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Radiation Chemical Studies with Cyclotron Beams. II. The Radiolysis of an Aqueous Ferrous Ammonium Sulfate Solution with Carbon- and Nitrogen-Ion Radiations[1)]

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The yield of ferric ions in the radiolysis of an aqueous ferrous ammonium sulfate solution has been determined in the very high LET (linear energy transfer) range. The radiations used were ions of carbon-12 and nitrogen-14, which were accelerated by means of the IPCR cyclotron and which had energies (E_s) of 31—77 MeV for C-ions and of 17—78 MeV for N-ions; the LET ranges for water were 24—46 eV/Å and 26—85 eV/Å respectively. From the plot of $G(Fe^{3+})E_s$ *vs.* E_s, the value for $G(Fe^{3+})$ at an infinite LET was found to be in the vicinity of 2.9. It has also been shown that there is a substantial difference in the instantaneous yield (G_i) between the two ion radiations of the same LET; this may be ascribed to the differences in the track structures of the heavy-ion radiations.

In most of the experimental work on the LET (linear energy transfer) effect in radiolysis, protons, deuterons, or helium ions have usually been used as radiation sources with a high LET.[1-8)] The maximum LET available in water, however, is approximately 7 eV/Å for protons and 25 eV/Å for helium ions. It is expected that a much higher LET can be obtained from fission fragments of ^{235}U (several hundred eV/Å), but they are attended with some inevitable experimental difficulties.

Schuler[9)] has used ^{12}C-ions accelerated with a HILAC and has made measurements of the yields for aqueous ferrous ammonium sulfate solutions; the energy of the C-ions was in the range of 54—102 MeV. Other heavy ions, such as ^{14}N- and ^{20}Ne-ions, have been used by Burns and his colleague for the radiolysis of liquid cyclohexane and benzene.[10)]

We have initiated radiolysis studies using heavy-ion radiations made available by the IPCR 160 cm cyclotron, which can accelerate several heavy ions at variable energies. While the previous paper[1)] of this series has reported the radiolysis of aqueous ferrous ammonium sulfate solutions with protons and helium ions, the present paper

1) Part I of this series: M. Matsui, H. Seki, T. Karasawa and M. Imamura, *J. Nucl. Sci. Tech.*, **7**, 97 (1970).

2) a) R. H. Schuler and A. O. Allen, *J. Amer. Chem. Soc.*, **77**, 507 (1955). b) R. H. Schuler and A. O. Allen, *ibid.*, **79**, 1565 (1957).

3) a) R. H. Schuler and N. F. Barr, *ibid.*, **78**, 5756 (1956). b) N. F. Barr and R. H. Schuler, *J. Phys. Chem.*, **63**, 808 (1959).

4) H. A. Schwarz, J. M. Caffrey, Jr., and G. Scholes, *J. Amer. Chem. Soc.*, **81**, 1801 (1959).

5) A. Appleby and H. A. Schwarz, *J. Phys. Chem.*, **73**, 1937 (1969).

6) A. R. Anderson and E. J. Hart, *Radiat. Res.*, **14**, 689 (1961).

7) G. L. Kochanny, Jr., A. Timnick, C. J. Hochanadel and C. D. Goodman, *ibid.*, **19**, 462 (1963).

8) For organic compounds, see, W. G. Burns and R. Barker, "Progress in Reaction Kinetics," Vol. 3, ed. by G. Porter, Pergamon Press, Oxford (1965), p. 303.

9) R. H. Schuler, *J. Phys. Chem.*, **71**, 3712 (1967).

10) a) W. G. Burns, W. R. Marsh and C. R. V. Reed, *Nature*, **218**, 867 (1968). b) W. G. Burns and C. R. V. Reed, *Chem. Commun.*, **1968**, 1468.

will concern the results with C- and N-ions, which had energies of 31—77 and 17—78 MeV respectively; a single result with 58 MeV ^{16}O-ions is also included.

By extrapolating the present results at very high LET's, one could obtain the value for $G(Fe^{3+})$ at an infinite LET and, therefore, the limiting yield of water decomposition, G_{-H_2O}. It has also been shown that there is a substantial difference in the instantaneous yield among C-, N-, and O-ions. This may be explained by the differences in the track structures of these heavy-ion radiations.

