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Gamma Radiolysis of Ceric Systems in Sulfuric Acid Solution

by

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Gamma Radiolysis of Ceric Systems in Sulfuric Acid Solution *

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It is known that ceric ions are reduced into cerous ions when ceric sulfate solutions are irradiated by γ rays in the presence of sulfuric acid.

In this work we have found that the amount of cerous ions produced depends on the concentration of sulfuric acid. The inital yield of cerous ions decreases from 3.08 to 2.35 when the acid concentration increases from 0.4 N to 1.6 N. The amount of ceric reduced was not proportional to the total dose and $G(Ce^{+3})$ decreased with decraesing $(Ce^{+4})/(Ce^{+3})$ ratios.

Both deaerated stannous and stannic solutions were found to be affected by γ rays. The stannic yield was 1.23 when stannous solutions were irradiated, while a stannous yield of 0.29 was determined in irradiated stannic solutions.

Stannic ions were found to affect the radiolysis of ceric sulfate solutions. In irradiated $Ce(SO_4)_2+1.6N\ H_2SO_4$ solutions containing up to 40 mN $SnCl_4$,the cerous yield decreased continuously from 2.35 to 1.80. When the $SnCl_4$ concentration increases further, however, the cerous yield goes up gradually and after reaching the original value at 60 mN $SnCl_4$, continues to increase at a lover rate.

Ferric ions have the same effect as the stannic ions on the radiolysis of ceric sulfate with the only difference that the value for the minimum of $G(Ce^{+3})$ was lower (1.5). The doses were measured spectrophotometrically using the Fricke dosimeter system.

In each case a reaction mechanism is suggested explaining satisfactorily the experimental results presented in this work.

INTRODUCTION

The ceric sulfate system has been studied extensively by several authors to improve its utilisation as a standard and reproducible dosimeter at high doses. Some of these authors [1–8] have tried to clarify the mechanism of ceric radiolysis under

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* Part of this work was presented to the International Congress of Radiation Research, held in Cortina d'Ampezzo in June 1966.

various conditions, while orthers [9–13] have emphasized the possibility of using the ceric system as a satifactory dosimeter. In most of the investigations with ceric systems, the effect of added substances was to increase the cerous yield. In order to extend the dose limit of the ceric dosimeter the cerous yield should be lowered. Clark and Coe [14] and Master and Challenger [8] have shown that with x–rays and β –rays silver and cupric ions have a decreasing effect on the cerous yield. Müñoz and Miró [13] have studied the effect of cupric ions in 0,8N H_2SO_4 on ceric reduction using gamma rays and found a decrease in cerous yield.

Considering the effects of silver and cupric ions, we decided to study in this work the effects of stannic and ferric ions on the radiolysis of ceric system. As the reactions of high valency ions such as ceric, stannic and ferric are affected by the acidity of the solution, we have first studied the radiolysis of ceric system in various concentrations of sulfuric acid.

The work done [15–17] on stannic and stannous systems is very limited and, in order to explain the effect of stannic ions on ceric reduction mechanism, we have also reconsidered the radiolysis of stannous and stannic systems.

EXPERIMENTAL

An 800 curie cobalt–60 source was used for all irradiations and the doses were measured by the Fricke dosimeter with $G(Fe^{+++}) = 15.6$. The dose rate was $2x10^{20}$ ev/lt–min. Triple distilled water, obtained by distillation from alkaline permanganate and acidic bichromate was utilised for the preparation of solutions. Most of the determinations were carried out in DU Beckman Spectrophotometer. The extinction coefficients of ceric and ferric ions were 5433 at 318 mμ and 2226 at 303 mμ respectively.

Procedure. The preparation, irradiation and analysis of stannous and stannic solutions were carried out in an inert atmosphere. The experiments to see the effect of stannic and ferric ions on cerous yield however were carried out in air. As stannous chloride is easily oxidised in air it was necessary to dissolve pure metallic tin in hydrochloric acid in the absence of oxygen. For this purpose the flask shown in Figure 2 was utilised. After the preparation of the solution the head (B) of the flask was removed and it was attached to the apparatus in Figure 3. The solution in flask I was transferred with the help of nitrogen gas pressure to flask II where it was degassed. Then the degassed solution in flask II was transferred to the irradiation cell (20 ml volume) shown in Figure 1 (a) with the help of helium gas pressure. Some of the cells were irradiated and the rest were kept as blank.

