[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Oxidation of Aqueous Ferrous Sulfate Solutions by Charged Particle Radiations

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Chemical yields are reported for the oxidation of aqueous ferrous sulfate solutions by H^3 β-particles, Po^{210} α-particles, and by the recoil products of the $B^{10}(n,\alpha)Li^7$ and $Li^6(n,\alpha)H^3$ nuclear reactions. Yields for the heavy-particle radiation are considerably lower than for the β-particles and decrease with decreasing energy.

The efficiency of a given type of ionizing radiation for inducing chemical action is indicated by a G-value, the number of molecules or equivalents of reaction product resulting per expenditure of 100 electron volts of energy by the ionizing radiation. The G-value for the X- or γ-ray-induced oxidation of ferrous ion in aqueous sulfuric acid solution has been cited at various values between 15 and 20[1] with a recent calorimetric measurement yielding 15.6 ± 0.3.[2] It is of practical importance for monitoring purposes, as well as of fundamental interest, to compare with this the analogous values for other types of ionizing radiation. In this study, chemical yields have been determined for the oxidation of ferrous ion in 0.8 N sulfuric acid solution, as induced by the β-radiation of tritium, the α-radiation of Po^{210}, and the recoil products of the $B^{10}(n,\alpha)Li^7$ and $Li^6(n,\alpha)H^3$ reactions.

Experimental

The water used was purified by a triple distillation procedure which has been described previously.[3] Recrystallized ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and reagent grade sulfuric acid, sodium chloride, boric acid and lithium sulfate ($Li_2SO_4 \cdot H_2O$) were used in preparation of the solutions. Ferric ion was determined using a Beckman Model DU quartz spectrophotometer with a one-cm. cell. At a wave length of 3020 Å., the concentration of ferric ion in millimoles per liter is given by 0.449 D, where D is the optical density of the solution.

The procedures employed for the irradiations were as follows.

A. **β-Particles.** $H^3 \rightarrow He^3 + \beta$.—Two tritium water solutions were used. The first was prepared and assayed in this Laboratory as previously described.[4] The second was a sample of known activity, obtained from Atomic Energy of Canada, Ltd., through the courtesy of T. J. Hardwick. Solutions of 0.10 curie/ml. of each of the tritium water solutions, 1.0 mN ferrous sulfate, 1.0 mM sodium chloride and 0.8 N sulfuric acid were placed in stoppered one-cm. absorption cells of the spectrophotometer, and ferric ion was determined as a function of time as the radiation-induced oxidation proceeded. The sodium chloride was added to eliminate possible catalytic effects due to organic impurities,[5] after initial experiments could not be reproduced.

B. **α-Particles.** $Po^{210} \rightarrow Pb^{206} + \alpha$.—A 27.5-millicurie sample of Po^{210} electroplated on platinum foil was dissolved in concentrated sulfuric acid by heating in a water-bath at 100°. Aliquots were made up into solution 0.5 mN in ferrous sulfate and 0.8 N in sulfuric acid, with a specific activity of 2.51×10^{-3} curies/ml. The activity was determined using a Simpson methane proportional counter with 52% geometry[6] on aliquots diluted 10,000-fold in 2 M nitric acid. The ferric ion was monitored spectrophotometrically in the same manner as in the tritium water experiment. Air-saturated and air-evacuated samples were run.[7] The evacuation technique has been reported previously.[3]

C. **Recoil Products—$B^{10}(n,\alpha)Li$.**[7]—Air-saturated solutions of 0.5 and 1.0 mN ferrous sulfate in 0.8 N sulfuric acid and several concentrations, 0.0 to 0.10 M of boric acid were irradiated in quartz cells by exposure to the neutron flux in the thermal column of the Argonne heavy water reactor for lengths of time ranging from 15 minutes to one hour. Three to four samples of differing boric acid concentration were irradiated simultaneously and in closely coincident positions. One sample of each such group contained no boric acid, affording a blank determination of the oxidation induced by the small γ-flux of the thermal column. Groups of samples were irradiated at two positions in the thermal column, corresponding to neutron fluxes of 6.9×10^9 and 1.3×10^{11} neutrons/cm.^{2} sec. A gold foil was irradiated with each group of samples for a determination of the thermal neutron flux by nuclear activation and standardized radioactivity counting techniques. Activation of a gold foil through cadmium showed the epi-thermal flux to be negligible.

D. **Recoil Products—$Li^6(n,\alpha)H^3$.**—A solution of 0.5 mN ferrous sulfate in 0.8 N sulfuric acid and 0.547 M lithium sulfate was irradiated with a group of boric acid samples as described above.

