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# ALPHA RADIOLYSIS OF AQUEOUS SOLUTIONS

M. V. Vladimirova

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## I. INTRODUCTION

Recent advances in nuclear chemistry, and in particular in the chemistry of the transuranium elements, have created a need for a better understanding of the effects of α-radiation on the physicochemical properties of a system. Furthermore, the high ionisation density of the α-radiation from radioactive elements offers a convenient simulation of the radiochemical processes occurring in solutions irradiated by fission residues. Hence the need for coordinating the experimental data relating to α-radiolysis is self-evident, particularly since the published results of different authors are often contradictory.

The decomposition of water under the influence of $\alpha$-particles was first observed at the beginning of the present century, but no systematic studies were made until the late 1940's. The first experiments relied on radon as a source of $\alpha$-radiation. The drawbacks of radon as an $\alpha$-emitter are obvious: heterogeneous radiation, short half-life, and the inconvenience of working with a gaseous material. $^{210}$Po is more convenient, being a practically pure $\alpha$-emitter (one $\gamma$ quantum per $10^5$ $\alpha$-disintegrations) with a half-life of 138 days. A further advantage of polonium is the very small mass of dissolved polonium needed to give high radiation intensities (1 curie of Po corresponds to $2.24 \times 10^{-4}$ g). The disadvantage of polonium is the fact that it cannot be used as an internal $\alpha$-source in weakly acid, neutral, and weakly alkaline solutions (pH 4–10) because of the extensive hydrolysis of its compounds. These solutions are studied with external polonium sources.

The first attempts at using dissolved polonium as a source of $\alpha$-radiation, in 1948, proved unsuccessful. Bonet-Maury and Lefort[1,2] failed to detect hydrogen peroxide in 0.8 $N$ $H_2SO_4$, in contrast to their experiments with radon[3,4]. Their conclusion that the polonium catalyses the decomposition of hydrogen peroxide was later confirmed[5,6]. On the other hand, Haissinsky and Anta[7,8], who studied the effect of $\alpha$-radiation from dissolved polonium on solutions of bivalent iron and quadrivalent cerium, found that the radiochemical yields for cerium reduction and for iron oxidation were indistinguishable from those obtained with radon radiation[9,10] or with an external polonium source[11,12]. The French workers subsequently established[13–15] that the decomposition of hydrogen peroxide is caused by various impurities introduced into the solution during preparation of the polonium from RaD, and not by polonium ions. Radiochemical yields of hydrogen peroxide similar to those obtained with radon radiation were achieved by using polonium purified by various methods.

At the present time polonium is prepared by irradiating bismuth with neutrons ($^{209}Bi + n_0 \rightarrow {}^{210}Bi \xrightarrow{\beta} {}^{210}Po$). Ershova and Vladimirova[16] have described a method of separating the polonium from the bismuth which gives polonium pure enough to be used as an internal $\alpha$-source. Polonium can also be used in external $\alpha$-sources. The construction and method of use of external polonium sources are discussed in papers by Miller and Wilkinson[12], Senvar and Hart[17], and Hart and Teranday[18].

Besides Po and Rn, other radioactive elements (Pu, Am, Cm, Np), and accelerated helium nuclei and $\alpha$-particles produced in various nuclear reactions, can be used as sources of $\alpha$-particles in radiation studies.

## II. RADIOLYSIS OF WATER AND AQUEOUS SULPHURIC ACID SOLUTIONS

### 1. Hydrogen Peroxide

Several workers have measured the radiochemical yield† of hydrogen peroxide in water and in 0.8 $N$ sulphuric acid (Table 1).

† The radiochemical yield is defined as the number of molecules, atoms, ions, free radicals, etc., formed (or consumed) when the system absorbs 100 eV of ionising radiation. It is standard practice to write the appropriate formula in parentheses after the letter $G$ (which denotes radiochemical yield).

TABLE 1. Radiochemical yield $G(H_2O_2)$.

| Composition of solution | Source of radiation | $G(H_2O_2)$ | Reference |
|---|---|---|---|
| Water | Rn | 0.94 | 19 |
| Water | Po (external) | 1.28 | 17 |
| Water + $O_2$* | Po (external) | 1.33 | 17 |
| Water + $O_2$ | Rn | 1.10 | 20 |
| 0.8 $N$ $H_2SO_4$ | Po (dissolved) | 0.95 | 15 |
| 0.8 $N$ $H_2SO_4$ | Po (dissolved) | 1.10 | 21 |
| 0.8 $N$ $H_2SO_4$ + $O_2$ | Po (dissolved) | 1.15 | 15 |
| 0.8 $N$ $H_2SO_4$ + $O_2$ | Po (dissolved) | 1.25 | 21 |
| 0.8 $N$ $H_2SO_4$ + $O_2$ | Po (dissolved) | 1.20 | 16 |

* The oxygen concentration corresponds to saturation with air under normal conditions.

It is clear from Table 1 that $G(H_2O_2)$ in water and in 0.8 $N$ sulphuric acid is close to unity. The large scatter of the $G(H_2O_2)$ values for the radiolysis of water is probably due to experimental error in the measurement of energy absorption when working with external sources of $\alpha$-radiation. In air-free solutions $G(H_2O_2)$ is lower than in aerated solutions.

Lefort[5] studied the effect of oxygen at concentrations ranging from $3 \times 10^{-5}$ M to $4 \times 10^{-4}$ M, but could not detect any difference in the value of $G(H_2O_2)$. Trumbore and Hart[21] found an increase in the yield of hydrogen peroxide from 1.10 to 1.70 molecules per 100 eV on varying the concentration of dissolved oxygen from 0 to 0.1 M in 0.8 $N$ sulphuric acid. They calculated the rate constant of the reaction $H + O_2 \rightarrow HO_2$, which they believe to be responsible for the increase in the yield of $H_2O_2$. $K(H + O_2) = 2.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

The influence of pH on the yield of hydrogen peroxide is examined in a number of papers. Bonet-Maury and Lefort[22] found that $G(H_2O_2)$ remains constant on changing the pH of water from 1 to 12. Vladimirova[23] observed a decrease in $G(H_2O_2)$ from 1.35 to 1.27 as the pH was varied from 7 to 2. Koulkes-Pujo[24] measured the yield of hydrogen peroxide over a wide range of pH: in neutral and acid media $G(H_2O_2) \simeq 1$, but in NaOH solutions and at pH 13–14 the yield is extremely small.

