[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Radiation Chemistry of Deaerated Ferrous Chloride Solutions[1]

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The oxidation of deaerated $FeCl_2$ solutions in 0.4 *M* HCl is qualitatively similar to the oxidation in H_2SO_4. However, the decrease in yield due to accumulation of Fe(III) as the reaction proceeds is much more marked in HCl solutions. In the presence of Fe(III), the yield approaches equivalence with the molecular H_2 formed by the radiation. This property allows accurate measurement of the hydrogen yield in 0.4 *M* HCl solutions and the variation of the yield with Fe(III) concentration. The ratio of rate constants for the reactions $H + Fe(III) \rightarrow H^+ + Fe(II)$ and $H + H^+ + Fe(II) \rightarrow H_2 + Fe(III)$ is found to be 170, and the molecular H_2 yield is found to vary according to the relation $G_{H_2} = 0.45 - 0.64(Fe^{III})^{1/3}$ where G_{H_2} is the number of H_2 molecules produced per 100 e.v. adsorbed in the solution.

The radiation induced oxidation of $FeSO_4$ solutions in 0.4 *M* H_2SO_4 has received considerable attention.[3] In particular, for Co^{60} γ-rays[3a] and high energy electrons,[3b] the yield in air-saturated solution is 15.5 Fe(II) ions oxidized per 100 e.v. absorbed in the solution. In deaerated solutions the yield is only 8.2.[3d,g] In a study of the oxidation of $FeCl_2$ in air-saturated 0.4 *M* HCl, the initial yield was 15.8 ions oxidized per 100 e.v., in agreement with H_2SO_4 solutions.[4] However, the yield decreased at high doses, showing that the Fe(III) chloride complexes compete effectively with oxygen for H atoms. The ratio of the rate constants for the reactions

$$H + Fe(III) \longrightarrow H^+ + Fe(II)$$
$$H + O_2 \longrightarrow HO_2$$

was found to be $k_{Fe(III)}/k_{O_2} = 0.21$ in 0.4 *M* HCl. This ratio was dependent on chloride concentration indicating that the various ferric complexes react at somewhat different rates. Fe(II), however, is not appreciably complexed in either HCl or H_2SO_4 solutions. To a first approximation, one might expect the $k_{O_2}/k_{Fe(II)}$ rate constant ratio, 1200 in 0.4 *M* H_2SO_4,[3d] to be the same in HCl solutions. The product of these two rate constant ratios should give the ratio of rate constants for H atoms reacting with Fe(III) *versus* Fe(II) in HCl solution, $k_{Fe(III)}/k_{Fe(II)} \simeq 0.21 \times 1200 \simeq 250$.

This ratio would apply in the kinetics of oxidation of Fe(II) in deaerated HCl solution. By analogy with H_2SO_4 solutions,[3f] we might expect the mechanism

$$H_2O \longrightarrow H_2, H_2O_2, H, OH$$
$$H + Fe(III) \longrightarrow H^+ + Fe(II) \quad (1)$$
$$H + H^+ + Fe(II) \longrightarrow H_2 + Fe(III) \quad (2)$$
$$OH + Fe(II) \longrightarrow OH^- + Fe(III) \quad (3)$$
$$H_2O_2 + 2Fe(II) \longrightarrow 2OH^- + 2Fe(III) \quad (4)$$

In HCl solutions, reaction 3 probably proceeds *via* the intermediate production of a chlorine atom, but this does not matter in the present work, as the net result in either case is the oxidation of one Fe(II). This mechanism and the equation of material balance, $2G_{H_2O_2} + G_{OH} = 2G_{H_2} + G_H$ lead to the equation for the rate of production of Fe(III) (including any H^+ concentration dependence of reaction 2 in the rate constant k_2)[3d]

$$\frac{d(Fe(III))}{d(dose)} = 2G_{H_2} + \frac{2G_H}{1 + \frac{k_1}{k_2}\frac{(Fe^{III})}{(Fe^{II})}} \quad (1)$$

As k_1/k_2 is of the order of 250 and G_{H_2} and G_H are approximately 0.4 and 3.7, respectively, then at $(Fe^{III})/(Fe^{II})$ ratios as small as 0.05, the rate of oxidation of Fe(II) should be governed principally by the magnitude of G_{H_2}. This suggests that a study of deaerated $FeCl_2$ solutions might lead to accurate measurements of G_{H_2} in acid solutions. The following work was performed to check the above mechanism and to study G_{H_2} and its possible dependence on Fe(III) concentration.