Experimental

The irradiation arrangement and experimental procedure were similar in outline to those described previously.[1] The ions accelerated in the cyclotron had a charge of +4.[11] The accelerated ions were withdrawn through a beam duct (10 m long) to a target. In the vicinity of the exit window of the duct, the ion beams were passed through a thin gold foil (2μ) and a small fraction of them were elastically scattered by it. The number of ions passing through the foil was thus monitored by counting the number of the scattered ions by a solid-state detector. Meanwhile, the beam currents of ions passing through the foil were determined with a Faraday cup. The number of ions collected in a Faraday cup was then calculated from the total charge, Q, and the average charge, $\langle z\rangle_f$, of ions collected in a Faraday cup after passing through the gold foil; the average charges of ions were obtained in a manner described below. As the number counted by the solid-state detector should be proportional to the number of ions collected in the Faraday cup, one can readily obtain the total number of ions deposited in the solution by assuming no loss of ions between the scattering foil and the solution. The ratio of the number of the scattered ions to that of the collected ions was determined before and after each run; the data were in agreement, within an error of 3%, for each run.

The incident energies of ions were obtained within an error of ±2% by $E_c(\mathrm{MeV})=0.107Af^2$, where A is the mass number of the ion and, f(MHz) the radio frequency of the cyclotron being operating. As the ion beams were passed through the scattering foil (2μ Au), the exit window (10μ Al), the air layer (10 mm), and the cell window (10μ mica), the incident energy, E_c, was reduced to E_s when the ions entered the solution. The initial energies of ions entering the solution, E_s, were estimated by the use of the range-energy relations given by Northcliffe.[12]

The principal difference between protons (or helium ions) and heavy ions is that the former can be regarded as charge-invariant over most of the energy region, while the latter can not. With an increase in the atomic number of the ion, there is an expansion of the velocity region in which charge variation is of importance. Northcliffe[13] summarized experimental equilibrium charge distribution data for several heavy ions. It seems that the data can be represented reasonably well by a single universal curve for each value of $z-z'$ (z: atomic number; z': net charge). In the present experiment, the total thickness of absorbers was sufficient to allow the heavy ions to be charge-equilibrated before entering the solution. We have calculated the average charge of ions entering the solution, $\langle z\rangle_s$, by taking weighted means of each fraction of ions having a charge, z', in a charge-equilibrated monoenergetic beam. Table 1 lists the values of z' and $\langle z\rangle_s$ for each ion used in this experiment.

A ferrous ammonium sulfate solution (10^{-2} M $Fe(NH_4)_2(SO_4)_2$, 10^{-3} M NaCl, 0.8 N H_2SO_4) in triply-

Table 1. Average charges, initial LET's and overall yields for heavy ions

Ion	E_c*1	E_s*2	Fraction of ions having charge z' of					$\langle z\rangle_s$	Initial LET (eV/Å)	$G(Fe^{3+})$
			+4	+5	+6	+7	+8			
^{12}C	54.1	31.0	2	23	75	—	—	5.7_3	45.5	3.8_3
^{12}C	73.5	57.0	0	8	92	—	—	5.9_2	30.0	4.1_1
^{12}C	74.2	58.0	0	8	92	—	—	5.9_2	29.6	4.2_0
^{12}C	91.5	77.0	0	4	96	—	—	5.9_6	23.7	4.9_1
^{14}N	51.8	17.0*3	3	29	49	19	—	5.8_4	84.7	3.3_9
^{14}N	52.7	17.0	3	29	49	19	—	5.8_4	84.7	3.4_3
^{14}N	66.8	35.5	0	6	36	58	—	6.5_2	59.8	3.7_7
^{14}N	82.2	61.5	0	1	17	82	—	6.8_1	42.3	4.1_2
^{14}N	96.6	78.5	0	0	12	88	—	6.8_8	35.5	4.4_6
^{16}O	91.7	58.0	0	0	4	33	63	7.5_9	59.2	4.3_2

*1 The energy of ions accelerated in the cyclotron.
*2 The energy of ions entering the solution.
*3 A Ni (3μ) scattering foil was used.