The influence of sulphuric acid concentration on the yield of hydrogen peroxide has also been investigated[23]. As the sulphuric acid concentration was varied from 0.4 M to 4.0 M, $G(H_2O_2)$ fell from 1.20 molecules per 100 eV to zero. The authors suggest that OH radicals from the tracks can take part in the reactions

$$HSO_4 + OH \rightarrow HSO_4 + OH,$$
$$H_2SO_4 + OH \rightarrow HSO_4 + H_2O,$$

when the concentration of sulphuric acid is increased. These reactions compete with the formation of hydrogen peroxide by recombination of the OH radicals. Good agreement with diffusion theory calculations for a cylindrical track was obtained. The rate constant for the reaction between hydrogen sulphate ions and OH radicals was calculated: $K(OH + HSO_4^-) = 0.7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

### 2. Gaseous Radiolysis Products

The yields of hydrogen and oxygen have been measured by several workers (see Table 2).

TABLE 2. Radiochemical yields of $H_2$ and $O_2$.

| Composition of solution | Source of radiation | $G(H_2)$ | $G(O_2)$ | Reference |
|---|---|---|---|---|
| Water | Rn | 1.8 | 0.42 | 19 |
| Water | Po (external) | 1.45 | 0.10 | 17 |
| Water + $O_2$ | Rn | 1.70 | | 20 |
| 0.8 $N$ $H_2SO_4$ | Rn | 1.80 | 0.40 | 19 |
| 0.8 $N$ $H_2SO_4$ | Po (dissolved) | 1.80 | 0.38 | 15 |
| 0.8 $N$ $H_2SO_4$ | Po (dissolved) | 1.40 | 0.07 | 21 |
| 0.8 $N$ $H_2SO_4$ | Po (dissolved) | 1.37 | 0.15 | 25 |
| 0.8 $N$ $H_2SO_4$ | Pu (dissolved) | 1.60 | | 26 |

TABLE 3.

| Particle energy, MeV | LET*, eV Å$^{-1}$ | $G(H_2)$ | $G(H_2O_2)$ | Reference |
|---|---|---|---|---|
| 32 | 2.2 | 0.97—1.15 | 1.20 | 30,33,34 |
| 22 | 3.0 | 1.14 | | 34 |
| 11 | 5.0 | | 1.24 | 30 |
| 5.3 | 13.0 | 1.40 | 1.20 | 31 |
| 3.4 | 17.5 | 1.45 | 1.30 | 17 |
| 1.5 | 22.0 | 1.65 | | 33 |

* LET = linear energy transfer.

The radiochemical yields for hydrogen and oxygen reported by different authors show a large scatter. The present writer believes that the measurement of oxygen yield presents a number of difficulties. The work of Hart[27] and Donaldson and Miller[28] has shown that the radical $HO_2$ is formed in the neighbourhood of the track, and decomposes to give oxygen ($HO_2 + H_2O_2 = OH + H_2O + O_2$). As hydrogen peroxide accumulates, a similar reaction can also take place in the bulk of the solution, producing additional oxygen. Hence, the oxygen yield will depend on the level of absorbed energy used in its measurement. The reasons for the scatter in the reported radiochemical yield of hydrogen are less obvious. The values $G(H_2)$ = 1.7–1.8 molecules per 100 eV are probably too high. According to Lefort[29], a hydrogen yield of 1.7 can only obtain in the presence of dissolved acceptors for OH radicals. This conclusion is at variance with Lefort's own results in Table 2, and confirms our view that $G(H_2)$ during $\alpha$-radiolysis is close to 1.40 molecules per 100 eV.

The influence of sulphuric acid concentration on the yields of hydrogen and oxygen was studied by Vladimirova and Ershova[25], who found that $G(H_2)$ per 100 eV of energy absorbed by the water increases from 1.37 to 1.55 molecules per 100 eV when the concentration of $H_2SO_4$ is raised from 0.4 to 4.0 M. Schwarz and coworkers[30], using accelerated particles, also observed a higher $G(H_2)$ in sulphuric acid than in water.

### 3. Influence of Dose Rate, $\alpha$-Particle Energy, and Amount of Energy Absorbed on the Yields of Hydrogen and Hydrogen Peroxide

Vladimirova and others[16,30] showed that $G(H_2O_2)$ keeps a constant value of 1.20 molecules per 100 eV when the concentration of dissolved polonium is varied from 0.1 to 12 mc ml$^{-1}$, corresponding to a change in dose rate from $1.9 \times 10^{13}$ to $2.3 \times 10^{15}$ eV ml$^{-1}$ s$^{-1}$. When the dose exceeds $1.5 \times 10^{20}$ eV ml$^{-1}$, $G(H_2O_2)$ gradually drops, and the amount of hydrogen peroxide tends towards a limiting concentration of the order of 0.01 M. For comparison, it may be noted that, according to Hochanadel[32], the steady-state concentration of hydrogen peroxide during $\gamma$-radiolysis in water is less than $10^{-6}$ M.

The radiochemical yield of hydrogen kept a constant value of 1.37 molecules per 100 eV when the dose rate was changed from $2 \times 10^{13}$ to $2 \times 10^{16}$ eV ml$^{-1}$ s$^{-1}$, *i.e.* by three orders of magnitude. The $G(H_2)$ value remained constant for doses ranging from $5 \times 10^{18}$ to $4 \times 10^{20}$ eV ml$^{-1}$.

It is clear from the results of Table 3 that the radiochemical yield of hydrogen peroxide, $G(H_2O_2)$, is practically independent of the energy of the $\alpha$-particles, whereas $G(H_2)$ increases as the energy of the particles decreases and as the linear energy transfer increases.