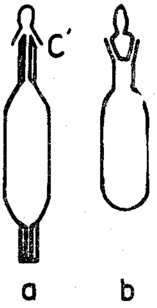

Fig. 1– Irradiation cells; a–for degassed solutions b– for aerated solutions.

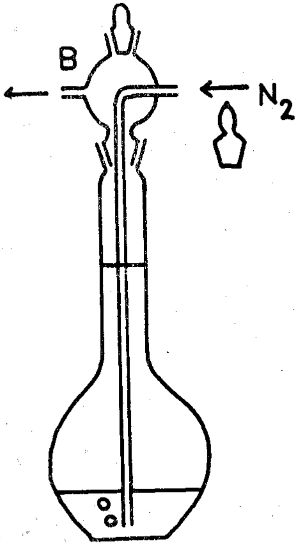

Fig. 2– Flask for the preparation of solutions under nitrogen.

A– For the spectrophotometric analysis of stannous ions in the solution the large glass container shown in Figure 4 was used. This container which was swept continuously with nitrogen, contained the measuring flasks. The irradiated solution was transferred into the flask shown in Figure 4 through the hole G. Then a suitable volume of this solution was added by a pipette to the other meassuring flask containing a known amount of ceric solution. After allowing ten minutes for the completion of the reaction the necessary dilution was made and the optical densities of the irradiated sample and blank were measured.

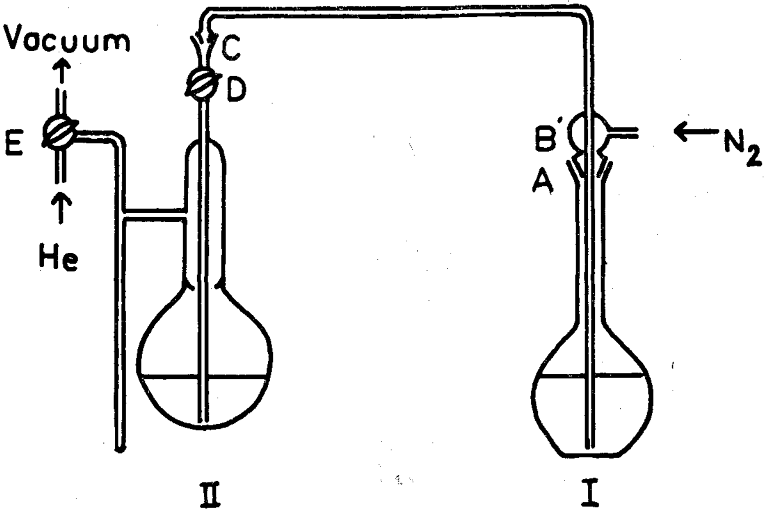

Fig. 3– Degassing of the solutions prepared under nitrogen.

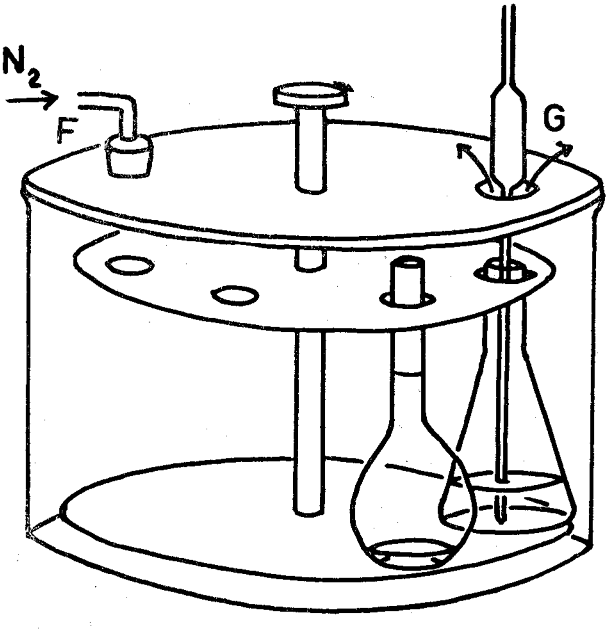

Fig. 4– Apparatus for the preparation of solutions before spectrophotometric meassurement, under nitrogen.

B– For the volumetric analysis of stannous ions the irradiated or unirradiated solution (prepared under nitrogen) was transfered into the flask shown in Figure 5 (a). Then a suitable volume of this was introduced by a pipette to the flask shown in Figure 5 (b), in which it was titrated with a standardised iodine solution.