Experimental

Standard solutions of reagent grade $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3 \cdot XH_2O$ and HCl were prepared. Aliquots of the stock solutions were added to the triply distilled water.[5] The HCl concentration was maintained near 0.4 *M*. In the worst case, about 5% of the Fe(III) was in the form of $FeSO_4^+$. Normally it was less than 1%.

The solutions were poured into tubes 15 cm. long and 10 mm. i.d. and deaerated by N_2 bubbling.[6] They were stoppered and irradiated in a cylindrical Co^{60} source.[7] The dose rate was approximately 2.5×10^{19} e.v./l. min.

With this procedure, the scatter in the data was slightly greater than was expected (amounting to ±3 μM Fe(III)) and all of the results appeared high by about 7 μM Fe(III). The effect was still present but smaller when 400 μM of Fe(III) was added. If 0.4 *N* HCl was irradiated, with neither Fe(II) nor Fe(III) added, an optical density increase of about 0.010 was noted at 350 mμ. The origin of this was not determined, but the results were found to be more reproducible if the 0.4 *N* HCl was prepared and pre-irradiated with about 10^5 roentgen before adding the stock iron solutions. This procedure was followed in all of the runs with added Fe(III). A blank correction, 7 μM of Fe(III), was subtracted from all of the data collected previous to this on solutions without added iron (Fig. 1).

The Fe(III) was estimated by measuring its absorption at 335 mμ in a Beckman DU ultraviolet spectrophotometer. (The molar extinction coefficient $\epsilon_{Fe(III)} = 1340$ in 0.408 *N* HCl.)[4] When Fe(III) was added initially, the irradiated solution was compared directly to the unirradiated solution in separate cuvettes by setting the instrument at 100% transmission when the unirradiated solution was in the light beam. With this method, small changes in the optical density could be measured even though the total optical density was greater than unity. The 3×10^{-3} and 10^{-2} *M* Fe(III) solutions were diluted 1:1 and 1:4 with 0.4 *N* HCl before comparing to avoid stray light effects at very high optical density.

Results and Discussion

The oxidation of deaerated Fe(II) in 0.4 *N* HCl is shown in Fig. 1 for 10^{-3} and 10^{-2} *M* Fe(II)

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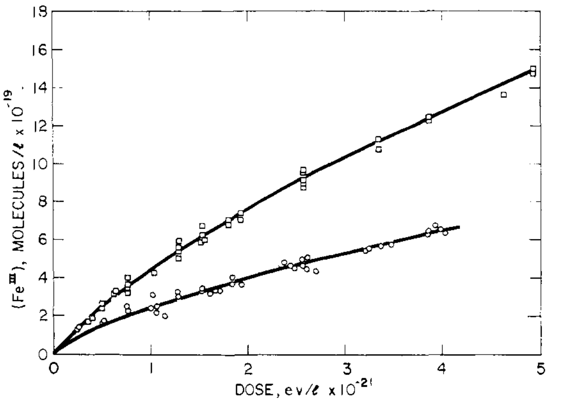

Fig. 1.—Oxidation of Fe(II) in deaerated 0.40 *M* HCl: ○, 10^{-3} *M* Fe(II); □, 10^{-2} *M* (Fe^{II}). A blank correction of 0.5×10^{19} molecules/l. has been subtracted from the data (see text). Curves are calculated from eq. 2.

The results agree qualitatively with the mechanism given in the introduction and expressed in eq. 1, *i.e.*, the rate of oxidation is not linear with dose and is greater in 10^{-2} *M* Fe(II) than in 10^{-3} *M* Fe(II). In order to obtain a quantitative comparison, eq. 1 is integrated with the assumption that (Fe^{II}) remains constant. This assumption does not alter the form of the equation and any change in the constants (which amounts to a few per cent.) is taken up in k_1/k_2. However the meaning of the equation is more obvious in this form.

$$2G_{H_2}(\text{dose}) = \Delta(\text{Fe}^{III}) - \frac{k_2G_H(\text{Fe}^{II})_0}{k_1G_{H_2}}$$
$$\ln\left[1 + \frac{G_{H_2}}{G_H + G_{H_2} + G_{H_2}\dfrac{k_1(\text{Fe}^{III})_0}{k_2(\text{Fe}^{II})_0}} \times \frac{k_1\Delta(\text{Fe}^{III})}{k_2(\text{Fe}^{II})_0}\right] \quad (2)$$

$\Delta(Fe^{III})$ is the increase in (Fe^{III}) concentration and $(Fe^{III})_0/(Fe^{II})_0$ is the initial ratio of concentrations. When no Fe(III) was added initially, this ratio amounted to 2.5×10^{-3} because of the Fe(III) contained in the reagent $FeSO_4{\cdot}7H_2O$. G_H was taken as 3.70[3d,4] and G_{H_2} was taken as 0.41. The only constant left, k_1/k_2, was varied to give the best fit with the data, yielding $k_1/k_2 = 170$. The curves drawn in Fig. 1 are calculated from eq. 2 with these constants and are in excellent agreement with the data. Furthermore, the value of k_1/k_2, 170, is in reasonable agreement with the value predicted in the introduction, 250, considering the experimental errors involved and possible effects of the two different media.