### 4. Influence of Dissolved Substances on the Yields of Hydrogen and Hydrogen Peroxide

Various authors have examined the influence of halide ions on $G(H_2O_2)$. Senvar and Hart[17] found that the radiochemical yield of $H_2O_2$ drops from 1.24 molecules per 100 eV to zero when the concentration of $I^-$ is varied from $10^{-5}$ M to 0.1 M. The authors' calculations satisfactorily accounted for the experimental results in terms of diffusion theory. Burton and Kurien[35] also reported a decrease in $G(H_2O_2)$ with increase in concentration of acceptors (bromide and chloride ions). Anta[15] studied the effect of various additives on the yield of hydrogen peroxide, and found a decrease (from 1.15 to 0.19 molecules per 100 eV) upon changing the concentration of chloride ions from $2.6 \times \times 10^{-3}$ M to $5 \times 10^{-2}$ M. Increasing the concentration of $NO_3^-$ ions from 0.003 M to 0.4 M lowered $G(H_2O_2)$ from 1.15 to zero. The author ascribes reducing properties to the OH radical, and accordingly believes that the decrease in $G(H_2O_2)$ is due to the reaction

$$OH + NO_3^- \rightarrow NO_2^- + HO_2 .$$

Lefort and Cottin[20,36] showed that addition of such substances as KBr, KCl, KI, $KBrO_3$, $KIO_3$, HCOOH, $KNO_3$, $K_2Cr_2O_7$, $KMnO_4$, $Ce(SO_4)_2$, $Cr_2(SO_4)_3$, $FeSO_4$, and $C_2H_5OH$ to 0.8 $N$ sulphuric acid lower the yield of $H_2O_2$ very significantly, whereas additions of $C_6H_6$, $NH_2NH_2$, acrylonitrile, phosphite, and arsenite do not decrease $G(H_2O_2)$. In all the solutions investigated $G(H_2)$ remained constant at the level 1.7–1.8 molecules per 100 eV. Vladimirova[25,31] has examined the effect of various acceptors for OH radicals (glucose, Methylene Blue, and hydrogen) on the radiochemical yield of hydrogen peroxide and hydrogen. When the concentration of glucose was increased from 0.001 to 0.01 M, $G(H_2O_2)$ rose to 1.60 molecules per 100 eV, but fell to 1.09 molecules per 100 eV when the glucose concentration was increased still further. An increase in Methylene Blue concentration from $1 \times 10^{-5}$ M to $7 \times 10^{-5}$ M also increases $G(H_2O_2)$ (to 1.5 molecules per 100 eV). A similar increase in $G(H_2O_2)$ was observed on saturating the solution with hydrogen. The author explains these results in terms of Pucheault's assumption[37,38] of a second heterogeneous region adjacent to the tracks, in which the molecular products formed in the tracks (but unable to diffuse into the bulk of the solution) are thought to react with free radicals, *e.g.*

$$H_2O_2 + OH \rightarrow HO_2 + H_2O , \quad (a)$$

$$H_2 + OH \rightarrow H + H_2O , \quad (b)$$

$$H_2O_2 + H \rightarrow OH + H_2O . \quad (c)$$

Reactions (a), (b), and (c) have been called "intratrack reactions" in the foreign literature. The term seems lacking in felicity, and should be abandoned in favour of

TABLE 4. Measurements of the yield of OH, H, and $HO_2$ radicals.

| System | $G(OH)$ | $G(H)$ | $G(HO_2)$ | Reference |
|---|---|---|---|---|
| Formic acid | 0.43 | 0.43 | | 40 |
| Iron sulphate | 0.46 | 0.46 | | 12 |
| Iron sulphate + copper sulphate ($Cu^{2+}$) | | 0.73 | 0.25 | 28 |
| Cerium sulphate + + thallium sulphate $Tl^+$ concn.: | | | | 39 |
| $3 \times 10^{-3}$ M | 0.40 | 0.59 | 0.21 | |
| $7 \times 10^{-3}$ M | 0.54 | 0.59 | 0.08 | |
| Iron sulphate | 0.95 | 0.65 | | 41 |
| Cerium sulphate | | 0.60 | | 42 |
| Thallium sulphate ($Tl^{3+}$) | 0.40 | 0.58 | | 43 |
| Cerium sulphate + formic acid | 0.50 | 0.37 | | 44 |
| Methylene Blue | | 0.70 | | 31 |

"track reactions". We shall denote the region within which these reactions proceed as the track region, to distinguish them from the track itself, which is the site of the recombination reactions OH + OH and H + H. The reality of track reaction (b) is confirmed by the experimental demonstration of the influence of sulphuric acid concentration on $G(H_2)$ (see p. 214), and also by the experiments with additions of glucose[25] in which $G(H_2)$ rose from 1.37 to 1.75 molecules per 100 eV for a change in glucose concentration from 0.001 M to 0.01 M.

Conditions such that the acceptors will react with the radicals: (1) in the bulk of the solution, (2) in the track region, or (3) in the track, can be established by addition, in various concentrations, of acceptors for OH or for H radicals. Under condition (1) the yield of radiolysis products should remain unchanged; condition (2) should lead to higher initial yields of molecular products, since reactions (a), (b), and (c) will be suppressed; condition (3) should lower the initial yield of molecular products.

### 5. Yields of Free-Radical Radiolysis Products

The conventional indirect methods of measuring yields of free-radical products are satisfactory only in experiments with "light" radiation of low ionisation density, to which homogeneous kinetics can be applied. With heavy particles the track effects become very significant, and the yields of products become sensitive to the concentrations of dissolved materials: under these conditions an indirect method gives very approximate values of the radiochemical yields of free-radical products. This is clearly shown by the results for various systems given in Table 4.

## III. RADIOLYSIS OF AQUEOUS SOLUTIONS OF INORGANIC AND ORGANIC COMPOUNDS

### 1. The $Fe^{2+}$–$Fe^{3+}$ System

The results for the $\alpha$-radiolysis of $\sim 10^{-3}$ M solutions of $Fe^{2+}$ in the presence of air, given in Table 5, show considerable scatter in the $G(Fe^{3+})$ values. The presently accepted value is 5.1–5.2 molecules per 100 eV.