11) Y. Miyazawa, T. Tonuma, I. Kohno, S. Nakajima, T. Inoue, A. Shimamura, K. Yoshida and T. Karasawa, *Japan J. Appl. Phys.*, **9**, 532 (1970).
12) L. C. Northcliffe, "Studies in Penetration of Charged Particles in Matter," Publication 1133, National Academy of Sciences-National Research Council, Washington, D. C. (1964), p. 173.
13) L. C. Northcliffe, *Ann. Rev. Nucl. Sci.*, **13**, (1963).

distilled water was used under aerated conditions. The irradiation cells were the same as those used previously;[1] the aperture of the cell (10 mm in diameter) was glazed with mica (10 μ thick), the range of which was estimated to be 2.7 mg/cm^2. The solution was stirred during irradiation by means of a magnetic stirrer at a speed of 36 rps.

The oxidation yields of ferrous ions (the number of Fe^{3+} ions oxidized by 100 eV of energy deposited in the solution) were calculated by the equation:[1]

$$G(Fe^{3+}) = 0.96\times10^7\times\frac{DV}{\varepsilon d}\times\frac{\langle z\rangle_f}{E_sQ}$$

where: D: the optical density at 304 nm,
ε: the molar extinction coefficient of Fe^{3+} at 304 nm in M^{-1} cm^{-1},
d: the optical path-length for D-measurement in cm,
V: the volume of the irradiated solution in ml,
E_s: the initial energy of ions entering the solution in Mev,
Q: the total charge collected in a Faraday cup in nanocoulomb, and
$\langle z\rangle_f$: the average charge of ions collected in a Faraday cup.

The initial LET values for ions with an energy of E_s and a net charge of z' were calculated by the reduced Bethe equations:

$$-\frac{dE}{dx} = \frac{22.2z'^2}{E_s}\log(2.75E_s) \quad \text{for } C^{+z'}\text{-ions}$$

$$-\frac{dE}{dx} = \frac{25.9z'^2}{E_s}\log(2.36E_s) \quad \text{for } N^{+z'}\text{-ions}$$

where the mean excitation potential (I) is assumed to be 66 eV for water and where $-dE/dx$ is expressed in eV/Å when E_s is in MeV. The effective values of $-dE/dx$ for ions with an average charge of $\langle z\rangle_s$ were obtained by taking the weighted means of the value for each z'-value; they are summarized in Table 1.[14]

Results and Discussion

The oxidation yield of ferrous ions was found to be linearly dependent on the dose. Some typical examples are given in Fig. 1; Figure 1 also shows that the yield is independent of the beam current in the range of 0.1—3 nA;[15] above 5 nA the yield decreases.

The radiation chemical yields ($G(Fe^{3+})$) were calculated from the slopes of these linear yield-dose plots and are summarized in Table 1. Figure 2 shows the dependence of the observed $G(Fe^{3+})$ value on the initial LET's of ions. The yields obtained by Schuler[9] with C-ions, also plotted in Fig. 2, indicate good agreement with the present C-ion data. It does not seem, however, that the data for the three ions are superimposable: the heavier the ion, the greater the yield. A similar discrepancy has also been observed between protons or deuterons and helium ions.[16] Furthermore, it seems that the yields at higher LET's can be extrapolated to a value lower than 3.6, which was assumed by Schuler and Allen[2b] to be a limiting yield at an infinite LET.

The $G(Fe^{3+})$-values have hitherto been determined by using accelerated protons, deuterons, and helium ions (LET as high as ~5 eV/Å) and

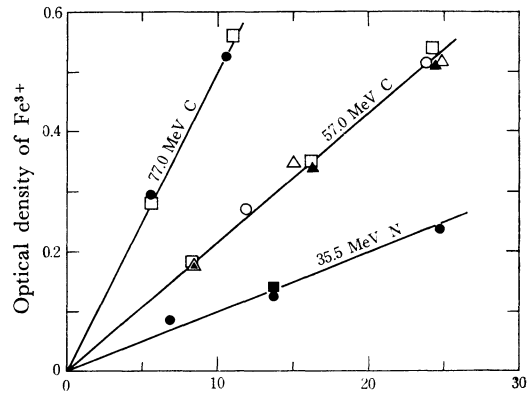

Fig. 1. Plots of Fe^{3+}-yield *vs.* number of ions scattered by a gold foil at various beam currents. The number of scattered ions is proportional to the total number of ions deposited in the solution. The optical densities (d=10 mm) were determined at 304 nm.
○, 0.1 nA; ●, 0.2 nA; □, 0.5 nA; ■, 0.7 nA; △, 1.5 nA; ▲, 3.0 nA