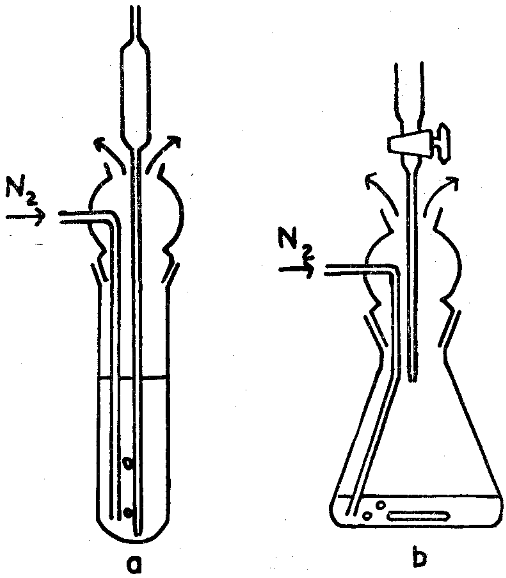

Fig. 5– Flasks for volumetric analysis of solutions under nitrogen.

C– For the spectrophotometric analysis of ceric ions containing stannic or ferric in air the irradiation cell shown in Figure 1 (b) was used and the optical densities of the sample and the blank were measured after proper dilution.

RESULTS AND CONCLUSIONS

I– Radiolysis of ceric sulfate solutions in various concentrations of sulfuric acid.

We have found experimentally that the radiolysis of ceric sulfate is affected by the concentration of sulfuric acid; therefore, we have irradiated ceric sulfate solutions, in air and in the presence of 0.4, 0.8, 1.2 and 1.6 N H_2SO_4. The results are given in Figure 6. The cerous yields corresponding to various

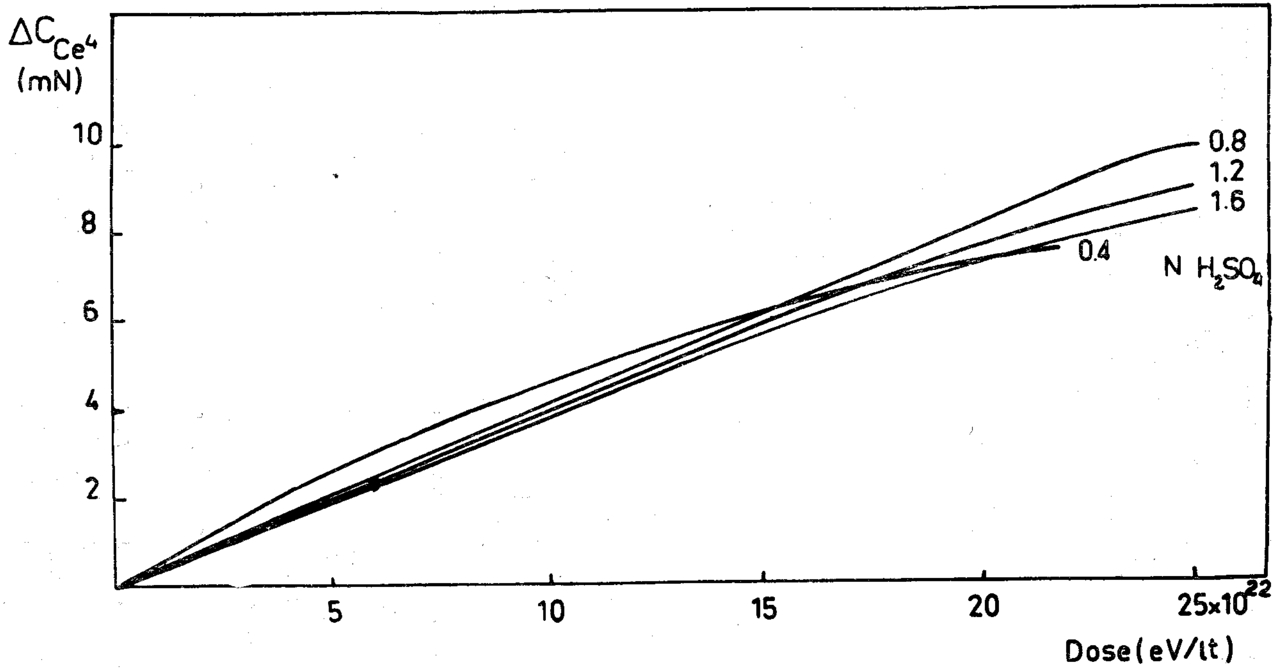

Fig. 6– Gamma radiolysis of ceric sulfate solutions with various con centrations of sulfuric acid.

