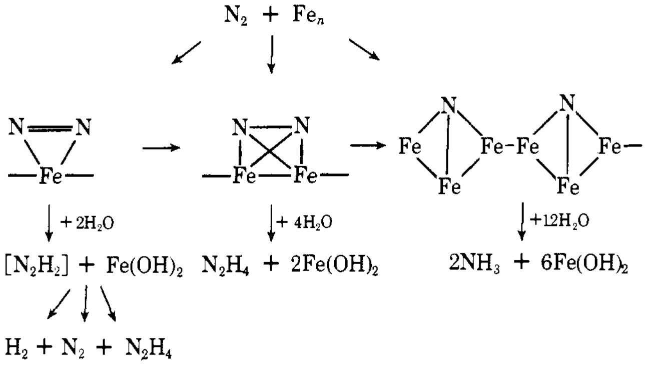


Figure 4. Pseudo-first-order rate plots of H_2 evolution. Experimental data are from Figure 2.

Scheme I. Postulated Mechanism of Reduction of Acetylene by Fe_n-Clusters Generated from $Fe(OH)_2$



Scheme II. Possible Mechanisms of Reduction of Molecular Nitrogen by Fe_n-Clusters Generated from $Fe(OH)_2$



action, i.e., before the precipitates become dark green. This kinetic behavior is consistent with a mechanism in which the dissolution of Fe^0 is rate determining. Acceptable first-order rate plots were also obtained for H_2 evolution in nickel-containing $Fe(OH)_2$ suspensions.

Reversibility and Catalysis. We have been unable thus far to find reductants or reaction conditions by which the present H_2-generating systems could be modified to become catalytic, i.e., to evolve H_2 continuously. The blue-green Fe^{2+}-Fe^{3+} oxides or hydroxides which remain after the spontaneous hydrogen evolution is complete could also not be reduced to $Fe(OH)_2$ with molecular H_2 at temperatures up to 100°. However, if $Fe(OH)_2$ is precipitated from acidic solutions of ferrous salts by addition of alkali under an atmosphere of hydrogen, the $Fe(OH)_2$ retains its white color for several days, whereas $Fe(OH)_2$ prepared under argon turns dark green. This shows that the disproportionation of $Fe(OH)_2$ either is inhibited or that the reaction is at least partly reversible. To obtain continuously functional H_2-evolving systems based on iron it is evidently necessary to find complexing agents which favor the disproportionation into Fe^0 and Fe^{3+}-Fe^{2+}-containing products, and simultaneously prevent the formation of the insoluble and thermodynamically stable Fe_3O_4 or hydrated precursors thereof.

Effects of Unsaturated Hydrocarbons, Carbon Monoxide, and Alkyl Halides. The observed inhibition of H_2 evolution from $Fe(OH)_2$ by unsaturated hydrocarbons and CO is plausibly attributed to their interaction with the elemental iron generated under the reaction conditions. Since C_2H_2 is reduced not only to C_2H_4 but also to C_2H_6 and traces of CH_4, reactions of C_2H_2 with one, two, or more iron atoms most obviously occur as well. We postulate that the iron atoms generated from $Fe(OH)_2$ aggregate and that the reactive species are Fe_n^0 clusters. The formation of the reduced products may subsequently proceed via carbide-like organoiron intermediates such as **1–3** (Scheme I), which undergo protolysis to $Fe(OH)_2$ and the hydrocarbon products. Our scheme is probably oversimplified but is not inconsistent with the experimental evidence and the known reactions of unsaturated organic substrates on the surface of metals. Plausible mechanisms of reduction of C_2H_4 by Fe_n^0 could be written in analogy to Scheme I. The formation of CH_4 as a reaction product in CO-inhibited, H_2-evolving $Fe(OH)_2$ systems is also suggestive of the presence of oligomeric Fe_n^0-clusters, since the reduction of one molecule of CO to CH_4 requires the transfer of six electrons. The reactions of CH_3I and C_2H_5I with $Fe(OH)_2$ suspensions yield CH_4 and C_2H_6 as the main products, either via free alkyl radicals or organoiron-halide intermediates.

