The Radiation-Induced Oxidation of Stannous Chloride in Aqueous Hydrochloric Acid

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(Received January 5, 1962)

Numerous investigators[1-6] in recent years have suggested a radical diffusion model for various radiation-induced chemical reactions in aqueous media. According to this model radiation-induced chemical reactions in aqueous solutions are initiated by radicals generated from water as a result of energy degradation processes. In fact, a few supporting evidences[7-9] have been presented in the study of the effect of gamma irradiation from cobalt-60 on ferrous sulfate in 0.8 N sulfuric acid.

For this model investigations of the radiation-induced oxidations or reductions of other inorganic compounds in aqueous media have been studied by many workers[10-14]. Solutions of oxidizing agents are reduced by gamma irradiation usually in a yield of about 2.3 atom-equivalents per 100 eV. While, these of common reducing agents are oxidized in the same yield as that of hydrogen gas formed, the radiation-induced oxidation of stannous to stannic ion was also investigated as one of these reactions and could be used for chemical dosimetry.

Aqueous hydrochloric acid solution of stannous ion, exposed to the gamma irradiation

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from cobalt-60, yields stannic ion and hydrogen gas as the products. This system is of particular interest because of the transfer of two electrons is involved in the oxidation of stannous to stannic ion. Since stannous ion is powerful reducing agent in aqueous solutions, it could be used as a scavenger for radicals produced in the irradiation of aqueous solution, and also as a chemical dosimeter.

Boyle, Weiner and Hochanadel[15)] have studied the irradiation of stannous ion in aqueous sulfuric acid and mixtures of stannous ion with ferrous and ferric ion. All their experiments were carried out in 0.8 N sulfuric acid. Amell[16)] studied the irradiation of stannous chloride in aqueous hydrochloric acid, but his study has to be extend further in detail in order to use this reaction for chemical dosimetry. Therefore, we have undertaken this investigation.

Experimental

Irradiations.—Cylindrical and basket style sources of cobalt-60 gamma rays, which have 1000 and 3800 curies respectively, were used. Energy absorption in solutions was determined with the Fricke ferrous sulfate dosimeter taking G as 15.6[9)]. Initial dose rate values for the two sources are shown in Table I. The dose rates were corrected for decay. All the irradiations were carried out at ambient temperature between 27 and 32°C.

For continuous measurements, a dropping mercury apparatus with mercury pool electrolysis cell was placed in the irradiation room, while lead wires were led outside from the room, and were connected with a polarographic recorder. The measurements of polarogram were taken periodically during the irradiations.

TABLE I. DOSE RATES ON THE VARIOUS POSITIONS AT THE IRRADIATION FACILITIES

Co-60 source curies	Distance from source to sample cm.	Dose rate $\times 10^{19}$ eV./l. min.
3800	15	10.3
3800	20	6.8
1000	12	3.7
1000	20.5	2.0

Preparation of Solutions.—Water used was prepared by at first distillation over acid permanganate, then over alkaline permanganate, and finally by ordinary distillation. This water was used throughout this experiment. Solutions used for irradiation were made oxygen free. Because of rapid air oxidation of stannous ion it was necessary to avoid oxygen during preparation, irradiation and analysis of the solution. Stock solution of stannous chloride was prepared by dissolving reagent grade stannous chloride in concentrated hydrochloric acid and diluting with water to the final desired concentrations for both stannous ion and the acid. These solutions were stored in nitrogen atmosphere to minimize the oxidation of the stannous ion by oxygen.

Standard solutions of stannic ion were prepared by dissolving reagent grade stannic chloride. The concentration of stannic ion was determined gravimetrically as stannic oxide.

Deaerated solutions of the stannous chloride (0.5~3 mM) in 6 N hydrochloric acid were used in most cases. The solutions were then irradiated and analyzed in the following method.

Analytical Methods.—The stannous and stannic ion were determined polarographically, using a Yanagimoto PA-101 polarography with the temperature controlled at 30±1°C. The reduction of stannic to stannous ion produces wave suitable for this analytical purpose when the supporting electrolyte was 6 N hydrochloric acid. This wave is diffusion controlled and occurring at a half-wave potential of −0.25 V. vs. S. C. E. The measurements were taken in mercury pool electrolysis cell. The diffusion constant for stannic ion used in this study were taken by $I=i_d/m^{2/3}t^{1/6}c=4.77\ \mu$A/mM.