There is some disagreement as to the influence of $Fe^{2+}$ concentration on $G(Fe^{3+})$: Lefort and Tarrago[39] and Miller and Wilkinson[12] found that a change in $Fe^{2+}$ concentration

TABLE 5. Radiochemical yield for the oxidation of iron in 0.8 $N$ $H_2SO_4$ by the $\alpha$-radiation of dissolved polonium.

| $G(Fe^{3+})$ molecules per 100 eV | Reference | $G(Fe^{3+})$ molecules per 100 eV | Reference |
|---|---|---|---|
| 6.0 | 7 | 5.1 | 21,46 |
| 6.2 | 45 | 5.2 | 44 |
| 5.6 | 41 | 5.08 | 47 |
| 5.5 | 39 | | |

from $2 \times 10^{-4}$ M to $10^{-2}$ M had no effect on the yield of oxidised iron, whereas Trumbore and Hart[21] reported an increase from 5.0 to 5.38 molecules per 100 eV following a change in $Fe^{2+}$ concentration from $2 \times 10^{-4}$ M to 2.5 $\times$ $\times 10^{-2}$ M. According to Miller and Wilkinson[12], $G(Fe^{3+})$ is not affected by increasing the sulphuric acid concentration from $5 \times 10^{-4}$ to 0.5 M.

The effect of dissolved oxygen concentration on $G(Fe^{3+})$ has been examined by several authors (Table 6). Trumbore and Hart[21] ascribe the increase in $G(Fe^{3+})$ to a higher yield of the $HO_2$ radical, which is formed when oxygen accepts H atoms in the tracks of the $\alpha$-particles. This view is supported by the experiments of Donaldson and Miller[28], who were able to decrease $G(Fe^{3+})$ to 2.1 molecules per 100 eV by adding $Cu^{2+}$ ions, which act as acceptors for H and $HO_2$ radicals, at a concentration of 0.01 M.

The oxidation of $Fe^{2+}$ is frequently used for the chemical assay of external sources of radiation. With polonium sources, the measurement of energy absorbed is a rather complex problem. It requires a knowledge of the degree of collimation of the beam of $\alpha$-particles, of the stopping power of the mica or other materials used to protect the active surface of the source, and lastly of the energy of the $\alpha$-particles which penetrate into the solution. The results of work on the variation of $G(Fe^{3+})$ with $\alpha$-energy, using external polonium sources, are summarised in Table 7. Starred values of $G(Fe^{3+})$ were obtained with accelerated helium ions.

It is evident from Table 7 that $G(Fe^{3+})$ increases with increase in $\alpha$-particle energy and with decrease in linear energy transfer. The significant discrepancies in the yields obtained by different workers for $\alpha$-particles of a given energy arise from the difficulty of calibrating external sources of $\alpha$-radiation.

### 2. The $Ce^{4+}$–$Ce^{3+}$ System

The radiolysis of sulphuric acid solutions of $Ce^{4+}$ has been adequately investigated. Values of $G(Ce^{3+})$ for aerated solutions are set out in Table 8.

TABLE 6. Effect of oxygen concentration on $G(Fe^{3+})$ in $3 \times 10^{-3}$ M solutions of $Fe^{2+}$ in 0.8 $N$ $H_2SO_4$.

| $O_2$ concentration, M | $G(Fe^{3+})$ | Reference | $O_2$ concentration, M | $G(Fe^{3+})$ | Reference |
|---|---|---|---|---|---|
| 0.0 | 3.47 | 12 | $1.1 \cdot 10^{-3}$ | 5.49 | 21 |
| 0.0 | 3.65 | 41 | $4.1 \cdot 10^{-3}$ | 7.6 | 21 |
| 0.0 | 3.53 | 47 | 0.1 | 8.5 | 21 |
| 0.0 | 3.57 | 21 | 0.4 | 9.8 | 21 |
| $2.2 \cdot 10^{-4}$ | 5.1 | 21 | | | |

TABLE 7. Variation of $G(Fe^{3+})$ with energy of $\alpha$-particles and helium ions and with linear energy transfer (LET).

| Energy, MeV | LET, eV Å$^{-1}$ | $G(Fe^{3+})$ | Reference | Energy, MeV | LET, eV Å$^{-1}$ | $G(Fe^{3+})$ | Reference |
|---|---|---|---|---|---|---|---|
| 32 | 2.2 | 8.1 * | 34,51 | 3.5 | 17.5 | 5.94 | 48,49 |
| 22 | 3.0 | 7.0 * | 34 | 3.0 | 18.0 | 5.70 | 48,49 |
| 11 | 5.0 | 6.5 * | 34 | 3.0 | 18.0 | 4.16 | 50 |
| 4.7 | 15.0 | 5.9 | 12 | 1.5 | 20.0 | 4.19 | 50 |
| 4.5 | 15.0 | 4.79 | 50 | 1.5 | 20.0 | 4.15 | 49 |
| 3.5 | 17.5 | 4.37 | 50 | 1.5 | 20.0 | 4.20 | 45 |
| 3.5 | 17.5 | 4.70 | 52 | 1.5 | 20.0 | 4.20 | 53 |

* These values were obtained with helium ions.

TABLE 8. Radiochemical yields of $Ce^{3+}$ in solutions of $Ce^{4+}$ salts in 0.8 $N$ $H_2SO_4$.

| Radiation source | $G(Ce^{3+})$ | Reference |
|---|---|---|
| Rn | 3.2 | 9 |
| Po (dissolved) | 3.3 | 54 |
| Po (dissolved) | 3.2 | 8 |
| Po (dissolved) | 3.2 | 42 |
| Po (dissolved) | 3.05 | 44 |
| Po (external, $E\alpha$ = 3.4 MeV) | 2.88 | 55 |

The agreement between the tabulated values is satisfactory. However, if the yields of $\alpha$-radiolysis products are inserted into the equation giving $G(Ce^{3+})$ for $\gamma$-radiolysis a value of 2.5–2.7 ions per 100 eV is obtained. This is much lower than the experimental values. The failure of the accepted reduction scheme for cerium to explain the $\alpha$-radiolysis results was also pointed out by Anta[15]. The constancy of the $Ce^{3+}$ yield with changes in $Ce^{4+}$ concentration between $10^{-5}$ M and $10^{-3}$ M, reported by Weiss and Miller[55], whether or not oxygen is present in solution, adds to the difficulty of interpreting the reduction mechanism of cerium.