Reduction of Molecular Nitrogen. The fact that nitrogen inhibits H_2 evolution from $Fe(OH)_2$ suspensions suggests that this substrate is also reduced. This was in turn confirmed by experiments using $^{30}N_2$-enriched N_2 as the substrate, as well as by direct colorimetric determinations of hydrazine and ammonia. The demonstrated formation of ammonia and of hydrazine from molecular nitrogen and reacting $Fe(OH)_2$ suspensions *represents one of the simplest examples for the reduction of N_2 under mild conditions in the presence of water.* Ammonia and hydrazine are undoubtedly formed by the hydrolysis of iron nitrides and dinitrides, various mechanistic possibilities are summarized in Scheme II. Since we have not been able as yet to obtain catalytic H_2-evolving systems based on $Fe(OH)_2$, we have also not succeeded so far in producing ammonia and hydrazine from nitrogen catalytically. However, it is possible to reduce the Fe^{3+}-Fe^{2+} hydroxides at the end of the reaction with SO_2 and to reprecipitate $Fe(OH)_2$ by the addition of alkali. Hence, a quasi-catalytic system for the reaction eq 6 and 7 is available:

$$N_2 + 2H_2O + 2SO_2 \rightarrow N_2H_4 + 2SO_4^{2-} \tag{6}$$

$$N_2 + 3H_2O + 3SO_2 \rightarrow 2NH_3 + 3SO_4^{2-} \tag{7}$$

The reduction of nitrogen in the present system obviously has nothing in common with the fixation of nitrogen by nitrogenase enzymes; in the latter, all substrate reactions are ATP dependent and occur at a molybdenum-active site.[8] Moreover, C_2H_2 is reduced by nitrogenase only to C_2H_4 and not to C_2H_6 or CH_4; in addition, C_2H_4 is not a substrate of nitrogenase. However, the possibility exists that some nitrogen is fixed in nature under anaerobic conditions in aging deposits of $Fe(OH)_2$; it is also not entirely inconceivable that certain primitive organisms fix nitrogen with molybdenum-free iron enzymes. It remains to be seen if the mechanism of H_2 evolution from $Fe(OH)_2$ suspensions is in any way related to the action of hydrogenase enzymes. We have recently shown[9] that H_2 is evolved from solutions of Fe^{2+} in the presence of S^{2-} and RS^-. To obtain more efficient H_2-evolving systems, further studies on the effects of sulfur ligands on the H_2 evolution from solutions or suspensions of Fe^{2+} species are obviously necessary and in progress. Last but not least, the present study may also be relevant with respect to the mechanism of iron corrosion, particularly under anaerobic conditions. The observed stimulation of the disproportionation of $Fe(OH)_2$ by ultraviolet light permits the interesting speculation that the corrosion of compact iron may be accelerated by uv light under certain conditions.

Experimental Section

Reagents and Chemicals. The ferrous salts used for the experiments were of Reagent ACS purity and obtained from Matheson Coleman and Bell. The $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ contained 0.003% Cu, 0.01% Fe^{3+}, 0.01% insoluble matter, 0.01% Mn, 0.003% PO_4^{3-}, 0.05% of substances not precipitated by NH_4OH, and 0.003% of Zn as maximum impurities. Independent analytical tests revealed the absence of detectable amounts of Ni, Co, and of platinum group elements. All other standard reagents and chemicals were highest available purity, all were used without further purification. The argon and nitrogen were 99.991% pure, both gasses were passed through alkaline pyrogallol solution to remove traces of oxygen.