Results

The β-particle induced oxidation of ferrous ion in air-saturated tritium water proceeded linearly over an irradiation time of three hours, with a rate of $(2.71 \pm 0.04) \times 10^{-6}$ N/min. at an activity of one curie/ml. The mean energy of the tritium β-decay is 5.69 ± 0.04 kev.[8] This yields a G-value of 12.9 ± 0.2 ferrous ions oxidized per 100 ev., in close agreement with the value of Hardwick.[9]

The α-radiation from Po^{210} induced the oxidation of ferrous ion in air-saturated solutions at a linear rate of $(1.22 \pm 0.04) \times 10^{-3}$ N/min. at an activity of one curie/ml. If one uses an α-particle energy of 5.30 Mev.,[10] and neglects the heavy nucleus recoil, a G-value of 6.2 ± 0.2 is obtained for the reaction induced in the presence of air.

The irradiation of boric acid solutions with thermal neutrons oxidized ferrous sulfate with yields which, after correction for the γ-ray induced blank, were linear with duration of irradiation, neutron flux level, and concentration of boric acid contained in the solution. The yield determined was $(45 \pm 4) \times 10^6$ ferric ions oxidized per neutron/cm.^{2} per mole of boric acid. The value for the thermal neutron absorption cross-section for boron was taken as 7.55×10^{-22} cm.^{2},[11] the nuclear

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absorption processes competing with the (n,α) reaction being negligible.[10,11] The disintegration energy of the reaction is 2.79 Mev., the lithium and helium ion products being accompanied by a γ-ray of 0.47 Mev. energy in 94% of the disintegrations.[12] Absorption of the γ-ray in the aqueous solution is small, and its contribution to the chemical reaction is neglected. This leaves a mean energy of 2.35 Mev. expended by the heavy particle products of the reaction, inducing the chemical oxidation. On this basis, 4.2 ± 0.4 ferrous ions are oxidized per 100 ev.

Similarly for the oxidation induced by the recoil products of the $Li^6(n,\alpha)H^3$ reaction, a yield of $(10.6 \pm 1.0) \times 10^6$ ferric ions per neutron/cm.^{2} per mole of lithium ion was observed. The thermal cross-section for neutron absorption in lithium, the only reaction of appreciable magnitude,[13,14] is 71 barns.[11] The products of the reaction are emitted with an energy of 4.80 Mev.,[15] there being no evidence of a γ-component.[16] From these data a G-value of 5.2 ± 0.5 is obtained.

A summary of the ferric ion yields and energy characteristics of the radiations is given in Table I.

Table I

Specific Yields for the Oxidation of Aqueous Ferrous Sulfate by Charged Nuclear Particles

Reaction	Nuclear particle	Energy, Mev.	$G_{Fe^{+++}}$ (oxygenated) (molecules/100 ev.)
$H^3 \rightarrow He^3$	β^-	0.00569	12.9 ± 0.2
$Po^{210} \rightarrow Pb^{206}$	α	5.30	6.2 ± 0.2
$B^{10}(n,\alpha)Li^7$	α Li^7	1.50^a 0.85^a	4.2 ± 0.4
$Li^6(n,\alpha)H^3$	α H^3	2.05 2.73	5.2 ± 0.5

^{a} Weighted mean values of long and short range particles.

Discussion

The ferric ion yields reported in Table I can be explained reasonably well from the free radical and molecular product yields deduced from other data. This fact augurs well for the quantitative stoichiometric aspects of current radiation chemistry theory although it adds nothing new to the detailed mechanism of free radical and molecular product formation.

According to current theory, the passage of ionizing radiation through aqueous solutions induces a primary dissociation of water into hydrogen atoms and hydroxyl radicals along the track of the particle. These free radicals are assumed to be formed along the track of the ionizing particles in geometrical distributions that are a function of the particle velocity and mass. Since the velocity of a given particle varies from an initial speed to a final speed of zero, the distribution of free radicals varies along the path of the particle. However, associated with each particle, or type of radiation, there will be an average yield and distribution of free radicals or active species. Some of these radicals escape recombination in the track and are available for reaction with solute molecules as free hydrogen and hydroxyl radicals. Let reaction 1 represent the reaction of free radicals escaping the primary recombination and G_1 represent the yield of this reaction

$$H_2O = H + OH \qquad (1)$$

It is further assumed that a certain proportion of the initial free radicals undergo recombination in the track or hot spot before reaction with solute occurs. Let net reaction 2 represent this process and G_2 designate its yield.

$$H_2O = {}^1/_2H_2 + {}^1/_2H_2O_2 \qquad (2)$$

At this point it is well to emphasize the fact that for the present it is impossible to state whether hydrogen and hydrogen peroxide are formed by the suggested recombination process or by an equivalent direct dissociation of two water molecules into hydrogen and hydrogen peroxide.