The reduction of cerium is known to be very sensitive to the presence of dissolved compounds. Lefort and Tarrago[39] and Weiss and Miller[55] have shown that the yield of $Ce^{3+}$ is slightly increased by $Tl^+$ ions added to the solution. Anta and Margu[56] found that an increase in nitric acid concentration from $2 \times 10^{-2}$ M to 3 M raises $G(Ce^{3+})$ from 3 to 10 ions per 100 eV.

### 3. Aqueous Solutions of Some Other Inorganic Substances

Nitrate–nitrite system. A qualitative study of this system was made by Lefort[5] and Haissinsky and Lefort[57], who showed that the oxidation of nitrite to nitrate proceeds faster than the reverse reduction process. Anta[15], working with 0.8 $N$ sulphuric acid solutions containing nitrate, found that $G(NO_2^-)$ is only 0.005 ions per 100 eV at a concentration of nitrate of 0.4 M. Kabakchi and coworkers[58,59] observed the formation of nitrite in yields ranging from 0.1 to 4 ions per 100 eV in aqueous solutions of nitrate (0.01 M to 6 M) subjected to $\alpha$-radiation from $^{239}Pu$. These large yields of nitrite may be attributed to the Griess reagent which was added to the solutions and stabilised the nitrite ions by combining with them.

$I^- - I_2$ system. Lefort[60] and Senvar and Hart[17] observed the formation of free iodine in their work on the radiolysis of KI solutions in 0.8 $N$ sulphuric acid. The latter workers showed that the combined yield of iodine and hydrogen peroxide remains constant (1.30 molecules per 100 eV) over the whole range of KI concentration used in the investigation.

Phosphate–phosphite system. Cottin[61] studied $\alpha$-radiolysis in this system, and observed phosphite oxidation with a yield depending on the concentration of phosphite in solution. Thus, $PO_4^{3-}$ yields of 0.26 molecules per 100 eV and 1.01 molecules per 100 eV were obtained for $HPO_3^{2-}$ concentrations of $2 \times 10^{-4}$ M and $5 \times 10^{-3}$ M respectively. Oxidation proceeds according to the reaction $HPO_3^{2-} + 2OH \rightarrow PO_4^{3-} + H_2O$.

Arsenite–arsenate system. Lefort and Haissinsky[62,63] found that arsenite is quantitatively oxidised to arsenate by the reaction $AsO_3^{3-} + 2OH \rightarrow AsO_4^{3-} + H_2O$.

$V^{4+} - V^{5+}$ system. Pucheault and Ferradini[37,64] proved that an equilibrium between the oxidised and the reduced form of vanadium is established in solution during $\alpha$-radiolysis.

$U^{6+} - U^{4+}$ system. Zalkind and Veselovskii[65] examined the effect of $\alpha$-radiation from radon on solutions of uranyl sulphate by an electrochemical procedure, and observed a non-equilibrium amount of $U^{5+}$ formed by the reduction of uranyl ion by H radicals. $U^{5+}$ is readily oxidised by OH radicals and by hydrogen peroxide: for this reason, no hydrogen peroxide or peroxidic compounds of uranium are found in solution at high concentrations of dissolved uranyl sulphate (1–1.5 M).

Haissinsky[66] studied the action of $\alpha$-radiation from Po on $U^{4+}$ solutions, and found that the oxidation yield depends on the initial concentration of $U^{4+}$. $G(U^{6+})$ = 3.9 molecules per 100 eV for a $3 \times 10^{-3}$ M concentration of $U^{4+}$; $G(U^{6+})$ = = 13.7 for a $9 \times 10^{-3}$ M concentration of $U^{4+}$.

### 4. Aqueous Solutions of Organic Compounds

Lefort and Haissinsky[68] observed, in their study of the radiolysis of aqueous hydrazine solutions (Table 9), that the yields of hydrolysis products depend on the acidity of the solution and on the hydrazine concentration, whilst the yield of hydrazine decomposition is independent of acidity (0.6 and 1.0 molecules per 100 eV for $10^{-4}$ M and $10^{-3}$ M concentrations respectively). They suggest the following scheme for the radiolysis of hydrazine:

$$N_2H_4 + 2H_2O_2 = N_2 + 4H_2O, \quad 2N_2H_4 + 2OH = N_2 + 2NH_3 + 2H_2O.$$

Hart[40] studied the $\alpha$-radiolysis of aqueous solutions of formic acid in order to characterise the relative yields of free-radical and molecular radiolysis products. In a $10^{-3}$ M solution, $CO_2$ and $H_2$ were obtained in yields of 0.43 and 1.57 molecules per 100 eV respectively. Assuming that the radiochemical process is $HCOOH + OH + H + O_2 = H_2O + CO_2 + H_2O_2$, Hart calculated that the $\alpha$-radiolysis yields 12% of free-radical products and 88% of molecular products.

Data on the $\alpha$-radiolysis of aqueous solutions of glycine[67], obtained with an external polonium source ($E$ = 4 MeV), are presented in Table 10. The concentration of $H_2O_2$ was monitored over a wide range of doses, and found to reach

TABLE 9. Radiochemical yield (molecules per 100 eV) of the radiolysis products of hydrazine.

| $N_2H_4$ concn., M | $10^{-4}$ | $10^{-3}$ | $10^{-4}$ | $10^{-3}$ |
|---|---|---|---|---|
| | neutral solution pH 8 | | acid solution 0.1 $N$ $H_2SO_4$ | |
| $N_2$ | 0.55 | 0.7 | 0.35 | 0.55 |
| $NH_3$ | 0.1 | 0.6 | 0.55 | 0.9 |
| $H_2O_2$ | — | — | 0.8 | 0.4 |
| $H_2$ | 1.6 | 1.7 | 1.65 | 1.65 |
| $O_2$ | 0.25 | 0.2 | 0.2 | 0.2 |

TABLE 10. Yield of radiolysis products of a 1 M aqueous solution of glycine.

| Radiolysis products | $G$, molecules per 100 eV | |
|---|---|---|
| | deaerated | in presence of air |
| $NH_3$ | 1.67 | 1.80 |
| $CH_2NH_2$ | 0.24 | |
| HCOCOOH | 1.1>0.64 | 1.23>0.84 |
| HCHO | 0.42 | 0.57 |
| $CH_3COOH$ | 0.16 | |
| $H_2O_2$ | >0.6 | ≃0.8 |

a steady-state level of about $1.5 \times 10^{-3}$ M at doses of the order of $2 \times 10^{20}$ eV ml$^{-1}$.

