

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Radiation Chemistry of Ferrous Chloride Solutions¹

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The radiation induced oxidation of ferrous ion in air-saturated 0.4 M HCl differs from the oxidation in 0.4 M H₂SO₄ in that the ferric iron production is not linear with dose. The initial yield is essentially the same, $G_{(\text{Fe}^{\text{III}})}$ (ions oxidized per 100 e.v. absorbed) being 15.8, but the kinetics indicate a competition between ferric iron and oxygen for H atoms. The effect of the competition is to decrease the yield, and the effect increases with increasing chloride ion concentration. The ratios of the rate constant for H atoms reacting with ferric iron and oxygen at the various chloride ion concentrations have been separated into the ratios for the individual species present, giving $k_{\text{Fe}^{\text{III}}}/k_{\text{O}_2} = 0.004$, $k_{\text{FeCl}^{\text{II}}}/k_{\text{O}_2} = 0.23$ and $k_{\text{FeCl}_2^{\text{I}}}/k_{\text{O}_2} = 0.48$.

Rigg, Stein and Weiss² have suggested that the kinetics observed in the oxidation of FeSO₄ solutions by X-rays in the pH range 1–3 are affected by the presence of ions in solution capable of complexing the ferric ion. The addition of fluoride and phosphate ions to the solution apparently makes the ferric iron less liable to reduction by H atoms.

The difference observed in the kinetics of oxidation of ferrous ion by γ -rays when the substrate is changed from sulfuric acid solution to hydrochloric acid solution apparently is also due to the form of complexing of the ferric ion. In air-saturated 0.4 M H₂SO₄, ferrous ions are oxidized with a yield of 15.5 ions per 100 e.v. absorbed in the system.³ Ferric production is linear with dose until all but a few per cent. of the oxygen in solution is used up.⁴ In air-saturated 0.4 M HCl, though the initial rate of oxidation is essentially the same, the ferric production is not linear with dose, falling off as the reaction proceeds.

The present paper is an elucidation of the kinetics of the ferrous chloride oxidation in terms of the nature and extent of complexing of the ferric ion.

Experimental

Reagent grade materials were used without further purification. The water was distilled four times as described previously.⁵ Solutions were equilibrated with air by shaking and with oxygen by bubbling. They were irradiated in a cylindrical Co⁶⁰ source at a dose rate of 3.02×10^{16} e.v./cc.-min. The dose rate was determined with the ferrous sulfate dosimeter taking the yield of ferrous oxidation as $G_{\text{Fe}^{\text{III}}}$ (ions per 100 e.v.) = 15.45 ± 0.11 .³

All analyses were performed on a Beckman DU ultraviolet spectrophotometer. Ferric iron was determined as the appropriate complex. At 23.8°, the following extinction coefficients were determined: in 0.4 M H₂SO₄, ϵ_{2170} 2170; in 0.246 M HCl, 0.20 M HClO₄, ϵ_{335} 1026; in 0.442 M HCl, ϵ_{335} 1358; in 0.434 M HCl, 1.00 M NaCl, ϵ_{335} 2010; in 0.441 M HCl, 0.60 M NaClO₄, ϵ_{335} 1366; in 0.40 M HClO₄, ϵ_{240} 4185. The solutions containing 1 M Cl⁻ were diluted 1:1 with NaCl solution such that the final Cl⁻ concentration was 1.436 M. The extinction coefficient of iron in chloride solutions has a temperature coefficient of about 2% per degree⁶; hence a thermostated Beckmann was used and the samples were allowed to equilibrate before reading. The extinction coefficient in HClO₄ agrees well with that reported by Bastian, Weberling and Palilla; ϵ_{240} 4160.⁷

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) T. Rigg, G. Stein and J. Weiss, *Proc. Roy. Soc. (London)*, **A211**, 375 (1952).

(3) (a) C. J. Hochanadel and J. A. Gormley, *J. Chem. Phys.*, **21**, 880 (1953); (b) R. H. Schuler and A. O. Allen, *ibid.*, **24**, 56 (1956).