Reactions 1 and 2 are, however, inadequate to account for the high chemical yields found in the oxidation of ferrous sulfate if the radical pair and molecular products yields for dilute solutions are used.[17] In view of recent experimental evidence by Dainton and Sutton[18] that hydrogen peroxide in excess of hydrogen is found in dilute ferrous sulfate solutions, Allen[19] has been led to posulate net reaction 3 in order to explain the stoichiometry of ferrous ion oxidation

$$H_2O = H + {}^1/_2H_2O_2 \qquad (3)$$

This reaction may arise as a result of the stabilization of the hydrogen atom by hydrogen, bisulfate of sulfate ions and permit the recombination of hydroxyl radicals within the expanding reaction spur. In any case, reaction 3 provides hydrogen atoms in excess of those formed in reaction 1. In the absence of more detailed information regarding the mechanism of free radical and molecular product formation, reactions 1, 2 and 3 state the empirical facts that hydrogen atoms in excess of hydroxyl radicals and hydrogen peroxide in excess of hydrogen are formed by the ionizing particles.

In aerated ferrous sulfate–0.8 N sulfuric acid solutions, decomposition of a water molecule by each of reactions 1 and 3 results in the oxidation of four ferrous ions, while one ferrous ion is oxidized per water molecule dissociated in 2. The yield of ferric ion is thus

$$G_{Fe^{+++}} = 4G_{(1)} + G_{(2)} + 4G_{(3)} \qquad (4)$$

where $G_{(1)}$, $G_{(2)}$ and $G_{(3)}$ are the yields of water molecules decomposed/100 ev. in stoichiometric reactions 1, 2 and 3, respectively. The relative proportions of water molecules decomposed by ionizing radiations depend on the ionization density characteristics of the radiation. Heavily ionizing nuclear particles induce principally 2, while high energy electrons (including β-particles and recoil electrons from γ-ray absorption) result in high yields of 1.[17]

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(17) E. J. Hart, "Radiation Research," in press.

(18) F. S. Dainton and H. C. Sutton, *Discs. Faraday Soc.*, No. 12, 121 (1952); *Trans. Faraday Soc.*, **49**, 1011 (1953).

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Allen's calculation of $G_{(3)}$[19] utilized data for $G_{(1)}$ and $G_{(2)}$ obtained by studies on hydrogen and hydrogen peroxide production in ferrous sulfate and ceric sulfate solutions. Reaction 3 has recently been experimentally confirmed by the formic acid–oxygen method of measuring radical pair yields and found to be highly dependent on hydrogen ion concentration in the *p*H range from 0.32 to 3.0.[20] At a *p*H of 3.0, the yield of reaction 3 is substantially zero. Reactions 1 and 2, on the other hand, are dependent on *p*H but to a lesser extent. The evidence for reaction 3 as deduced from the formic acid–oxygen data depends on measurements of radiation yields of carbon dioxide, hydrogen and hydrogen peroxide formed and oxygen reacted. Interpretation of the yields of these data obtained in the *p*H range from 0.32 to 3.0 requires the use of reaction 3.

In view of this dependence on *p*H, it is not possible to use the values for $G_{(1)}$ and $G_{(2)}$ measured by the formic acid–oxygen method in 0.001 N sulfuric acid and apply them directly to the present ferrous sulfate irradiations which were run at *p*H 0.5 in 0.8 N sulfuric acid. However, by using the values of 2.35, 0.46 and 1.42 reported by Hart[20] for $G_{(1)}$, $G_{(2)}$ and $G_{(3)}$ for Co^{60} γ-rays at *p*H 0.32, a value for $G_{Fe^{+++}}$ of 15.5 is obtained from eq. 4. This excellent agreement with the experimental value of 15.6 indicates that one may calculate ferric ion yields from $G_{(1)}$, $G_{(2)}$ and $G_{(3)}$ obtained from formic acid–oxygen results provided measurements have been carried out at the proper *p*H. Allen's computed values for Co^{60} γ-rays are 2.86, 0.96 and 0.78 for $G_{(1)}$, $G_{(2)}$ and $G_{(3)}$, respectively.[19] The principal difference lies in the value employed for $G_{(2)}$ and this value in turn affects $G_{(3)}$. $G_{H_2O_2}$ formed initially through reactions 1 and 2 in the present work equals $1/2(G_{(2)} + G_{(3)})$ or 0.94 and lies in the upper range reported by Dainton and Sutton[18] for the molecular hydrogen peroxide yield, designated $G^{M}_{H_2O_2}$ by them, of 0.55–0.94.