Vladimirova observed[31,69], in her study of the $\alpha$-radiolysis of aqueous Methylene Blue solutions, that the yield of bleached dye varies exponentially with energy absorbed. Depending on the experimental conditions, the decolorisation can proceed reversibly or irreversibly. During irreversible bleaching of Methylene Blue in 0.8 $N$ sulphuric acid solution, the variation of the radiochemical yield with dye concentration shows three distinct regions. The author points out that the OH radicals, which are responsible for the irreversible bleaching, can be accepted in three different regions: the bulk of the solution, the track region, and the track. Complete acceptance of the OH radicals in the bulk of the solution occurs at a Methylene Blue concentration of $5 \times 10^{-5}$ M. Vladimirova suggests that the irreversible bleaching of Methylene Blue could be used in the dosimetry of dissolved polonium.

Alexander and Rosen[70,71] irradiated solutions of proteins and tryptophan, and found that the molecular products of $\alpha$-radiolysis are more reactive than the radical products of $\gamma$-radiolysis. They suggest that the action of $\alpha$-particles produces hydrogen peroxide in an active form (possibly an isomeric form) of lifetime $10^{-5}$ s and oxidising power similar to that of ozone. This is apparently the reason for the more drastic biological effects of $\alpha$- than of $\gamma$-radiation.

## 5. Solutions of Compounds of the Transuranium Elements

A whole review article could be written on the $\alpha$-radiolysis of solutions of the transuranium elements. Therefore we shall only briefly consider the main published data.

The use of $\alpha$-radiation from the transuranium elements $^{239}$Pu, $^{237}$Np, and $^{241}$Am for studying radiation processes in water or other media is complicated by the large concentration of these elements ($10^{-3}$–$10^{-2}$ M) needed to produce even comparatively modest dose rates in the solution ($\sim 10^{15}$ eV ml$^{-1}$ s$^{-1}$). Thus the radiation effects in the medium are masked by chemical reactions between the emitters themselves and the radiolysis products of water. The only exception is $^{242}$Cm, which has a half-life of 167 days, *i.e.* close to that of polonium. The only reported use of curium as a source of radiation is a private communication from Miller on the value of $G(H_2O_2)$ in dilute sulphuric acid. Anta showed[15] that this agrees closely with the $G(H_2O_2)$ values given by polonium and radon radiation, which is not surprising, since the energy of $\alpha$-particles from curium (and from the other transuranium elements) is not very different from the energy of the particles from polonium or radon.

Radiation processes in solutions of compounds of the transuranium elements are usually investigated by observing changes in the valence state of these elements brought about by their own $\alpha$-radiation (self-reduction) or by radiation from polonium, which offers higher dose rates. From the results, the yields of molecular and free-radical radiolysis products in the given medium can be calculated. The values thus obtained (Table 11) agree satisfactorily with the radiochemical yields observed in experiments with polonium and radon radiation, with the exception of the calculated yield of $H_2O_2$ in 0.2 M $HClO_4$: according to Anta[15], $G(H_2O_2)$ in 0.4 M $HClO_4$ should be 1.35 molecules per 100 eV.

Plutonium salt solutions. The most extensive study of the $\alpha$-radiolysis of various solutions of plutonium salts ($Pu^{6+}$) was reported by Pages[26,73,74] and by Artyukhin[75,76]. It was shown that $Pu^{6+}$ is reduced to $Pu^{3+}$ in 0.1 M perchloric acid, and to $Pu^{4+}$ in 0.1–0.4 M sulphuric acid. In either solution the yield of $Pu^{6+}$ reduction is 3.2 equiv. per 100 eV. In a 1.5 M sulphuric acid solution the reduction yield drops to 2.4. Pages assumes that the reduction of $Pu^{6+}$ involves mainly hydrogen peroxide: $Pu^{6+} + H_2O_2 \rightarrow Pu^{4+} + O_2 + 2H^+$. By using polonium radiation, Pages demonstrated that the reduction of plutonium varies with dose rate. At the highest dose rates the reaction shows an induction period during which no reduction occurs. This is explained by the very fast accumulation of hydrogen peroxide, which fails to react with the plutonium ions.

TABLE 11. Yield of radiolysis products in solutions containing Pu and Am.

| Solution | Radiation source | $G(H_2O_2)$ | $G(H_2)$ | $G(H)$ | Reference |
|---|---|---|---|---|---|
| $H_2SO_4$ 0.1 – 0.4 M | $^{239}$Pu | 1.35 calc. | 1.60 expt. | | 26 |
| $H_2SO_4$ 0.1 M | $^{241}$Am | 1.18 expt. 1.16 calc. | | 1.86 calc. | 72 |
| $H_2SO_4$ 1.0 M | $^{241}$Am | 0.69 expt. 0.54 calc. | | 1.87 calc. | 72 |
| $HClO_4$ 1.0 M | $^{239}$Pu | 1.35 calc. | 1.60 expt. | | 26 |
| $HClO_4$ 0.2 M | $^{241}$Am | 0.78 calc. | | 1.73 calc. | 72 |

TABLE 12. Yields for the reduction of Am in acid solutions.