Figure 2 illustrates the effect of adding Fe(III) initially. The rate of Fe(II) oxidation is approximately linear in these solutions, as is predicted by eq. 2. Applying eq. 2 to the data in Fig. 2, we can obtain precise values of G_{H_2}. The logarithmic term in the equation is small compared to $\Delta(Fe^{III})$ and was computed assuming a value of 0.40 for G_{H_2}. This simplified the calculation of this term and can introduce only a negligible error, 0.5% in the worst case. The best values of G_{H_2} obtained are given in Table I. G_{H_2} decreases as Fe(III) increases, which is to be expected as analogous to the behavior of G_{H_2} in solutions of other solutes[8] capable of reacting with hydrogen atoms.

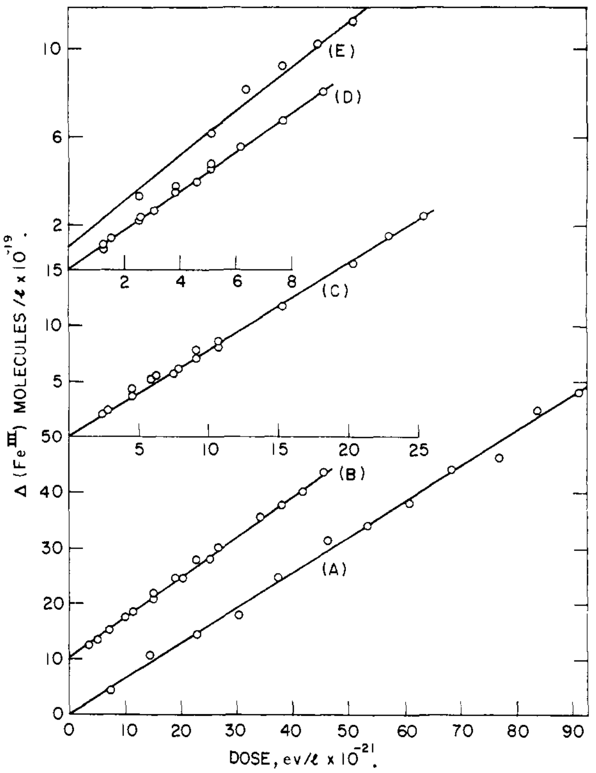

Fig. 2.—Oxidation of Fe(II) in deaerated 0.40 *M* HCl containing added Fe(III): (A), (Fe(III)) = 0.996×10^{-2} *M*; (B), (Fe(III)) = 3.80×10^{-3} *M*; (C), (Fe(III)) = 0.940×10^{-3} *M*; (D), (Fe(III)) = 3.96×10^{-4} *M*; (E), (Fe(III)) = 1.24×10^{-4} *M*. For curve A, (Fe(II)) = 3×10^{-3} *M*; for all others, (Fe(II)) = 1×10^{-3} *M*. Note the displacement of the curves on the ordinate. Curves D and E have been raised 10 and 1 units from their respective origins.

In the radical diffusion mechanism proposed to explain the appearance of H_2 and H_2O_2 among the products of the radiolysis of aqueous solutions,[8a,9,10] H atoms and OH radicals are assumed to be the only products formed initially. These are formed in small spurs, each containing an average of about three dissociated water molecules, and widely separated in the case of γ-rays. The radicals diffuse out of the spurs, occasionally encountering one another to form H_2, H_2O_2 or H_2O. If they escape this fate, they can react with a solute present. Thus, in the present case, the combination reaction of two H atoms is in competition with diffusion

$$H + H \longrightarrow H_2$$

TABLE I

CALCULATED G_{H_2} IN SOLUTIONS CONTAINING Fe(III) (FROM EQUATION 2)

(Fe^{III}) av, *M*	G_{H_2}
1.94×10^{-4}	0.420
4.55×10^{-4}	.405
1.09×10^{-3}	.375
3.08×10^{-3}	.360
1.05×10^{-2}	.315

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away from each other and reaction with Fe(III), reaction 1. Addition of Fe(III) to the solution will tend to repress the combination reaction, as is characteristic of competing reactions, lowering the H_2 yield.