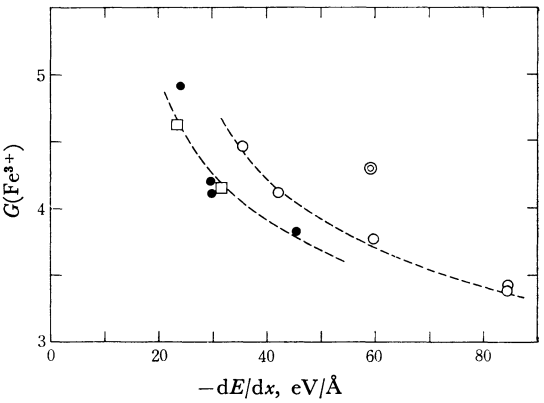

Fig. 2. A plot of the observed $G(Fe^{3+})$ *vs.* reciprocal LET. The initial LET values were calculated by the equations described in the text.
●, C-ions; ○, N-ions; □, C-ions by Schuler (Ref. 9); ◎, O-ions

14) Table 1 also contains a single result with O-ions; the experimental procedure was quite similar to that for C- or N-ions. The initial LET for O-ions is given by $(-dE/dx)=(29.6\ z'^2/E_s)\log(2.06\ E_s)$.

15) The beam currents determined by the use of a Faraday cup.

16) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," Van Nostrand, Princeton, N. J. (1961), p. 54.

the recoil particles from (n,α) reactions of Li and B (~25 eV/Å).[17] These results indicate that the $G(Fe^{3+})$ decreases as the LET of the radiation is increased. No experimental value of $G(Fe^{3+})$ at the LET's higher than the above value has been reported except for those by Schuler with C-ions (LET's as high as ~30 eV/Å) shown in Fig. 2.[9] The present results indicate that the $G(Fe^{3+})$ still decreases at LET's above 30 eV/Å.

The integrated yield of ferric ions produced by an ion with E_s is given by:

$$G(Fe^{3+}) \times E_s = \int_0^{E_s} G_i dE \qquad (E_s \text{ in } 100\,eV)$$

where G_i represents an instantaneous yield at a a given energy. In Fig. 3 the values of $G(Fe^{3+}) \times E_s$ for C-, N-, and O-ions are plotted as a function of E_s; the data of Schuler with C-ions[9] are also included. It seems that, in unexpected contrast to Fig. 2, all the data fit a universal curve, as is shown in Fig. 3. The instantaneous yields, G_i, for given values of E_s are readily obtained from the slopes at the corressponding points on this curve, *i.e.*,

$$G_i(Fe^{3+}) = \frac{d[G(Fe^{3+})E_s]}{dE_s}$$

The values of $G_i(Fe^{3+})$ thus obtained are plotted as a function of the reciprocal LET in Fig. 4 for C-, N-, and O-ions. The dotted line in Fig. 3 represests the tangent at an infinite LET, which gives $G_i(Fe^{3+})=2.9$.

As may be seen in Fig. 3, the data for C- and N-ions and probably for O-ions apparently fit a single universal curve within the limits of experimental error. This is presumably adventitious; the curves may not coincide with each other at higher E_s's. Figure 4 clearly indicates the existence of substantial differences in $G_i(Fe^{3+})$ among these ions at the same LET. These differences may be explained by assuming the different contribution of high-energy secondary electrons; the heavier ion ejects the more energetic secondary electrons. The net yield is, therefore, a combination of the yields for the "core" of the track and for the emergent secondary electrons. The higher yields of heavier ions can thus be understood by assuming the effective expansion of the heavy-ion tracks; such a model has been proposed by Mozumder *et al.*[18] A similar effect observed with deuterons and helium ions has been discussed in terms of the kinetics of secondary electron production.[19] Further experimental study on this effect due to the quality of heavy ions is in progress by using C-, N-, and O-ion radiations.

