THE ACTION OF α-PARTICLES ON SOLUTIONS CONTAINING FERROUS AND CUPRIC IONS

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Results have recently been published by Hart of a study of the kinetics of the oxidation, under ^{60}Co γ-ray irradiation, of ferrous ions in sulphuric acid solution when cupric ions are present. We have extended Hart's work, studying the same oxidation process under irradiation by ^{210}Po α-particles. With this radiation, two trends already discernible in the γ-ray work become more evident. They are (i) the occurrence of a reaction involving OH and H_2O_2 within the tracks to give HO_2, and (ii) interference of Cu^{2+} ions with the recombination of hydrogen atoms to give " molecular " hydrogen. In this study particular emphasis is directed on these intra-track reactions, with results which illustrate the now widely recognized naïvéte of the practice of dividing the products of irradiation of water into only two classes: (i) molecular, and (ii) radical.

The common assumption concerning the primary products of the decomposition of water by ionizing radiation is that they consist of H_2, H_2O_2, OH and H, the first two being regarded as " molecular " products in the sense that the yields of them are largely unaffected by the addition of substrates to the solution, the last two as " radical " products in that they are free to react with substrates according to homogeneous kinetics. Following Burton, let us define an apparent *G*-value for any chemical species as the number of atoms or molecules of that species which may be identified chemically per 100 eV of energy absorbed. A negative *G*-value on the same basis thus represents the number of atoms or molecules of that particular species disappearing per 100 eV absorbed. We thus quote *G*-values for the decomposition of water by any one type of radiation as G_{H_2}, $G_{H_2O_2}$, etc., bearing in mind that the overall stoichiometry demands the equality

$$-G_{H_2O} = G_H + 2G_{H_2} = G_{OH} + 2G_{H_2O_2}. \quad (1)$$

Consider next the elementary reactions involving these products and the following species: ferrous, ferric, cupric and cuprous ions and oxygen molecules. They are:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH^- \quad (2)$$
$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (3)$$
$$H + O_2 \rightarrow HO_2 \quad (4)$$
$$HO_2 \rightleftharpoons H^+ + O_2^- \quad (5a)$$
$$Cu^{2+} + O_2^- \rightarrow Cu^+ + O_2 \quad (5b)$$
$$Cu^+ + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+} \quad (6)$$
$$HO_2 + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \quad (7)$$
$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \quad (8)$$
$$H + Cu^{2+} \rightarrow H^+ + Cu^+. \quad (9)$$

We may write the resultant of (5*a*) and (5*b*) as (5), thus,

$$HO_2 + Cu^{2+} \rightarrow Cu^+ + H^+ + O_2. \quad (5)$$

In solutions in relatively dilute sulphuric acid of pH 2, in which the equilibrium (5*a*) is shifted towards dissociation so that reaction (5*b*) is important, it has been shown by Barb *et al.* that the ratio k_5/k_7 is about 15.[1] Hence in aerated solutions containing sufficient (tenfold) excess of cupric ions over ferrous, less than 1 % of the HO_2 radicals formed by (4) act as oxidizing agents, virtually all of them ultimately reducing Fe^{3+} according to (5) and (6). Furthermore, the fast reaction (9) may compete with reaction (4) for H atoms in the first place, in which case nearly all H atoms will ultimately reduce ferric ions, either by (4), (5) and (6), or by (9) and (6). Referring back to the stoichiometric eqn. (1), and bearing in mind reactions (2) and (3) involving the products on the right-hand side of this equation, we derive the equality $G_{Fe^{3+}} = 2G_{H_2}$ for these circumstances; and we also note that there should be no consumption or evolution of oxygen during the reaction.

In airfree solutions $\geqslant 10$ mM in cupric ion, all H atoms react according to (9), and the ferric yield and overall stoichiometry should thus be almost the same as in the aerated case.