doses are calculated from this figure are shown in Figure 7. It is seen from this figure that initial cerous yields are different for various sulfuric acid concentrations. Furthermore, when the concentration of sulfuric acid increases, the decrease of $G\,(_{Ce}{}^{+3})$ with the dose occurs at a higher rate. For 0 .8 N H_2SO_4, for instance, $G\,(_{Ce}{}^{+3})$ remains constant with dose, until almost all the ceric ions are consumed. For 1 .6 N H_2SO_4, $G\,(_{Ce}{}^{+3})$ begins to decrease at lower doses.

The reaction mechanism for the γ radiolysis of ceric system is [12]:

$$H_2O \xrightarrow{\gamma} H,\ OH,\ H_2,\ H_2O_2$$

$$Ce^{+4} + H \longrightarrow Ce^{+3} + H^{+} \qquad (1)$$

$$Ce^{+4} + H_2O_2 \longrightarrow Ce^{+3} + H^{+} + HO_2 \qquad (2)$$

$$Ce^{+4} + HO_2 \longrightarrow Ce^{+3} + H^{+} + O_2 \qquad (3)$$

$$Ce^{+3} + OH \longrightarrow Ce^{+4} + OH^{-} \qquad (4)$$

which leads to the following equation for $G\,(_{Ce}{}^{+3})$:

$$G\,(_{Ce}{}^{+3}) = G_{H} + 2\,G_{H_2O_2} - G_{OH}$$

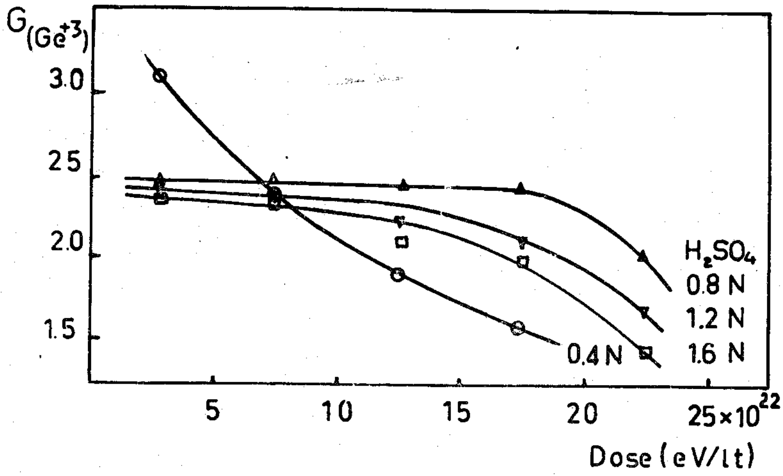

Fig. 7– The changes of $G(_{Ce}{}^{+3})$ in various concentrations of sulfuric acid, with dose.

The theoretical value found from this equation for the cerous yield in 0 .8 N H_2SO_4 is 2 .3 which agrees with the experimental results. The dependence of $G\,(_{Ce}{}^{+3})$ on sulfuric acid concentration can be explained by the above mentioned reaction steps. H+ is produced by reactions (1), (2) and (3) and consumed by (4). Actually reaction (4) for acidic solutions can be writen as follows:

$$Ce^{+3} + OH + H^{+} \longrightarrow Ce^{+4} + H_2O$$

Accordingly, reaction (4) is favored when the acid concentration is high while reactions (1)–(3) are hindered. This means that $G(_{Ce^{+3}})$ should decrease with increasing acid concentration, which is what we have found. The higher the acid concentration the sooner the lowering of $G(_{Ce^{+3}})$ is as shown in Figure 7. This observation also can be explained with the effect of H+ on reaction (4). The curve for 0 .4 N H_2SO_4 in Figure 7 does not agree with the other three, the reason for this discrepency could be the higher possibility of hydrolysis for ceric ions compared with cerous ions at low acid concentration.