Sworski has noted the empirical relation that the molecular yields tend to decrease linearly with the cube root of the solute concentration.[11] This relation breaks down with large changes in G_{H_2}[8d] but should be valid in the range covered in this work. A cube root plot of the data of Table I is given in Fig. 3. The linearity is in agreement with the other systems. Since this cube root relation is empirical, a comparison is also given in Fig. 3 with a one parameter curve representing an approximate solution of the diffusion-combination mechanism outlined above.[8a] The agreement with the prediction of this mechanism is considered good in view of the approximations that were made in calculating the curve.

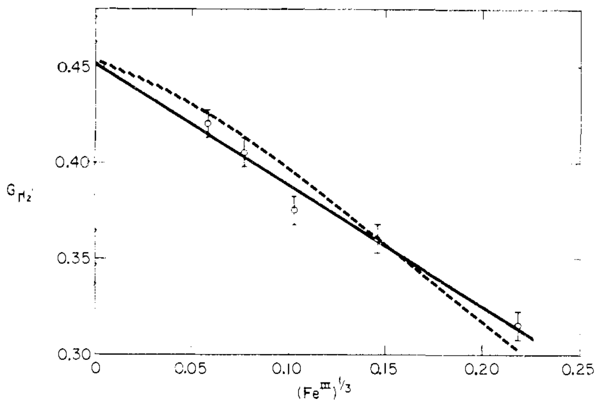

Fig. 3.—The variation of the hydrogen yield with Fe(III) concentration; G_{H_2} is calculated from eq. 2, and Fe(III) is the average concentration present during the irradiation. The dotted line is the curve predicted by a radical diffusion mechanism.

This is the first demonstration of the validity of the cube root relation for hydrogen yields in highly acid solutions, indicating that the possible reaction[3c] does not interfere with the solute dependence.

$$H + H^+ \longrightarrow H_2^+ \qquad (5)$$

Rothschild and Allen have suggested that this reaction is very rapid, competing effectively with O_2 for H atoms.[3f] If a new reaction scheme is proposed for our system in which the H atom assumes another form, such as H_2^+, the kinetics will remain unchanged, except that the rate constant ratio determined by us will apply to the new species rather than the H atom.

Another point of interest in Fig. 3 is the extrapolated value of G_{H_2} at "zero" Fe(III) concentration. This value, $G_{H_2} = 0.45$, is the same as is found in neutral solutions, $G_{H_2} = 0.45$. Mahlman and Boyle have obtained the same yield in dilute KBr solutions in 0.4 N H_2SO_4.[12] Previously it was believed that the H_2 yield was approximately 15% lower in the acid solutions.[5,13] The measurements leading to this conclusion were made principally in solutions saturated with O_2 or containing iodine or ceric ion. These solutes react efficiently with H atoms and would be expected to lower the H_2 yield somewhat. As was mentioned in the Introduction, the ratio of rate constants for H atoms reacting with O_2 *versus* Fe(III) is 4.8. A solution containing 1.3×10^{-3} M O_2 would be expected to correspond to a Fe(III) solution 4.8 times this concentration, or 6.2×10^{-3} M Fe(III). From Fig. 3, the value of G_{H_2} predicted for this concentration is 0.34, in excellent agreement with the observed value of Ghormley and Hochanadel of 0.35.[8b] This appears to be an adequate explanation for the previously observed low yields. The value of G_{H_2} used in eq. 1, 0.41, is in agreement with Fig. 3 since the average Fe(III) concentration in Fig. 1 is about 10^{-4} M.

The H_2 yield in neutral O_2-saturated solution is somewhat higher, 0.40.[8b] Since the yields in the absence of O_2 are the same, O_2 is apparently more effective in reducing G_{H_2} in acid solution. The yields probably vary with the cube root of the O_2 concentration, and the ratio of the slope of the curve in acid solution to the slope in neutral solution is $(0.45 - 0.35)/(0.45 - 0.40) = 2$. The ratio of the effectiveness in the two cases is the cube of this, hence O_2 is 8 times more effective in acid solution. From the radical-diffusion model, this factor is proportional to $(k_{O_2}r_0^2)/D$,[8a] where k_{O_2} is the rate constant for the reaction of H atoms with O_2, r_0 is the average radius of a spur of radicals when it is formed, and D is the diffusion coefficient of the hydrogen atoms. However, any increase in D is likely to be reflected in an increase in k_{O_2}. Thus either the rate constant or radius of the spur or both could be increasing in going to acid solution.

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