Experimental observations carried out with γ-radiation by Hart[2] and by ourselves, which are in excellent agreement, confirm that this interpretation contains a large measure of the truth. With ^{60}Co γ-rays the yield of ferric ions is found to be very similar in aerated and airfree solutions initially 1 mM in Fe^{2+}, 10 mM in Cu^{2+} and 10 mN in H_2SO_4. Using a G-value for ferric ion of 15·5 for the ferrous sulphate dosimeter with γ-rays, $G_{Fe^{3+}}$ is found to be 0·64 in airfree solution, while $2G_{H_2}$ is 0·69.[2] The small discrepancy between these yields has, however, been shown by Hart[2] to be balanced by the evolution of oxygen, which, as we have seen, should not appear at all on the basis of this mechanism. With the α-radiation from ^{210}Po, we have now found that the corresponding discrepancy is in the same direction but much larger, viz. $G_{Fe^{3+}} = 2{\cdot}1$, $2G_{H_2} = 3{\cdot}1$; and that in airfree solution it is again balanced by oxygen evolution in stoichiometric equivalence. Closer examination reveals a dependence on ferrous ion concentration which remains unexplained by such a simple mechanism.

Following a suggestion originally made by Hart,[2] we believe that these results can be interpreted only by assuming that certain reactions between radicals and molecular products, in particular the following,

$$OH + H_2O_2 \rightarrow HO_2 + H_2O, \tag{10}$$

take place in local regions of high radical concentration during the expansion of the tracks, and that they are neither " radical " reactions in the sense that they can be treated by homogeneous kinetics, nor " molecular " in the sense that they are unaffected by the addition of substrates. Furthermore, from the behaviour of the system at higher cupric ion concentrations we obtain evidence that reaction (9) is able to interfere with the recombination of H atoms within the tracks according to (11),

$$H + H \rightarrow H_2. \tag{11}$$

This effect, which has recently been noted with γ-radiation,[3] has not been reported earlier for α-particles.

EXPERIMENTAL

PURITY OF MATERIALS

The α-emitter used was ^{210}Po, which was obtained in solution in sulphuric acid containing neodymium carrier from the Radiochemical Centre, Amersham. As described in an earlier publication,[4] the preparations from this source proved to be free of organic contaminants. The solutions were used as soon as possible after preparation to minimize the contamination with colloidal silica which results when solutions containing α-emitters are stored for extended periods in glass vessels. Hydrogen peroxide which accumulates in solution was destroyed when necessary by heating before use. The health hazards associated with the use of solid carrier-free preparations of polonium are enormously reduced when carrier-containing solutions are used. Separate studies using ^{60}Co γ-radiation showed that the neodymium carrier did not induce any spurious chemical effects in the ferrous + cupric system.

In the light of the experience gained in earlier work, analytical grade ferrous sulphate, cupric sulphate crystals and sulphuric acid were used without further purification. Before use the water was distilled freshly from alkaline permanganate, through a 1-m length of silica tubing at about 800° C.

ANALYTICAL METHODS

As in the work of Barb *et al.*,[1] the concentrations of ferrous and cupric ions are given as those of the corresponding sulphates. Such neglect of the extent of ionic dissociation will cause an overestimate of the true concentrations of the ions, but since the dissociation constants of the two salts are closely similar,[5] the qualitative conclusions reached herein are unaffected.

The ferric ion concentration in the solutions was measured spectrophotometrically using the absorption at 304 $m\mu$, in conformity with current practice. Dewhurst's values of the extinction coefficient as a function of pH and temperature, measured with the same equipment, were used.[6] At this wavelength the decadic molar extinction coefficient of cupric ion is less than 3 cm^{-1} both in 0·8 N and 10 mN H_2SO_4, and interference by this ion with the estimation of ferric ion is ordinarily negligible.