(4) Jerome Weiss, H. A. Schwarz and A. O. Allen, *International Conference on the Peaceful Uses of Atomic Energy*, Geneva, Switzerland, 1955.

(5) E. R. Johnson and A. O. Allen, *THIS JOURNAL*, **74**, 4147 (1952).

(6) D. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942).

(7) R. Bastian, R. Weberling and F. Palilla, *Anal. Chem.*, **28**, 429 (1956).

Some of the work was performed with added ferric iron initially, in which case the irradiated solution was compared directly with the unirradiated solution in the spectrophotometer, giving the change in optical density of the solution instead of absolute values of the optical density. Thus small changes in ferric concentration of the order of 10–20% could be determined with a precision of about 1%.

In order to check the spontaneous air oxidation of ferrous chloride, a solution of 10^{-3} M FeCl₂ in 0.4 M HCl was saturated with O₂ and allowed to stand overnight. The initial ferric iron concentration was 52 μ M increasing to 57 μ M in 18 hours. Since all solution preparations and analyses were performed in less than six hours, this source of error is negligible.

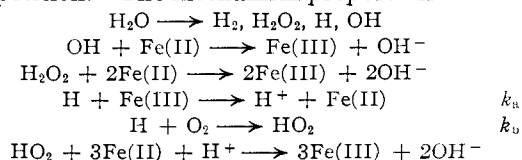
Results and Discussion

In Fig. 1, ferric production in solutions 10^{-3} M in ferrous ion is given as a function of dose and of substrate composition. In 0.4 M HCl, air saturated, the rate of ferric production decreases as the dose increases. In oxygen-saturated solution, ferric iron production is almost linear with dose in the range studied and the initial rates (calculated by a method to be given later) are given in Table I.

TABLE I
FERROUS ION OXIDATION YIELDS

Conditions	Yield
10^{-3} M FeCl ₂ in 0.4 M HCl, O ₂ satd.	15.8 ± 0.3
10^{-3} M FeCl ₂ in 0.4 M HCl, 1.0 M NaCl, O ₂ satd.	$15.8 \pm .3$
10^{-3} M Fe(ClO ₄) ₂ in 0.4 M HClO ₄ , O ₂ satd.	$15.7 \pm .3$

The oxygen effect suggests a ferric ion–oxygen competition. The mechanism proposed is



The first step represents the products formed by the action of radiation on water. The third and last steps are not mechanistic but indicate the overall stoichiometry. This mechanism is essentially the same as the one proposed by Weiss for FeSO₄ at higher pH,² with the addition of the known production of H₂ and H₂O₂ in the first step.⁸

The expression for the rate of ferric iron production derived on the basis of this mechanism and the stoichiometry $2G_{\text{H}_2} + G_{\text{H}} = 2G_{\text{H}_2\text{O}_2} + G_{\text{OH}}$ (G_X represents the number of molecules or radicals of X produced per 100 e.v. absorbed in the system) is

$$\frac{d(\text{Fe}^{\text{III}})}{d(\text{dose})} = 2G_{\text{H}_2} + \frac{4G_{\text{H}}}{1 + \frac{k_a(\text{Fe}^{\text{III}})}{k_b(\text{O}_2)}} \quad (1)$$

(8) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

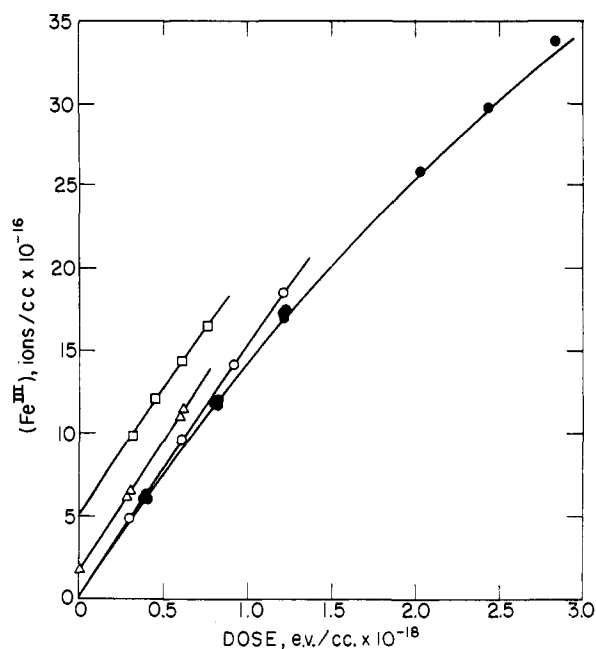
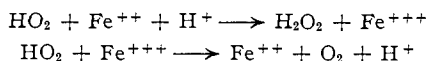