| $H_2SO_4$, M | $-G(AmO_2^{2+})$ | $HClO_4$, M | $-G(AmO_2^{2+})$ | $HNO_3$, M | $-G(AmO_2^{2+})$ |
|---|---|---|---|---|---|
| 0.1 | 4.18 | 0.2 | 4.18 | 0.5 | 7.1 |
| 1.0 | 2.95 | 2.0 | 3.31 | 3.0 | 8.9 |
| 2.0 | 2.59 | 4.0 | 3.31 | 6.0 | 9.0 |
| 4.0 | 2.09 | 6.0 | 3.52 | 9.0 | 10.6 |
| 6.0 | 1.86 | 9.0 | 2.9 | 14.3 | 6.0 |
| 10.0 | 2.28 | 12.0 | 0.0 | | |

In 0.1–0.5 M solutions of nitric acid Artyukhin and Pages found no reduction of plutonium over a very long period, but after 25–50 days the reduction became very fast. The reduction of plutonium is insensitive to the acidity of the medium between the pH limits 2–5. The reduction yield is markedly affected by the concentration of nitrate ions[75]: as the $NO_3^-$ concentration is increased from 0.1 *N* to 5.0 *N* (at pH 3), the reduction yield rises from 4 to 6.5 equiv. per 100 eV. The authors consider that reduction of $Pu^{6+}$ in nitrate solutions involves hydrogen peroxide and nitrous acid:

$$2PuO_2^{2+} + H_2O_2 \rightleftarrows 2PuO_2^+ + 2H^+ + 2O\,,$$
$$2PuO_2^{2+} + HNO_2 + H_2O \rightleftarrows 2PuO_2^+ + NO_3^- + 3H^+.$$

Artyukhin explains the retardation of the reduction of $Pu^{6+}$ in more concentrated nitric acid by an increase in the rate of reaction of $PuO_2^+$ with $NO_3^-$.

Americium salt solutions. The valence changes of americium caused by its own $\alpha$-radiation are discussed in detail in the papers by Yakovlev and Kosyakov[77,78] and by Zaitsev *et al.*[72] When mixed solutions of $Am^{6+}$ and $Am^{5+}$ in sulphuric or perchloric acid are reduced, the $Am^{5+}$ remains unaffected until the whole of the $Am^{6+}$ has been reduced. In nitric acid, reduction of $Am^{5+}$ is very slow. Reduction yields for $Am^{6+}$ in different acid solutions are set out in Table 12.

The following scheme for the reduction of $Am^{6+}$ is proposed:

$$AmO_2^{2+} + HO_2 \rightarrow AmO_2^+ + O_2 + H^+\,,$$
$$AmO_2^{2+} + H_2O_2 \rightarrow AmO_2^+ + HO_2 + H^+.$$

The decrease in reduction yield at higher sulphuric acid concentrations is ascribed to the increasing effect of the reaction $HSO_4^- + OH \rightarrow HSO_4 + OH^-$, which competes for OH radicals and therefore lowers the yield of hydrogen peroxide. The decrease in reduction yield of $Am^{6+}$ in concentrated perchloric acid solutions is explained by the authors in terms of the inhibiting effect of $Cl_2$ and $ClO_2$, which are produced by decomposition of the acid itself. The increase in reduction yield in nitric acid solutions is said to be due to secondary products formed by the action of free radicals upon nitric acid.

Neptunium salt solutions. The self-reduction of neptunium ($Np^{6+}$) in perchloric acid solutions was studied by Zielen *et al.*[79] At neptunium concentrations of the order of 0.2 M the reduction yield is 6.4 molecules per 100 eV, and does not vary with perchloric acid concentration within the limits investigated (0.5–1.7 M). This high reduction yield is attributed to the high concentration of neptunium in solution: in the investigations discussed above the concentration of plutonium and americium was never higher than $10^{-2}$ M.

## IV. MECHANISM OF $\alpha$-RADIOLYSIS

Available experimental data on the $\alpha$-radiolysis of aqueous solutions can be satisfactorily described by the concepts of the free-radical theory of radiolysis, leading to a fairly accurate mechanism for the process.

The high ionisation density associated with $\alpha$-particles gives rise to a considerable local concentration of free radicals along the tracks: $[OH] \simeq 0.1$ M; $[H] \simeq 0.01$ M. The recombination of radicals in the tracks (by the reactions OH + OH and H + H) leads to the formation of molecular products. Whereas the mechanism of formation of hydrogen peroxide is beyond doubt, various statements regarding the formation of molecular hydrogen appear to the present writer to be based on contradictory experimental data. The apparent constancy of $G(H_2)$ in 0.8 *N* sulphuric acid containing various solutes led Haissinsky to conclude, for example[80], that hydrogen is formed directly by the reaction $H_2O^- \rightarrow H_2 + O^-$. However, the results of Donaldson and Miller[28] on the acceptance of H atoms by $Cu^{2+}$ ions, and Vladimirova's observations[25,31] that H atoms are accepted by $NO_3^-$ ions and by Methylene Blue, force the conclusion that the hydrogen is produced by recombination.

Hart estimated that about 88% of the radicals during $\alpha$-radiolysis recombine to give molecular products, the proportion of free radicals in the product being only 12%.

Pucheault[37,38] made a significant contribution to a deeper understanding of the mechanism of $\alpha$-radiolysis by his detailed study of the track region and track reactions.

In what follows, we shall attempt to present the mechanism of $\alpha$-radiolysis of water on the basis of the experimental results reported for systems containing 0.8 *N* sulphuric acid.