Gas analyses were carried out with a vacuum-apparatus comprising a McLeod gauge, an attached platinum filament for combustion, and cold fingers maintained at − 78° C for condensation of water vapour. The apparatus of this type used in earlier work[4] was modified to attain greater sensitivity and accuracy; details of the modifications will be described in a further publication. In this it will be shown that values were obtained of the molecular yield of hydrogen from aerated sulphuric acid solutions, irradiated by ^{60}Co γ-rays, in excellent agreement with the recent refined measurements of Schwarz *et al.*[7]

IRRADIATION METHODS

The stock polonium solutions contained about 10 mC ^{210}Po and about 1 mg neodymium carrier in about 6 ml of 0·1 N H_2SO_4. At the start of the irradiation a weighed quantity of this preparation was added to a weighed quantity of a solution containing Fe^{2+}, Cu^{2+}, and H_2SO_4 in such quantities that the desired concentrations of all three solutes were attained on mixing. At the same time the polonium content of the stock solution was estimated by making up a weighed aliquot in a weighed quantity of 0·8 N sulphuric acid containing 1 mM Fe^{2+}, placing this directly into a 1-cm spectrophotometer cell, and measuring the ferric ion concentration at intervals. A neck, 5-6 cm long, was sealed to the top of each cell used, to avoid the spread of α-ray contamination. A *G*-value of 6·2 for ferric ion production was assumed,[8] this being considered appropriate to that of the full length of the polonium α-ray track. The value of 5·9 of Miller and Wilkinson was obtained with α-particles whose range in the liquid had been shortened by previous absorption in mica and an argon gas phase.[4]

The rate of production of ferric ion in the aerated solutions containing Fe^{2+} and Cu^{2+} was followed spectrophotometrically in a similar manner. In aerated solutions containing cupric ions, corrections for spontaneous oxidation were made using polonium-free solutions of identical ferrous and cupric concentration, made up simultaneously with the radioactive solutions.

Glass electrode measurements showed that the pH of solutions 10 mN in H_2SO_4 was changed by no more than 0·2 pH unit when these were made 30 mM in Fe^{2+} and 50 mM in Cu^{2+}, so that the effect of solute concentration on pH was small.

In work with de-aerated solutions, the active solution was left sealed to the vacuum-apparatus used for gas analysis during irradiation. De-aeration was carried out with the solution attached to a refluxing trap filled with powdered solid carbon dioxide. This allowed the water to reflux satisfactorily *in vacuo* without condensing undesirable impurities from other parts of the apparatus. To check on this point, ferrous sulphate solutions were de-aerated in this way, sealed off from the line, and irradiated with ^{60}Co γ-rays. The ratio of ferric ion yields in aerated and airfree solutions initially 10 mM in ferrous and 0·8 N in sulphuric acid was found to be 1·89 ± 0·02, in agreement with the generally accepted value for this quantity.[9] After analysis of the evolved gases had been carried out on the irradiated airfree solution, air was admitted and the solution transferred to a spectrophotometer cell for measurement of ferric ion. Glass surfaces which had been contaminated with polonium were cleaned by several rinses with 10 % hydrofluoric acid, the subsequent disposal of the active wash-liquor being facilitated by immediate precipitation of fluoride ion with calcium.

RESULTS

SOLUTIONS 10 mM IN Cu^{2+} AND 10 mN IN H_2SO_4

Ferric ion concentration against time curves obtained in aerated solutions of different initial ferrous ion concentrations with the above constant concentrations of cupric ion and sulphuric acid are presented in fig. 1, which shows also the comparable curve for the normal dosimeter solution initially containing ferrous ion only in 0·8 N H_2SO_4. The linearity and identical slopes of the curves with initial ferrous ion concentrations equal to 1 mM and 0·3 mM are evident. Furthermore, in the 0·3 mM case the curve remains linear until the ferrous ion concentration has been reduced to 50 μM. There is thus no evidence of a dependence of yield on the ferrous ion concentration from 1 mM downwards in media containing 10 mM Cu^{2+} and 10 mN H_2SO_4.