$G_{(1)}$, $G_{(2)}$ and $G_{(3)}$ have not been measured in formic acid–oxygen–0.8 N sulfuric acid for ionizing radiations other than Co^{60} γ-rays. However, it is possible to estimate $G_{(3)}$ from eq. 4 for a known $G_{Fe^{+++}}$ provided a satisfactory estimate of $G_{(1)}$ and $G_{(2)}$ can be made for the ionizing radiation concerned. $G_{(1)}$ and $G_{(2)}$ have been measured for Po^{210} α-rays in formic acid–oxygen–0.8 N sulfuric acid and these results can be used directly in eq. 4. Correction in the values of $G_{(1)}$ and $G_{(2)}$ for tritium β-rays and $B^{10}(n,\alpha)Li^7$ recoil radiations determined in 0.001 N sulfuric acid must be made in order to estimate $G_{(3)}$ from our ferric yields obtained using these radiations. Since reactions 1 and 2 are affected by *p*H for γ-rays, it is assumed that they are influenced in a similar manner for all types of radiation regardless of the relative proportions of 1 and 2. The ratio $G_{(1)}(1\ N\ H_2SO_4)/G_{(1)}(0.001\ N\ H_2SO_4)$ is 0.83 and the ratio $G_{(2)}(1\ N\ H_2SO_4)/G_{(2)}(0.001\ N\ H_2SO_4)$ is 0.64 for Co^{60} γ-rays. In calculating $G_{(3)}$ from eq. 4 it is assumed that $G_{(1)}$ and $G_{(2)}$ in 0.8 N sulfuric acid for a given radiation can be obtained from $G_{(1)}$ and $G_{(2)}$ measured in 0.001 N sulfuric acid by multiplying by 0.83 and 0.64, respectively. The values so calculated for tritium β-rays and the $B^{10}(n,\alpha)Li^7$ radiations appear in Table II and are designated $G_{(1)}$(calcd.) and $G_{(2)}$(calcd.).

TABLE II

FREE RADICAL AND MOLECULAR PRODUCTS YIELDS IN 0.8 N SULFURIC ACID SOLUTION

Radiation	Co^{60} γ-rays	H^3 β-rays	Po^{210} α-rays	B^{10} $(n,\alpha)Li^7$
Energy (Mev.)	*ca.* 0.5^a	0.00569	5.30	2.35
$G_{Fe^{+++}}$ (exp.)	15.6	12.9	6.2	4.2
$G_{(1)}$ (calcd.)	2.35^b	1.95	0.43^b	0.22
$G_{(2)}$ (calcd.)	0.46^b	0.65	3.14^b	2.01
$G_{(3)}$ (calcd.)	1.42^b	1.11	0.34	0.32

[a] Mean energy of Compton recoil electrons. [b] Experimental values. The experimental $G_{(1)}$ and $G_{(2)}$ for H^3 β-rays, Po^{210} α-rays and $B^{10}(n,\alpha)Li^7$ radiation are obtained from ref. 18 and the calculated values obtained according to the procedure given in the text.

It can be seen from Table II that the yields for reactions 1 and 2, as determined by the formic acid method, do not account quantitatively for the experimental $G_{Fe^{+++}}$ values without the assumption of reaction 3. The values for $G_{(3)}$ are somewhat different from those calculated by Allen. The absolute magnitude of $G_{(3)}$ decreases with increasing track density of ionization of the ionizing particle.

It is not possible to calculate accurately the independent G-values for the oxidation induced by the α-particles and recoil products of the neutron reactions, at the various energies, but if it is assumed that the effective density of ionization for the α-particle is less than that of the lithium fragment in the boron reaction and greater than that of the tritium fragment in the lithium reaction, an estimation can be made. In such a case the composite G-value as measured will represent a minimum value for the 1.47 Mev. α-particle of the $B^{10}(n,\alpha)Li^7$ reaction and a maximum for the 2.05 Mev. α-particle of the $Li^6(n,\alpha)H^3$ reaction, as indicated in Fig. 1. The $G_{Fe^{+++}}$ for α-radiation can be seen to increase from a value somewhat over four in the one Mev. range to a value of six for a five Mev. particle.