Dissolved oxygen was removed satisfactorily by bubbling nitrogen through the solution for 10 min. before each polarographic determination. The nitrogen stream was purified by bubbling through alkaline pyrogallol solution and distilled water.

The polarographic measurements were made both by the ordinary method and continuous measurement method. The former determined diffusion current difference between non-irradiated sample and irradiated sample. This difference corresponds to conversion value from stannous to stannic ion. Analyses generally were made within half an hour after taking out the sample from the irradiation room. Continuous measurements were taken during the irradiations, where variation of measurements appeared to have no effect on diffusion current.

Results and Discussion

The effects of irradiation time, initial stannous ion concentration, stannic ion concentration and dissolved oxygen on the yield were investigated.

Irradiation Time.—Figure 1 shows a fews plots of stannic ion formed against irradiation time. The amount of stannic ion formed from stannous ion in hydrochloric acid is proportional to that of energy absorbed up to at least 5×10^{22} eV./l. and is essentially independent of dose rate. The G-values obtained from stannic ion formation are shown in Table II. The continuous measurement method gave a variety of formation curves of stannic ion. A few typical curves for stannic ion formation are shown in Fig. 2. However, in most cases we obtained curve similar to B, which indicate that the rate of oxidation is a linear function of irradiation time over the range we studied.

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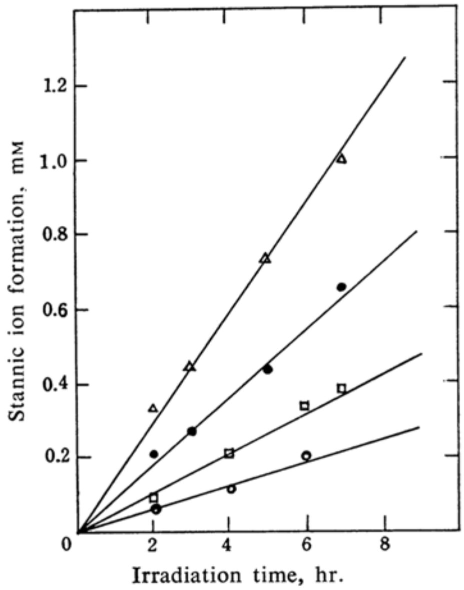

Fig. 1. Formation of stannic ion in deaerated solution of 6 N hydrochloric acid.

Initial stannous chloride concentration; 0.5 $\sim 3\times10^{-3}$ M

Dose rate; △ 10.3×10^{19} eV./l. min.
● 6.8×10^{19} eV./l. min.
□ 3.7×10^{19} eV./l. min.
○ 2.0×10^{19} eV./l. min.

Table II. The G-values for stannic ion formation

Deaerated solutions of the stannous chloride in 6 N hydrochloric acid were irradiated.

Dose rate $\times10^{19}$ eV. /l. min.	Oxidation rate mM/hr.	G-value
10.3	0.146	1.4_1
6.8	0.091	1.3_5
3.7	0.052	1.4_1
2.0	0.031	1.5_7
2.0	0.021	1.0_1[a]

a) In 0.8 N hydrochloric acid

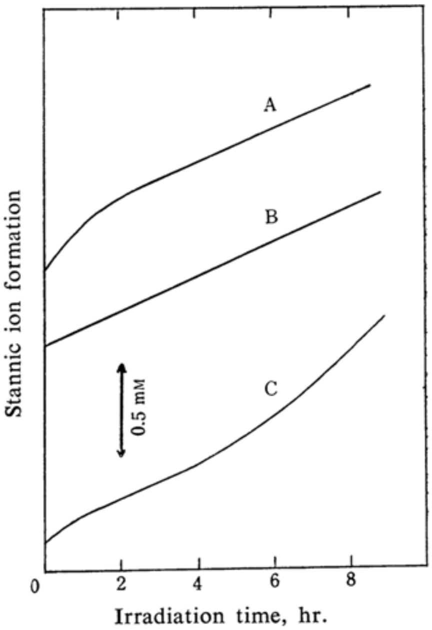

Fig. 2. Various formation curves of stannic ion on continuous measurement method.
Initial concentration;
A Sn(II) 2.87 mM, Sn(IV) 0.43 mM
B Sn(II) 2.16 mM, Sn(IV) 0.14 mM
C Sn(II) 1.57 mM, Sn(IV) 1.03 mM
Dose rate; 6.8×10^{19} eV./l. min.