Fig. 1.—Rate of oxidation of $10^{-3} M$ ferrous ion: ●, $0.416 M$ HCl, air saturated; ○, $0.416 M$ HCl, O_2 saturated; □, $0.42 M$ HCl, $1.00 M$ NaCl, O_2 saturated; Δ, $0.41 M$ $HClO_4$, O_2 saturated.

In order to test this mechanism, ferrous chloride solutions containing varying amounts of ferric chloride were irradiated both air saturated and oxygen saturated. The hydrogen yield is assumed to be the same in HCl solutions as in H_2SO_4 solutions, $G_{H_2} = 0.35$.⁹ A precise value is not required, since $G_{Fe(III)}$ is always a factor of 10 to 20 larger than G_{H_2} . Rearranging equation 1, it is seen that $1/(G_{Fe(III)} - 2G_{H_2})$ should be a linear function of the Fe(III) concentration to O_2 concentration ratio. This is shown in Fig. 2. The O_2 dependence rules out a competition between the



two reactions which have been proposed by Barb, Baxendale, George and Hargrave¹⁰ in a study of the ferrous sulfate- H_2O_2 reaction in sulfuric acid solutions. This mechanism would be O_2 independent.

Ferrous perchlorate solutions in $0.4 M$ $HClO_4$ containing varying amounts of ferric perchlorate were also irradiated, giving the lowest curve of Fig. 2. In this system, ferric iron apparently has little effect.

Equation 1 may be integrated if it is assumed that

$$-\frac{d(O_2)}{dt} = \alpha \frac{d(Fe^{III})}{dt}$$

Actually, α varies during the run, but it may be calculated to be within 3% of 0.239 at all doses studied in Fig. 1. Performing the integration, we have [for the case $(O_2)_0 \gg \alpha(Fe^{III})_0$; i.e., $(O_2) = (O_2)_0 - \alpha(Fe^{III})$]

(9) J. A. Ghormley and C. J. Hochanadel, *Radiation Research*, **3**, 227 (1955).

(10) W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans Faraday Soc.*, **47**, 462 (1951).

$$\begin{aligned} \text{dose} &= \frac{C}{B} \{ (Fe^{III}) - (Fe^{III})_0 \} + \frac{(B - AC)(O_2)_0}{B^2} \times \\ &\ln \left[1 + \frac{B}{A(O_2)_0 + B(Fe^{III})_0} \{ (Fe^{III}) - (Fe^{III})_0 \} \right] \end{aligned}$$

where $A = G_{Fe(III)}$, $B = 2k_a/k_b G_{H_2} - \alpha G_{Fe(III)}$, $C = k_a/k_b - \alpha$, the superscript and subscript zero's refer to initial yields and concentrations. For small ferric concentration this equation is expanded into

$$\begin{aligned} \text{dose} &= \frac{1 + C(Fe^{III})_0/(O_2)_0}{A + B(Fe^{III})_0/(O_2)_0} \{ (Fe^{III}) - (Fe^{III})_0 \} \\ &+ \frac{k_a/k_b (A - 2G_{H_2})}{2 \{ A + B(Fe^{III})_0/(O_2)_0 \}^2} \{ (Fe^{III}) - (Fe^{III})_0 \}^2 \end{aligned}$$

Initial slopes in the oxygen-saturated solutions were calculated using this equation, and are given in Table I. All yields are the same within experimental error, but they are about 2% larger than is observed with ferrous sulfate in $0.4 M$ H_2SO_4 . This could easily be experimental error. This is of interest in view of the observation that the net water decomposition yield ($G_H + 2G_{H_2}$ or $1/4 \{ G_{Fe(III)} + 6G_{H_2} \}$) increases by about 20% going from neutral solution to $0.4 M$ H_2SO_4 .⁸ From these results it appears that the increase is specific for the hydrogen ion and is independent of the negative ion in solution.