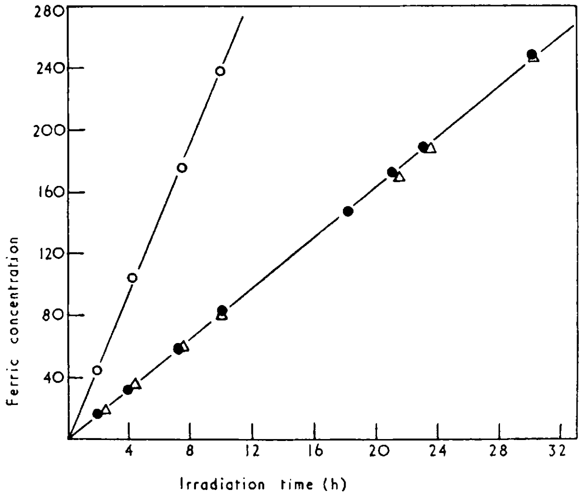

FIG. 1.—Ferric concentration (μM/l.) against irradiation time curves obtained from aerated solutions containing ^{210}Po. Open circles, solution initially 1·1 mM in ferrous ion and 0·8 N in H_2SO_4; closed circles, solution initially 0·3 mM in ferrous ion, 10 mM in cupric, and 10 mN in H_2SO_4; triangles, solution initially 1·45 mM in ferrous ion, 10 mM in cupric, and 10 mN in H_2SO_4.

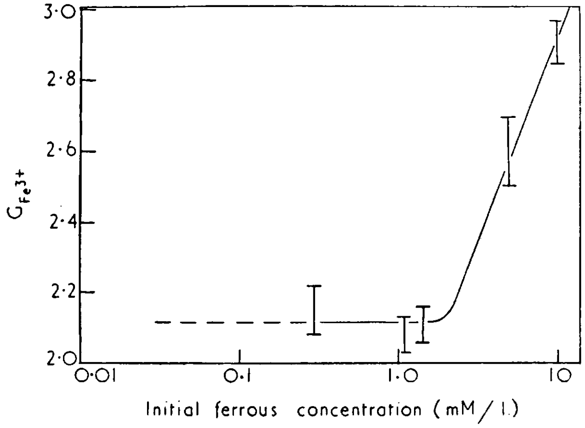

FIG. 2.—Ferric yield against initial ferrous concentration curve obtained from aerated solutions containing ^{210}Po. All solutions were 10 mM in cupric ion and 10 mN in H_2SO_4; standard deviations represented by length of vertical lines.

In fig. 2 the ferric ion yields obtained from the slopes of curves such as those of fig. 1 are plotted as a function of the initial ferrous ion concentration of the solutions. All the solutions were aerated and contained 10 mM Cu^{2+} and 10 mN H_2SO_4 as in fig. 1. From fig. 2 it appears that when the initial ferrous ion concentration rises above ~ 2 mM at constant [Cu^{2+}] the ferric yield rises sharply.

SOLUTIONS 10 mN IN H_2SO_4 WITH Cu^{2+} MAINTAINED IN TENFOLD EXCESS OVER Fe^{2+}

The results with 10 mN H_2SO_4 solutions containing a tenfold excess of Cu^{2+} over Fe^{2+} are presented in fig. 3. Here the observed *G*-values for Fe^{3+}, H_2 and O_2 are plotted as a function of solute concentration. With this constant ratio of [Cu^{2+}] to [Fe^{2+}] the HO_2 radicals formed act almost quantitatively as reducing agents as explained in the introduction.