II– Radiolysis of stannous chloride

The most suitable conditions for the irradiation of stannous chloride solution prepared under nitrogen atmosphere were found to be 20 mN stannous chloride in∼2N hydrochloric acid. The results are shown in Figure 8. The experimental data in this Figure give a stannic yield of $G\ (_{Sn^{+4}}) = 1.23$. This is in reasonably good agreement with the value of 1 .45 found by Amell [16] in 3N hydrochloric acid. Boyle and coworkers [15] have found a value of 0 .49 in sulfuric acid solution. Considering the reaction mechanism proposed by Amell and by Boyle and coworkers, one can write the following reaction spteps:

$$Sn^{+2} + OH \longrightarrow Sn^{+3} + OH^{-} \qquad (5)$$

$$Sn^{+2} + H \longrightarrow Sn^{+1} + H^{+} \qquad (6)$$

$$Sn^{+3} + Sn^{+3} \longrightarrow Sn^{+4} + Sn^{+2} \qquad (7)$$

$$Sn^{+1} + Sn^{+3} \longrightarrow 2Sn^{+2} \qquad (8)$$

$$Sn^{+4} + Sn^{+1} \longrightarrow Sn^{+3} + Sn^{+2} \qquad (9)$$

$$Sn^{+2} + H_2O_2 \longrightarrow Sn^{+3} + OH + OH^{-} \qquad (10)$$

$$Sn^{+2} + H + H^{+} \longrightarrow Sn^{+3} + H_2 \qquad (11)$$

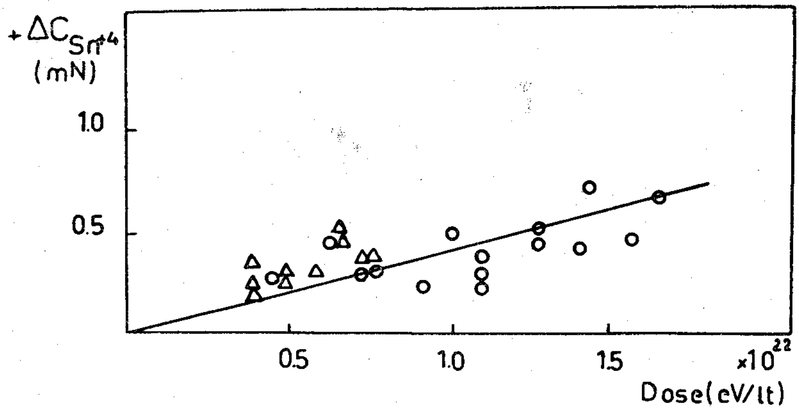

Fig. 8– Results of gamma radiolysis of acidic stannous chloride solution.

In reaction (6) Sn^{+2} is reduced while in reaction (11) it is oxidised. Assuming that (11) does not occur:

$$G(Sn^{+4}) = G_{H_2O_2} + 1/2\ G_{OH} - 1/2\ G_H = G_{H_2} = 0.45$$

The values found in hydrochloric acid solutions by us and by Amell for $G(Sn^{+4})$ are much higher. On the other hand, assuming that reaction (11) occurs rather than (6)

$$G(Sn^{+4}) = G_{H_2O_2} + 1/2\ G_{OH} + 1/2\ G_H = 4.1$$

The value found in this work (1.23) and that of Amell (1.45) are in between the above values of 0.45 and 4.1, which proves once again that both reactions (6) and (11) occur but at various ratios depending on the acid concentration.

III– Radiolysis of stannic chloride

20 mN stannic chloride solutions in 1.6 N H_2SO_4 prepared under nitrogen were used for irradiation. This concentration of sulfuric acid was found to be most suitable for working with the ceric – stannic systems. The results are given in Figure 9. The yield is $G(Sn^{+2}) = 0.29$

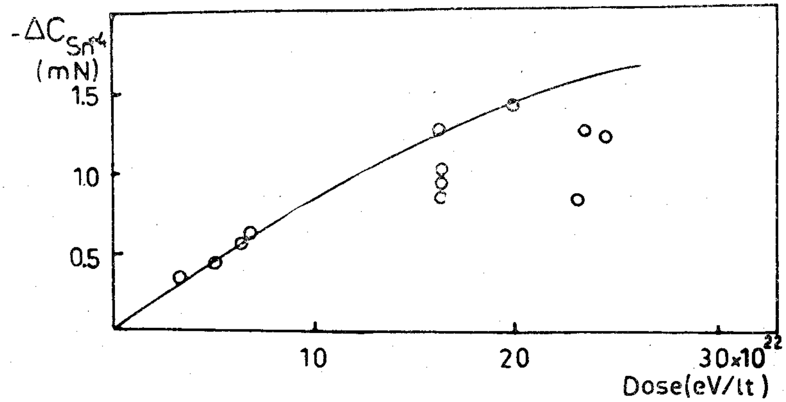

Fig. 9– Results of gamma radiolysis of acidic stannic chloride solution.