The oxidation yield of ferrous ions in an aerated aqueous solution is given by the equations:

$$G(Fe^{3+}) = G_{OH} + 3G_H + 2G_{H_2O_2}$$
$$= G_{-H_2O} + 3G_H = 2G_{H_2} + 4G_H$$

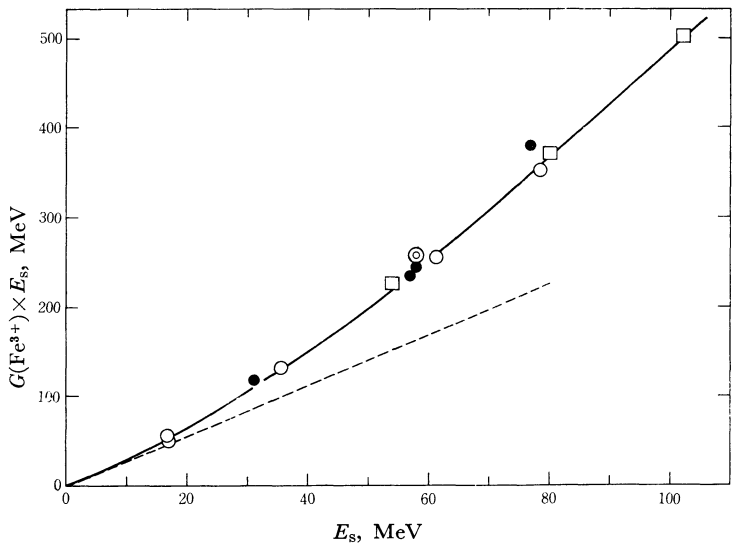

Fig. 3. A plot of the integrated yield of ferric ions *vs.* energy of the heavy ions entering the solution. The dotted line represents the limiting yield of $G(Fe^{3+})=2.9$ at an infinite LET.
●, C-ions; ○, N-ions; □, C-ions by Schuler (Ref. 9) ◎, O-ions

17) W. R. McDonell and E. J. Hart (*J. Amer. Chem. Soc.*, **76**, 2121 (1954)) have obtained $G(Fe^{3+})=5.2$ and 4.2 for $^6Li(n, \alpha)^3H$ and $^{10}B(n,\alpha)^7Li$ recoils and R. H. Schuler and N. F. Barr (Ref. 3a) 5.69 and 4.22, respectively.

18) a) A. Mozumder, A. Chatterjee and J. L. Magee, *Advan. Chem. Ser.*, **81**, 27 (1968). b) A. Mozumder, *Advan. Radiat. Chem.*, **1**, 1 (1969).

19) R. E. Faw and H. J. Donnert, *Nucl. Instr. Methods*, **58**, 307 (1968).