Standard Experimental Technique. All experiments were performed in reaction flasks of 38-ml total capacity, manufactured by Pierce Chemical Co., Rockford, Ill. The flasks were sealed with silicon rubber seals and flushed with argon for 20 min. Aliquots of freshly prepared solutions of $FeSO_4$ or $Fe(NH_4)_2SO_4$ in carefully argon-deoxygenated, doubly distilled deionized water were injected into the reaction flasks in amounts corresponding to 100 μmol of Fe. In most experiments, 0.2 ml of 0.5 M solutions was added in this manner. Subsequently, 4.6 ml of deionized water or of freshly prepared deoxygenated solutions of glucose, glycerol, sucrose, etc., was added. The concentration of the stock solutions of the latter was adjusted to bring the final concentrations of the reaction solutions to the levels indicated in the tables or legends of the figures. To initiate the reactions, 0.2 ml of deoxygenated 1 N aqueous NaOH was injected. The reaction flasks were either exposed to uv light emitted from a mercury vapor lamp (Blak-Ray, Model 100A), at a distance of 20 cm or covered with aluminum foil for the dark experiments. The dark experiments were always performed simultaneously, and to eliminate temperature differences, the Al-foil covered flasks were placed under the uv light source as well. Hydrogen evolution from the $Fe(OH)_2$ suspensions was monitored by GLC, using a Hewlitt-Packard Series 700 laboratory gas chromatograph equipped with a column of 6 ft length, filled with molecular sieve (5 A), operating at 27^0. Gas samples of 0.2 ml volume were withdrawn by means of a syringe for this purpose. Hydrocarbon production in the experiments with gaseous reducible substrates such as C_2H_2, C_2H_4, and CO was also monitored by GLC, using a phenylisocyanate-Porasil, 80–100 mesh column at 27 °C.

Nitrogen Reduction Experiments. Nitrogen reduction by reacting $Fe(OH)_2$ suspensions was demonstrated by precipitating 100 μmol of $Fe(OH)_2$ in the manner outlined above, but in reaction vessels previously filled with $^{30}N_2$-enriched N_2. After completion of the reaction (18 h), the aqueous phase was transferred into one compartment of a Rittenberg flask, carefully degassed, and subjected to hypobromite oxidation as outlined in ref 10. The nitrogen evolved was collected by means of a Toepler pump and analyzed mass spectrographically for $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$. The $^{29}N_2$ was corrected for natural abundance from the measured peak height of $^{28}N_2$. The yields were determined by comparison with the peak height measured for $^{30}N_2$ released upon hypobromite oxidation of a $^{15}NH_4Cl$ standard. The colorimetric assays for NH_3 were performed by the method outlined in ref 11. Since iron salts interfere with this assay, the iron hydroxides were first removed by filtration or centrifugation. Hydrazine was determined with *p*-dimethylaminobenzaldehyde.[12] The hydrazone was extracted with 5 ml of CH_2Cl_2, and the absorbance was measured at 458 nm. The reagent solution was prepared by dissolving 10 g of *p*-dimethylaminobenzaldehyde in 50 ml of concentrated HCl and bringing the volume to 500 ml by addition of absolute ethanol. The assay can be carried out in the presence of iron salts provided that Fe^{3+} is reduced to Fe^{2+} by addition of sodium bisulfite solution, followed by gentle heating and subsequent acidification with 1 F HCl. It is important to remove all SO_2 prior to the assay.

Magnetic Measurements. For the magnetic measurements, $Fe(OH)_2$ precipitates were prepared as outlined above, i.e., by adding NaOH to solutions of $FeSO_4$ in water or water–sucrose under argon. The precipitates were dried under reduced pressure and pressed into pellets of 23-25 mg weight. White $Fe(OH)_2$ was found to be free of ferromagnetic impurities. The green Fe^{2+}-Fe^{3+} hydroxide or aquated oxide, isolated after H_2 evolution was as yet incomplete, contained a ferromagnetic component corresponding to 0.55 mol % Fe^0. After subtracting the ferromagnetic contribution, the magnetic susceptibility was 39×10^{-6} cm^3/g, corresponding to a μ_{eff} of 2.9 μ_B. The measurements were performed by the Faraday method.

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References and Notes

(1) This paper is dedicated to the memory of Dr. Oscar Baudisch (1881–1950), who aroused the interest of the senior author in the reactions of $Fe(OH)_2$ during a visit to Europe in 1947.
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