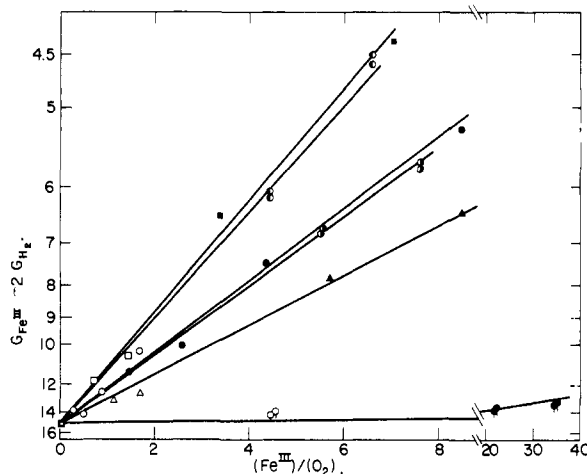


Fig. 2.—Rate of oxidation of 10^{-3} ferrous ion in ferric-oxygen mixtures. $G_{Fe(III)} - 2G_{H_2}$ is plotted as the reciprocal coordinate: ■, $0.43 M$ HCl, $1.00 M$ NaCl, air saturated; □, same, O_2 saturated; ●, $0.43 M$ HCl, $0.60 M$ NaCl, air saturated; ○, $0.43 M$ HCl, air saturated; ⊙, same, O_2 saturated; ▲, $0.43 M$ HCl, $0.6 M$ $NaClO_4$, air saturated; △, $0.245 M$ HCl, air saturated; Δ, same, O_2 saturated; ⊙, $0.41 M$ $HClO_4$, air saturated; ⊙, same, O_2 saturated.

Milling, Stein and Weiss¹¹ have observed that the ferrous oxidation yield is increased by the addition of $HClO_4$ in deaerated solution. This effect amounts to 2 or 3% in $0.4 M$ $HClO_4$, and is attributed to direct action of the radiation on the perchlorate ion. This effect is not evident in this work, perhaps due to the presence of oxygen.

The slopes of the curves in Fig. 2 (which are proportional to k_a/k_b) are seen to increase with increasing chloride ion concentration. The extent to which the ferric iron is complexed also increases

(11) B. Milling, G. Stein and Joseph Weiss, *Nature*, **170**, 710 (1952).

with increasing chloride ion concentration. Rabinowitch and Stockmeyer have determined the association constants for the first three chloride complexes to be (at $\mu = 1$ and 25°) $K_1 = 3.7$, $K_2 = 1.1$ and $K_3 \cong 0.03$.⁶ They also determined the variation of K_1 with ionic strength. The relative solution compositions at the various chloride ion concentrations (calculated assuming K_2 to vary with μ in a similar manner to K_1) are given in Table II along with values of k_a/k_b determined from Fig. 2.

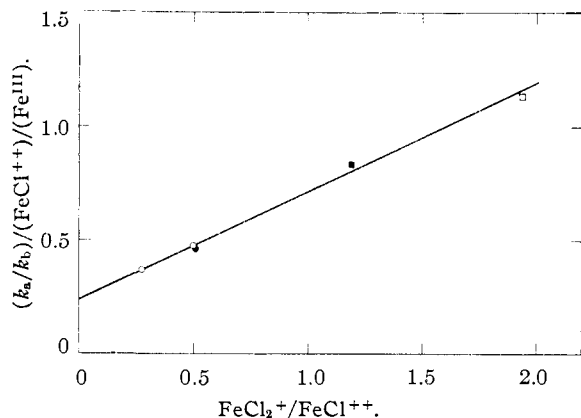
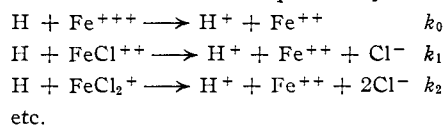


Fig. 3.—Ferric iron-oxygen competition constant as a function of extent of single and double complexing: O, $\mu = 0.45$; ●, $\mu = 1.05$; □, $\mu = 1.45$.