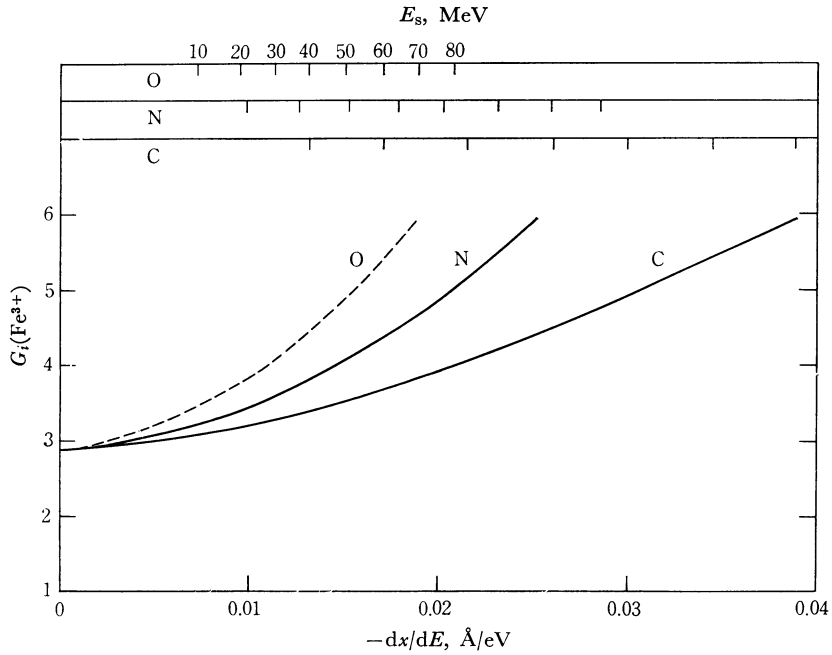

Fig. 4. Dependence on reciprocal LET of the instantaneous yields for C- and N-ions obtained from Fig. 3. Probable dependence for O-ions is also shown.

At an infinite LET, the free radical yields will vanish;[6,20] $G(Fe^{3+})$ will, therefore, approach G_{-H_2O} or $2G_{H_2}$. Schuler and Allen[2b] have assumed the limiting $G(Fe^{3+})=3.6$ from the values for G_{-H_2O} $(=3.6)$ or $2G_{H_2}(=3.4)$ in the radiolysis of an aqueous solution with $^{10}B(n,\alpha)^7Li$ recoil particles. As has been mentioned above, the present results gave the value of 2.9 for the limiting $G(Fe^{3+})$ at an infinite LET, which would mean $G_{-H_2O}\simeq 2.9$ according to the above argument.[21]

According to Allen,[22] the G_{-H_2O} for the 0.8 N H_2SO_4 solution decreases with an increase in the LET to about 3.6 at about 5 eV/Å; then it becomes constant in the higher LET range. In a neutral solution the G_{-H_2O} increases with an increase in LET above 5 eV/Å. However, Anderson and Hart,[6] who investigated the LET dependence of the initial yields from water using a formic acid solution saturated with oxygen, found that the value for G_{-H_2O} decreases with an increase in LET down to 2.4—2.6 for helium ions of about 10 MeV (LET ~5 eV/Å), and then increases slightly.

The present results indicate that the G_{-H_2O} in the 0.8 N H_2SO_4 solution seems substantially lower than the 3.6 estimated by Schuler and Allen.[2b] Although some discussions have been made concerning the value of G_{-H_2O} at very high LET's[21-24] and concerning the difference in that value between acid and neutral solutions,[6] more data should be accumulated in the higher LET region, and the variation in the value of G_{-H_2O} at LET's above 5 eV/Å is still open to question.

The authors wish to express their gratitude to the members of the cyclotron operation group, and also to Hiroshi Seki and Takahisa Imai for their experimental assistance.

20) A. Kuppermann, "Radiation Research 1966," ed. by G. Silini, North-Holland Publ. Co., Amsterdam (1967), p. 212.

21) In the high-LET tracks, some reactions between molecular products and free radicals may be taken into consideration. The most noteworthy reaction of them may be: $H_2O_2+OH\rightarrow H_2O+HO_2$ (*cf.* Ref. 16, p. 51). The formation of HO_2 in the α-ray tracks has been reported by Donaldson and Miller (*Trans. Faraday Soc.*, **52**, 652 (1956) and Appleby and Schwarz (Ref. 5). However, the rate constant of this reaction is not high (4.5×10^7 M^{-1} ses^{-1}, Schwarz, *J. Phys. Chem.*, **66**, 255 (1962)) and the yield has not been established. If this reaction is assumed to occur at all, the $G(Fe^{3+})$ is given, by assuming the material balance suggested by Allen (Ref. 16, p. 51(, by $G(Fe^{3+}(=G_{-H_2O}+G_{HO_2}$ at an infinite LET, yielding the value of G_{-H_2O} lower than 2.9.

22) A. O. Allen, Ref. 16, p. 58.

23) C. J. Hochanadel, "Comparative Effects of Radiation," ed. by M. Burton, J. S. Kirby-Smith and J. L. Magee, John Wiley & Sons, New York (1960), p. 151.

24) M. Anbar, "Fundamental Processes in Radiation Chemistry," ed. by P. Ausloos, Interscience, New York (1968), p. 651.