Fricke and Hart[17,18] irradiated with X-rays air-free solutions of a number of common reducing agents. The pH for the most of these solutions was varied over a wide range from 2 to 11. In most cases the amounts of reducing agents oxidized are equivalent to $G_{H_2}=0.5=G_{H_2O_2}-(G_H-G_{OH})/2$. While in air-free ferrous sulfate solutions ferrous ion is oxidized in a yield of $G(\mathrm{Fe(III)})=8.2=G_H+G_{OH}+2G_{H_2O_2}$[7-9].

Boyle et al.[15] reported that the yield of $G(\mathrm{Sn(IV)})=0.49$ is equivalent to G_{H_2} in 0.8 N sulfuric acid solutions by the gamma irradiation, indicating that oxidation is done by H_2O_2 and OH and reduction by H.

In aqueous hydrochloric acid the yield $G(\mathrm{Sn(IV)})=1.50$ was shown by Amell[16]. It is interesting to note the marked difference of G-values between 0.8 N sulfuric acid and hydrochloric acid. This difference was explained by Amell that stannous ion forms many different complex ions with chloride ion as the concentration is changed, thus be changing the reacting species which have both different oxidation potentials and different rates of reaction.

Using the values for the individual radical and molecular yield generated from water, the following sequence should give rise to the G-value.

$$H_2O \rightsquigarrow H + OH + H_2O_2 + H_2 \qquad (1)$$

$$\mathrm{Sn(II)} + OH \rightarrow \mathrm{Sn(III)} + OH^- \qquad (2)$$

$$\mathrm{Sn(III)} + OH \rightarrow \mathrm{Sn(IV)} + OH^- \qquad (3)$$

$$2\,\mathrm{Sn(III)} \rightarrow \mathrm{Sn(II)} + \mathrm{Sn(IV)} \qquad (4)$$

The results can be interpreted to mean that the tin is being oxidized by OH only while H does not react with anything, but merely combine with itself to forms H_2. In view of the abundant evidences for the general high reactivity of H and OH, it seems quite unlikely that these radicals can wait around to

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[17] H. Fricke and E. J. Hart, *J. Chem. Phys.*, 3, 365 (1935).
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combine with one another in the presence of such chemically reactive species as stannous chloride. More likely, the H atoms can reduce Sn(II) to Sn(I), and can also oxidize Sn(II) to Sn(III) as follows.

$$\mathrm{Sn(II)} + \mathrm{H} \rightarrow \mathrm{Sn(I)} + \mathrm{H}^+ \qquad (5)$$

$$\mathrm{Sn(II)} + \mathrm{H} + \mathrm{H}^+ \rightarrow \mathrm{Sn(III)} + \mathrm{H}_2 \qquad (6)$$

$$\mathrm{Sn(I)} + \mathrm{Sn(III)} \rightarrow 2\,\mathrm{Sn(II)} \qquad (7)$$

The oxidation-reduction potential calls for all of these stannous ions to be oxidized by hydrogen peroxide. Nevertheless, the reaction between stannous ion and hydrogen peroxide is apparently slow, and $G(\mathrm{Sn(IV)})$ to be equal to $G_{\mathrm{OH}}/2+G_{\mathrm{H_2O_2}}$ if this reaction is occurring.

Hydrochloric acid in contrast to sulfuric acid, is relatively less stable to irradiation. Chloride ion does not react effectively with OH in neutral solutions, probably because of the reaction

$$\mathrm{Cl}^- + \mathrm{OH} \rightarrow \mathrm{OH}^- + \mathrm{Cl} \qquad (8)$$

is endothermic. However, the reaction

$$\mathrm{Cl}^- + \mathrm{OH} + \mathrm{H}^+ \rightarrow \mathrm{H_2O} + \mathrm{Cl} \qquad (9)$$

is exothermic and chloride ion does react with OH in acid solution. The rate of reaction of Cl^- with OH would therefore be expected to increase with acid concentration and in fact, it is found that chloride ion changes as chlorine radical and the radical reacts with stannous ion the higher acid concentration.