The following reaction steps are proposed:

$Sn^{+4} + H \longrightarrow Sn^{+3} + H^{+}$ (12)
$Sn^{+4} + H_2O_2 \longrightarrow Sn^{+3} + HO_2 + H^{+}$ (13)
$Sn^{+4} + HO_2 \longrightarrow Sn^{+3} + H^{+} + O_2$ (14)
$Sn^{+3} + Sn^{+3} \longrightarrow Sn^{+4} + Sn^{+2}$ (7)
$Sn^{+2} + H_2O_2 \longrightarrow Sn^{+3} + OH + OH^{-}$ (10)
$Sn^{+2} + OH \longrightarrow Sn^{+3} + OH^{-}$ (5)

Considering that hydrogen peroxide can act as an oxidising and reducing agent it is possible to write:

$$G(_{Sn^{+2}}) = 1/2\ G_H - 1/2\ G_{OH} + G_{H_2O_2}\ \frac{k_{13}(Sn^{+4}) - k_{10}(Sn^{+2})}{k_{13}(Sn^{+4}) + k_{10}(Sn^{+2})}$$

We know that $1/2\ (G_H - G_{OH}) = 0.35$, while our experimental value for the stannous yield is $G(_{Sn^{+2}}) = 0.29$. This could be an indication that the net effect of hydrogen peroxide on $G\ (_{Sn^{+2}})$ should be a lowering effect and that it should have a small negative value. This is possible only if reactions (13) and (10) occur to the same extent. As the concentration of stannous ions is very small at the beginning of the radiolysis of the stannic solution, k_{13} (Sn^{+4}) can be smaller than k_{10} (Sn^{+2}) only if $k_{10} \gg k_{13}$. Therefore in many cases the negligence of k_{13} compared with k_{10} can be justified.

IV– Radiolysis of ceric sulfate in the presence of stannic and ferric chlorides.

10 mN ceric sulfate solutions in 1 .6 N H_2SO_4 were irradiated in the presence of various concentrations of stannic and ferric chlorides. Stannic chloride concentrations up to 320 mN were used. The total dose given to each sample was 4 .17x10^{22} ev/lt. The results are shown in Figure 10. G (Ce^{+3}) first decreased with increassing $SnCl_4$ concentration and went through a minimum value of G (Ce^{+3}) = 1 .8 at 40 mN $SnCl_4$. Then as the concentration increased further G (Ce^{+3}) increased rapidly until a concentration of 80 mN $SnCl_4$, beyond which the rate increase slowed down gradually until 120 mN $SnCl_4$. Between 120 mN and 320 mN $SnCl_4$ G(Ce^{+3}) continued to increase linearly.

Figure 10 also shows the effect of $FeCl_3$ on ceric sulfate radiolysis. Ferric chloride acts in the same way as $SnCl_4$ but the effect is stronger and gives a minimum value of G(Ce^{+3}) = 1 .5.

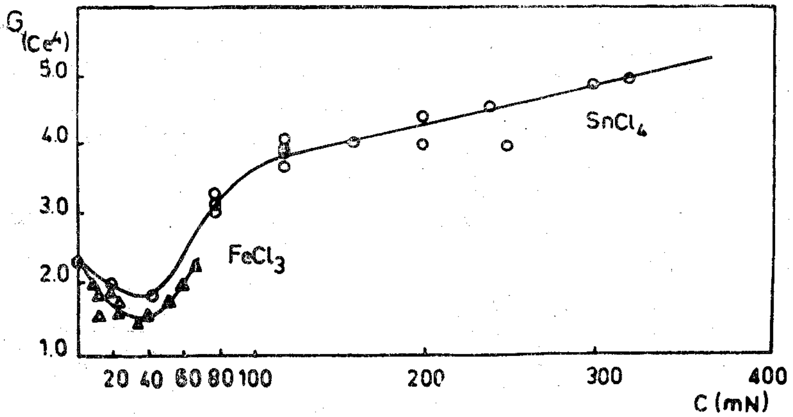

Fig. 10– The effect of stannic and ferric chlorides on the gamma radiolysis of acidic ceric sulfate solution.