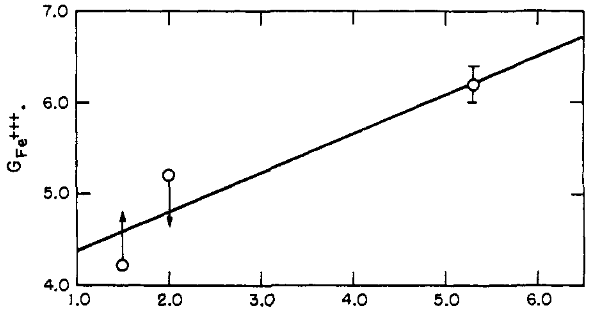

Fig. 1.—Variation of yield with energy for the α-radiation induced oxidation of ferrous ion in 0.8 N sulfuric acid solution.

This interpretation is in agreement with the work of Toulis, who found the yields of hydrogen and hydrogen peroxide in the decomposition of water decreased as the energy of cyclotron-

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(20) E. J. Hart, to be published.

accelerated protons and helium ions was increased.[21]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Kinetics of Precipitate Formation: Barium Sulfate[1]

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In the early stage of precipitation, the reaction is limited by nucleation and the slow growth of the newly-formed crystals. The sharp termination of the induction period arises from the autoinductive nature of the growth process. Autoinduction arises because the rate of growth is kinetically dependent upon the surface, and, as growth proceeds, the surface increases causing the rate of growth to increase. The precipitation process is interpreted as being initially controlled by the nucleation reaction and finally controlled by the growth reaction. During the first part of the induction period, only a few crystals are present and they grow so slowly that precipitation does not appear to take place. Near the end of the induction period, the "oldest" crystals attain considerable surface area and begin to grow rapidly. At the end of the induction period these crystals begin to reduce the concentration of the solution so rapidly that the smaller crystals are never able to reach a comparable size. After the "oldest" crystals begin to grow rapidly, they dominate the further precipitation and the precipitate approaches homogeneity with respect to crystal size. Theoretical equations based on these concepts have been derived and are well supported by experimental data. The first part of the precipitation process is represented by a relationship which takes into account the simultaneous nucleation and growth reactions. The equation fits the experimental data very well for times up to approximately twice the length of the induction period. For the remainder of the precipitation process the nucleation reaction is considered to be negligible and the rate equation involves only the growth reaction operating on a respective fixed number of particles. From consideration of the equations, and the experimentally determined constants, it has been found that the number of crystals is constant in the activity range examined.

Introduction

In the course of precipitate formation from very dilute solutions, two stages are observed: the induction period and the growth period. In the induction period, metastable systems of relatively great supersaturations may exist for considerable lengths of time without producing a visible precipitate. The induction period is terminated rather abruptly by the appearance of the precipitate. The growth stage follows during which precipitation occurs relatively rapidly, the particles grow, and the supersaturation is relieved.

From the standpoint of reaction mechanism, precipitate formation is considered to be a two-step process, the steps being nucleation and growth. The nucleation step involves the buildup of clusters, clusters being those entities which are part of the mother phase and which tend to dissociate. The nucleation step is culminated as the entities attain a critical size, beyond which the stability pattern is reversed and the particles tend to grow. The entities which have attained the critical size are called nuclei and are a new phase. The growth stage involves their development.

The empirical equation

$$I = \lambda C_0^{-n} \qquad (1)$$

has been fitted to the induction period data of many slightly soluble salts by some investigators.[2-6] In equation 1, I is the induction period, C_0 is the initial molar concentration, λ and n are constants. Christiansen and Nielsen[7] proposed that n was related to the order of the nucleation reaction. LaMer[8] has discussed this proposal with respect to the data of LaMer and Dinegar.[9] Duke[10] as well as Turnbull[11] proposed that the nucleation process takes place only during mixing and that growth of these first nuclei is responsible for the induction period and growth behavior. Christiansen and Nielsen[12] derived equations treating the nucleation and growth processes separately and fitted their equations to the data of Tovborg Jensen.[3] Large deviation from the theoretical curve during the first part of the precipitation process was attributed to the invalidity of the assumption that the crystals were of the same age.

Processes in the Induction Period.—The rate of growth of a single crystal may be represented by

$$\frac{da}{dt} = -k(C_0 - C)^{2/3} \times a^q \qquad (2a)$$

where a is mean ionic activity, $\sqrt{(Ba^{++})(SO_4^{=})}$, at time t, C_0 and C are molar concentrations of barium sulfate available for precipitation at the initial time and at time t, respectively, and k and q are constants. The term in the parentheses is in molar concentration units since it relates mass to

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[1] Material in this paper has been taken from the Ph.D. thesis of J. D. O'Rourke and was presented before the Colloid Division at the 124th Meeting of the American Chemical Society in Chicago, Sept. 1953.

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