On the other hand, the increase of *G*-value at higher acid concentrations is probably due to the direct deposition of energy by irradiation into the chloride ion. This becomes important at higher concentrations of hydrochloric acid, and leads to oxidation in a higher yield over that of the formation of radicals from water alone.

$$\mathrm{Cl}^- \rightsquigarrow \mathrm{Cl} \qquad (10)$$

$$\mathrm{Sn(II)} + \mathrm{Cl} \rightarrow \mathrm{Sn(III)} + \mathrm{Cl}^- \qquad (11)$$

$$\mathrm{Sn(III)} + \mathrm{Cl} \rightarrow \mathrm{Sn(IV)} + \mathrm{Cl}^- \qquad (12)$$

Effect of Initial Stannic Ion Concentration.—To determine the effect of the initial concentration of stannous ion on the oxidation, various solutions were prepared for irradiation. These solutions differed only in stannous ion concentration. The results of these concentration are shown in Fig. 1. Within these concentrations (0.5∼3 mM) there is no effect of stannous ion concentration on the oxidation.

Effect of Stannic Ion Concentration.—The concentration of stannic ion was varied to determine this effect. After the stannous ion is half depleted, stannous ion is oxidized at the rate which depends on stannic ion as shown by Fig. 2–C curve. The *G*-value as a function of stannic ion is given in Fig. 3.

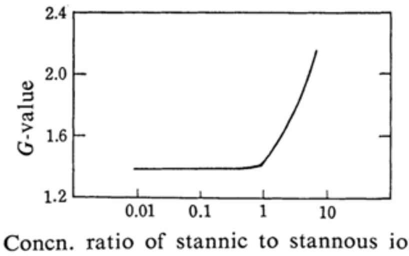

Fig. 3. Effect of stannic ion concentration.
Sn(II)+Sn(IV) ; 1.57×10^{-3} M in 6 N HCl
Dose rate ; 3.7×10^{19} eV./l. min.

The *G*-value from the radiation-induced oxidation of stannous and stannic ion mixtures is significantly higher than that obtained by stannous ion alone. Although we can offer no statisfactory explanation for this difference, it is probably due to the catalytic effect of stannic ion in the reaction of stannous ion with hydrogen peroxide.

Dissolved Oxygen. — Various experiments showed that the oxidation of stannous ion by irradiation is greatly increased when oxygen or air is present. This is seen in Fig. 2–A. After oxygen is depleted, formation curve shows linearity. Thoroughly bubbled solution by purified nitrogen gas does not show any increase of oxidation.

Application for Dosimetry

The good reproducible data obtained on the determinations of stannic ion suggest that this system can be used as a dosimeter for higher doses of irradiation. The analysis of stannous or stannic ion can be performed conveniently. However, it should be pointed out that even though the oxidation of stannous ion is pre-

TABLE III. REPRODUCIBLE RESULTS OF CHEMICAL DOSIMETRY

Irradiation dose	Conversion value	Reproducibility	
		Range	Standard deviation
×10⁵ r.	mM	mM	mM
4.20	0.66 0.59 0.58 0.57	0.09	0.04
2.79	0.42 0.36 0.34 0.37	0.08	0.03
1.51	0.18 0.21 0.22 0.22	0.04	0.02
0.82	0.14 0.11 0.13 0.13	0.03	0.01

sented to be the reaction only with OH radical, the quantities of products involved are still quite small. Consequently, for doses less than 10^4 r., microtechniques would have to be employed. By irradiating 1 cc. of 6 N hydrochloric acid solution of stannous ion one would expect only 1.4×10^{-5} mmol. of stannic ion to be produced by 10^4 r.

Summary

The radiation-induced oxidation of stannous to stannic ion in aqueous hydrochloric acid has been studied and that this system is proposed as a chemical dosimeter for higher doses.

The amount of oxidation is proportional to the energy absorbed and the yield of stannic ion is independent of dose rate and initial stannous chloride concentration over a wide range studied, but increases when stannic conconcentration is high or oxygen is present. Mechanism for this oxidation based on G-values is discussed in terms of the primary decomposition products of water radiolysis. The results can be interpreted to mean that the stannic ion is oxidized only by OH radical. This system could be used for a chemical dosimeter having 8% reproducibility.

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