We propose the following reaction steps to explain these results:

$$\begin{array}{llr}
Ce^{+4} + H \longrightarrow & Ce^{+3} + H^{+} & (1) \\
Ce^{+4} + H_2O_2 \longrightarrow & Ce^{+3} + HO_2 + H^{+} & (2) \\
Ce^{+4} + HO_2 \longrightarrow & Ce^{+3} + O_2 + H^{+} & (3) \\
Ce^{+3} + OH \longrightarrow & Ce^{+4} + OH^{-} & (4) \\
Sn^{+4} + H \longrightarrow & Sn^{+3} + H^{+} & (12) \\
Sn^{+4} + HO_2 \longrightarrow & Sn^{+3} + H^{+} + O_2 & (14) \\
Sn^{+3} + Sn^{+3} \longrightarrow & Sn^{+4} + Sn^{+2} & (7) \\
Sn^{+2} + OH \longrightarrow & Sn^{+3} + OH^{-} & (5) \\
Sn^{+3} + Ce^{+4} \longrightarrow & Sn^{+4} + Ce^{+3} & (15) \\
Sn^{+2} + Ce^{+4} \longrightarrow & Sn^{+3} + Ce^{+3} & (16) \\
Cl^{-} + OH \longrightarrow & Cl + OH^{-} & (17)
\end{array}$$

The possible reaction steps of ceric ions (1–4) are taken from the mechanism of Harlan and Hart[12]. The reaction of stannic ion with OH is not possible because OH is an oxidising agent. The reaction of stannic ion with H_2O_2 (reaction 13) can be neglected for reasons mentioned in part III ($k_{13} \ll k_{10}$). Furthermore, Boyle and coworkers [15] have shown that even (10) is a slow reaction. In the presence of oxgen almost all H radicals are in the form of HO_2, therefore, reaction (14) predominates. The reaction of H with Sn^{+2} (reaction 6) can be neglected because the concentrations of ceric and stannic are much higher than the concentration of stannous in the solution. Reaction (5) is included because stannous ions can compete with cerous ions for OH radicals.

The reaction steps proposed above lead to the following relationship:

$$G(Ce^{+3}) = G_H \frac{k_3(Ce^{+4})}{k_3(Ce^{+4}) + k_{14}(Sn^{+4})} + G_{H_2O_2}\left[1 + \frac{k_3(Ce^{+4})}{k_3(Ce^{+4}) + k_{14}(Sn^{+4})}\right]$$

$$-G_{OH} \frac{k_4(Ce^{+3})}{k_4(Ce^{+3}) + k_5(Sn^{+2}) + k_{17}(Cl^{-})}$$

In the absence of $SnCl_4$ all three fractions in the equation are equal to unity and we obtain the theoretical equation of $G(_{Ce}{}^{+3})$. With the increase of Sn^{+4} concentration the fractions in the first two terms become smaller than unity and this causes a decrease in $G(_{Ce}{}^{+3})$ as we have found experimentally. On the other hand, as the chloride concentration increases together with the stannic concentration, the fraction in the third term decreases because, in this case, the reaction

$$OH + Cl^- \longrightarrow OH^- + Cl \qquad (17)$$

takes place at a higher rate and becomes important as shown by Sworski [18].This decrease in the third term causes an increase in $G(_{Ce}{}^{+3})$, which takes place after 40 mN $SnCl_4$. When the concentration of $SnCl_4$ is increased further, hovever, the Cl^- concentration increases four times as much as Sn^{+4}. This allows the third term to be more effective after a certain concentration of $SnCl_4$.

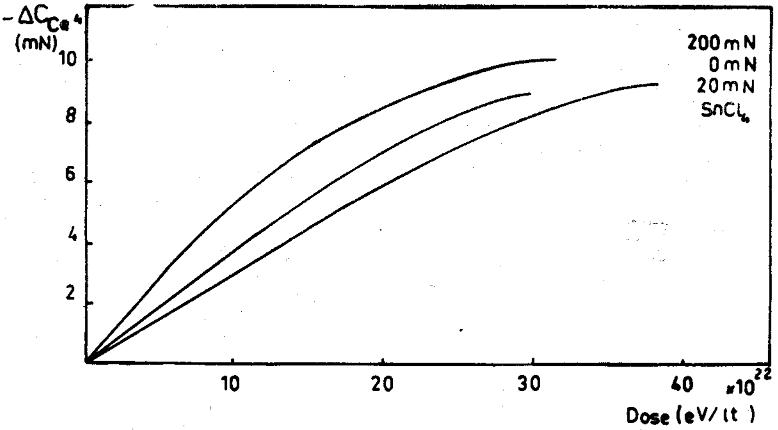

Fig. 11– Irradiation of ceric solutions in the presence of various concentrations of stannic chlorides.