Yields‡ of molecular products:

$$G^{O_2}(H_2O_2) = 1.20,\ G(H_2O_2) = 1.0,\ G_{H_2O_2} = 1.75,\ G(H_2) = 1.40\,,$$

$$G^{Fe^{2+}}(H_2) = 1.60,\ G_{H_2} = 1.80.$$

Yields of track reactions:

$$G_{(a)} = G_{HO_2} = G(HO_2) = 0.2,$$
$$G_{(b)} = G_{H_2} = G(H_2) = 0.4,$$
$$G_{(c)} = G_{H_2O_2} = G_{(a)} - G(H_2O_2) = 0.35.$$

The present writer believes that the scheme should include a fourth track reaction (*d*), which provides an alternative path for the formation of hydrogen peroxide in solution: $2H + O_2 = H_2O_2$

$$G_{(d)} = 2\,[G^{O_2}(H_2O_2) - G(H_2O_2)] = 0.4\,.$$

Yield of H and OH radicals. In the absence of dissolved oxygen it seems preferable to determine the yield of OH radicals starting from data on the oxidation of $Fe^{2+}$. The yield of $Fe^{3+}$ in a vacuum is 3.6 molecules per 100 eV. The yield of hydrogen in a solution containing $Fe^{2+}$ ions is higher than in 0.8 *N* sulphuric acid by 0.2. Since it is known that an equivalent amount of hydrogen is evolved

‡ The superscript after the symbol *G* refers to the compound present in solution. Initial yields of the radiolysis products of water are designated by the symbol *G* with the appropriate subscript, *e.g.* $G_{H_2O_2}$.

when iron is oxidised by H radicals in the absence of oxygen, we may assume that $G(H)$, the yield of H radicals reacting with $Fe^{2+}$, is 0.2 molecule per 100 eV.

$G(Fe^{3+})$ in a vacuum is described by the equation

$$G(Fe^{3+}) = 2G(H_2O_2) + G(OH) + 3G(HO_2) + G(H).$$

Hence $G(OH)$ = 3.6 - 2.0 - 0.6 - 0.2 = 0.8 molecule per 100 eV. To find $G(H)$ in 0.8 $N$ $H_2SO_4$, we use the material balance equation

$$-G(H_2O) = 2G(H_2O_2) + G(OH) + 3G(HO_2) = 2G(H_2) + G(H).$$

Hence $G(H)$ = 2.0 + 0.8 + 0.6 - 2.8 = 0.6 molecule per 100 eV.

In the presence of dissolved oxygen the yields of OH and H can be calculated from the two equations

$$G^{O_2}(Fe^{3+}) = 2G^{O_2}(H_2O_2) + G^{O_2}(OH) + 3G(HO_2) + 3G^{O_2}(H),$$
$$-G^{O_2}(H_2O) = 2G^{O_2}(H_2O_2) + G^{O_2}(OH) + 3G(HO_2) = 2G(H_2) + G^{O_2}(H) + G(d).$$

Inserting known numerical values, we find

$$G^{O_2}(OH) = 0.7, \quad G^{O_2}(H) = 0.5 \text{ molecule per 100 eV.}$$

Yield of water decomposition. The observed yield of water decomposition in the presence and in the absence of dissolved oxygen can be deduced from the material balance equation:

$$-G(H_2O) = 3.4 \text{ molecules per 100 eV}, \quad -G^{O_2}(H_2O) = 3.7.$$

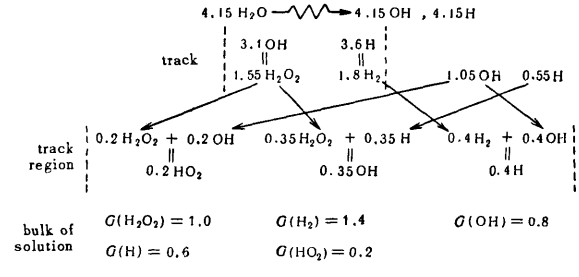
To calculate the initial yield of water decomposition, allowance must be made for the track reactions:

$$-G_{H_2O} = -G(H_2O) + G_{(b)} + G_{(c)}.$$

Inserting the appropriate values for the yields of the track reactions and of the water decomposition we find

$$-G_{H_2O} = 4.15 \text{ molecules per 100 eV}, \quad -G^{O_2}_{H_2O} = 4.45.$$

These results enable us to put forward the following scheme for the mechanism of $\alpha$-radiolysis:




The scheme shows the further transformations of free-radical and molecular products after their formation from ionised water molecules. Thus, the initial yield for the decomposition of water during $\alpha$-radiolysis is 4.45 molecules per 100 eV, *i.e.* the same as for $\gamma$-radiolysis. It is significantly higher than the previously accepted value of 3.6 molecules per 100 eV, which characterises the observed yield. The observed yield for the decomposition of water, as well as the observed yields of free-radical and of molecular products, may vary with the concentration of various solutes, but the initial yield for the decomposition of water should remain constant.

From these results we may conclude that the initial yield for the decomposition of water should be independent of the type of radiation used. The only difference in the mode of action of the various types of radiation concerns the magnitude of the linear energy transfer: with radiations having a small linear energy transfer all the decomposed water molecules can be easily accounted for in terms of processes occurring in the solution, whereas with radiations with a large linear energy transfer the initial radiolysis products are partly decomposed in the track region.

In his development of the hypothesis of track reactions and the track region Pucheault[81] attempted to demonstrate the likelihood of reactions $(a)$, $(b)$, and $(c)$, and to estimate the relative sizes of their regions. The removal of radiolysis products from the tracks, and their collision probabilities, depend on their diffusion coefficients $D$ (other conditions being equal). Introducing the notation

$$\frac{1}{\beta_a} = \frac{D_{H_2O_2}}{D_{OH}}, \quad \frac{1}{\beta_b} = \frac{D_{H_2}}{D_{OH}}, \quad \frac{1}{\beta_c} = \frac{D_{H_2O_2}}{D_H},$$

and using the relation $D = \sqrt{1/M}$, we obtain

$$\beta_a = \sqrt{\frac{34}{17}} = 1.41, \quad \beta_b = \sqrt{\frac{17}{2}} = 2.93 \text{ and } \beta_c = \sqrt{\frac{34}{1}} = 5.83.$$

In other words, reaction $(a)$ is the most probable. After a detailed analysis of the geometry of the process, in which the volume $V$ within which reactions $(a)$, $(b)$, and $(c)$ can occur is expressed in terms of the appropriate value of $\beta$, Pucheault finds that $V(a) = 40\,V(b) = 100\,V(c)$. These relative sizes of the reaction region, however, are not borne out by the experimental finding that reactions $(a)$ and $(b)$ have almost identical yields, or by Allen's calculation[82], according to which $K(a) \simeq K(b)$.

Various arguments aimed at explaining these discrepancies are advanced in Pucheault's book[81].


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U. D. C. 541.132:546.3-19

# ELECTRODEPOSITION OF ALLOYS

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