In order to account for the reaction of H atoms with the various ferric complexes, the fourth step in the mechanism should be replaced by the series



k_a is then given by

$$k_a(\text{Fe}^{\text{III}}) = k_0(\text{Fe}^{+++}) + k_1(\text{FeCl}^{++}) + k_2(\text{FeCl}_2^+) + \dots \quad (2)$$

All terms above k_2 have been dropped, since the concentration of the higher complexed species in solution is negligibly small.

In HClO_4 solutions, the ferric iron is probably not complexed. Hence $k_a/k_b = k_0/k_b = 4 \times 10^{-3}$. Since this is small compared to k_a/k_b observed in chloride solutions, we neglect $k_0(\text{Fe}^{+++})$ in equation 2 and find

$$\frac{k_a/k_b}{(\text{FeCl}^{++})/(\text{Fe}^{\text{III}})} = k_1/k_b + k_2/k_b \frac{(\text{FeCl}_2^+)}{(\text{FeCl}^{++})} \quad (3)$$

TABLE II

SOLUTION COMPOSITION AND FERRIC-OXYGEN COMPETITION CONSTANTS AS FUNCTIONS OF CHLORIDE ION CONCENTRATION AND IONIC STRENGTH
(H^+) = 0.40 M

(Cl ⁻), M	μ	Fe ⁺⁺⁺	FeCl ⁺⁺	FeCl ₂ ⁺	FeCl ₃	k_a/k_b
0.000	0.42	1.000	0.004
.245	.45	0.445	0.436	0.118	0.001	.159
.443	.45	.274	.486	.237	.003	.226
.436	1.05	.292	.471	.234	.003	.218
1.037	1.05	.105	.403	.477	.015	.336
1.436	1.45	.054	.313	.607	.026	.355

In Fig. 3, the first member of this equation is found to be linear with $(\text{FeCl}_2^+)/(\text{FeCl}^{++})$. k_1/k_b and k_2/k_b are found to be 0.23 and 0.48, respectively, from the intercept and slope. There is no large effect of ionic strength, which is not surprising, as the activity coefficients are probably near their minimum value. No errors are given for these values since it is difficult to assess the errors in the solution composition. The relative magnitude of these values undoubtedly is dependent on the activity coefficients of the complexes and reasons for k_2 being twice k_1 are subject to criticism on this basis.

There is insufficient quantitative information on rate constants of H atoms reacting with iron complexes to make a significant correlation or devise a general mechanism. Several qualitative observations can be found in the literature. Rigg, Stein and Weiss studied the effect of fluoride and phosphate on the FeSO_4 oxidation at high pH,² but unfortunately their system was complicated by the presence of the FeSO_4^+ complex which they could not include in their calculations, although they suspected its presence. However, their results indicate that $k_{\text{FeOH}^{++}}/k_{\text{O}_2}$ is of the order of unity while $k_{\text{FeF}^{++}}/k_{\text{O}_2}$ and $k_{\text{FePO}_4}/k_{\text{O}_2} \ll 1$. Since ferric iron production is a linear function of dose in the irradiation of FeSO_4 in 0.4 M H_2SO_4 until the O_2 concentration is reduced to a few micromolar, it may be concluded that $k_{\text{FeSO}_4^+}/k_{\text{O}_2} < 10^{-3}$.⁴ $\text{Fe}(\text{CN})_6^{\equiv}$ production in $k_4\text{Fe}(\text{CN})_6$ solutions is just equal to the H_2 yield ($G \sim 0.4$)¹² indicating that any oxidation by OH radicals is counterbalanced by reduction by H atoms. Tentatively, this suggests that $k_{\text{Fe}(\text{CN})_6^{\equiv}}$ is large.

UPTON, N. Y.

(12) H. Fricke and E. J. Hart, *J. Chem. Phys.*, **3**, 596 (1935).