The lower rate of increase after 120 mN $SnCl_4$ is difficult to explain. The lowering of the rate can happen in two ways only, reactions (1)–(3) should be suppressed or reaction (4) should be enhanced. The latter is impossible because of reaction (17), but the first case is possible because H radicals, for instance, may be consumed by

$$H + Cl \longrightarrow HCl \qquad (18)$$

The results of radiolysis of ceric system for three different stannic concentrations corresponding to different parts of the curve (0, 20, 200 mN $SnCl_4$) in Figure 10, are given in Figure 11. The curve for 20 mN $SnCl_4$ is the lowest and the one for 200 mN is the highest as expected. The lowest curve is almost linear while the highest curve reflects great changes in the value of cerous yield. All these results are in good agreement with the relationship suggested above for $G(_{Ce^{+3}})$.

It is concluded from our results and particularly from Figure 10 that the cerous yield can be lowered to some extent by the additions of $SnCl_4$ or $FeCl_3$ to 10 mN ceric sulfate in 1.6 N H_2SO_4. It might be worthwhile to investigate further the effects of other high valency cations as well as Sn^{+4} and Fe^{+3} under various conditions for a possible improvement of the ceric dosimeter system.

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ÖZET

Sülfürik asidli ortamda serium (IV) iyonlarından Co–60 gama ışınları etkisiyle serium (III) meydana gelmesi, ortamdaki H_2SO_4 konsantrasyonuna bağlıdır. H_2SO_4 konsantrasyonu 0.4 N den 1.6N e kadar değiştirilince $\sim 10^{20}$ ev/lt dak lık doz hızı için başlangıçtaki $G(Ce^{+3})$ değerleri 3.08 den 2.35 e düşmektedir. Ayrıca her bir asid konsantrasyonunda meydana gelen serium (III) miktarı toplam doz ile linear olarak değişmemekte ve çözelti içinde Ce^{+4} azalıp Ce^{+4}/Ce^{+3} oranı büyüdükçe $G(Ce^{+3})$ değeri küçülmektedir. Bu fark asid konsantrasyonu arttıkça artmaktadır.

Sn(IV) ve Sn(II) ihtiva eden asidli çözeltiler ayrı ayrı Co–60 γ ışınları etkisi ile değişikliğe uğramaktadırlar. Bu etki Sn(II) çözeltileri halinde daha fazladır, $G(Sn^{+4}) = 1.23$ kadardır. Normal şartlarda serium (IV) ve kalay (IV) ihtiva eden çözeltilerde bir reaksiyon olmadığı halde serium(IV)çözeltilerinin radyolizi esnasında ilâve edilen $SnCl_4$ $G(Ce^{+3})$ değerini değiştirmektedir. 1,6 N H_2SO_4 lü ortamda 10 mN Ce^{+4} ihtiva eden çözeltilerde $G(Ce^{+3})$ değeri ilâve edilen $SnCl_4$ belli bir konsantrasyona gelinceye kadar küçülmekte, bir minimumdan geçmekte fakat Sn(IV) konsantrasyonu daha da arttırılacak olursa önce hızlı sonra yavaş bir şekilde artmaktadır. $SnCl_4$ yerine $FeCl_3$ alınarak yapılan deneylerde demir (III) ün de serium (IV) sistemine aynı şekilde fakat biraz daha fazla tesir ettiği görülmektedir.

Verilen doz miktarları için G=15,6 alınmak sureti ile Fricke dozimetresinden, konsantrasyon tâyinlerinde ise spektrofotometrik metodlardan faydalanılmıştır.

Nihayet bu araştırmada bulunmuş olan denel sonuçları izah eden reaksiyon mekanizmaları verilmekte ve denel sonuçlar ile bu mekanizmaların uygunluklarının gayet iyi olduğu gösterilmektedir.

AVIS IMPORTANT

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" sera publiée dorénavant sous forme de fascicules à l'arrivée de chaque article. Le tome 13 de la série B, continuant par ce fascicule, sera complété par le dernier fascicule à paraître avant le 31 décembre 1966.

Prix de l'abonnement annuel pour 1966 :

Turquie : 15 TL ; Etranger : 30 TL.

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