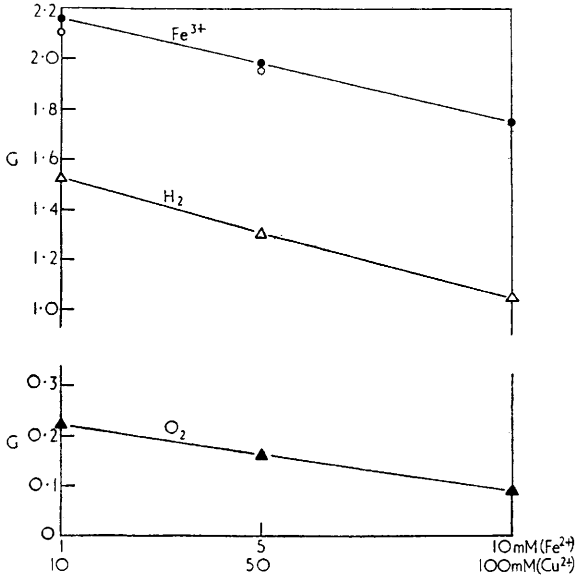

FIG. 3.—Yields of ferric ion, hydrogen and oxygen from airfree solutions containing ^{210}Po, as a function of initial ferrous and cupric concentrations, the ratio of these concentrations remaining constant at 1 : 10. All solutions were 10 mN in H_2SO_4. Closed circles, $G_{Fe^{3+}}$ based on mass balance; open circles, measured $G_{Fe^{3+}}$ in aerated solution.

The yields of ferric ion obtained by direct measurements in airfree solutions agreed within 4 % in all cases with those obtained by calculation from the overall mass balance: while both were identical within experimental error with the ferric ion yields in aerated solution, which are also plotted in fig. 3. Results in aerated solutions 10 mM in Fe^{2+} and 100 mM in Cu^{2+} could not be obtained owing to the high rate of spontaneous oxidation in these solutions.

SOLUTION IN 1 N H_2SO_4 CONTAINING 1 mM Fe^{2+} AND 10 mM Cu^{2+}

An airfree solution of this composition was irradiated in order to determine qualitatively the effect of pH on the system. The results indicated a rise in ferric ion yield and a fall in oxygen yield as compared with similar solutions in 10 mN H_2SO_4, while the yield of H_2 remained essentially unchanged. The figures during the oxidation of a total of 175 μM of ferrous ion were: $G_{H_2}^{Fe-Cu} = 1·57$, $G_{O_2}^{Fe-Cu} = 0·065$, $G_{Fe^{3+}}^{Fe-Cu}$ (measured) = 2·85, $G_{Fe^{3+}}^{Fe-Cu}$ (calculated from mass balance) = 2·88; though these *G*-values were not necessarily identical with the initial values at the start of the oxidation, as this is known not to be linear with time under these conditions.[2]

DISCUSSION

In solutions 10 mM in Cu^{2+} and 10 mN in H_2SO_4 the results of fig. 1 and 2 show that there is no dependence of the ferric ion yield on ferrous ion concentration from 1·6 mM downwards. In this range the overall stoichiometry of the reaction thus remains unchanged, and is represented by the results of fig. 3 for the concentrations 1 mM Fe^{2+} and 10 mM Cu^{2+}, i.e. $G^{Fe-Cu}_{Fe^{3+}} = 2{\cdot}1$, $G^{Fe-Cu}_{H_2} = 1{\cdot}55$, $G^{Fe-Cu}_{O_2} = 0{\cdot}23$. The only explanation of this evolution of oxygen which in our view is consistent with all the experimental facts is that presented in the introduction, viz. that there is a reaction between OH and H_2O_2 during the period of expansion of the tracks according to (10), and that the HO_2 formed reacts according to (5) or (7) depending on the pH of the solution and the ratio of $[Cu^{2+}]$ to $[Fe^{2+}]$. Hence the fall in oxygen yield just cited in 1 N H_2SO_4 containing a tenfold excess of $[Cu^{2+}]$ over $[Fe^{2+}]$, when $k_7[Fe^{2+}] > k_5[Cu^{2+}]$. Reaction (10) clearly cannot take place in the body of the solution, as the steady-state concentrations of both OH and H_2O_2 are too low. Comparison of the yields of these products with the estimated volume of the track at an early stage of its expansion shows, however, that the local concentrations of both species are momentarily at least 0·1 M, and to postulate such a reaction is then entirely plausible.

If this interpretation is correct, we can speak of HO_2 as being a primary product of the irradiation, G_{HO_2} being equal to the observed G_{O_2} for the concentration-independent region of fig. 2, viz. 0·23. The yields of the primary products of the α-ray-induced decomposition of dilute sulphuric acid solutions containing Cu^{2+} and Fe^{2+} are then represented by the following equation:

$$-G_{H_2O} = G_H + 2G_{H_2} - G_{HO_2} = G_{OH} + 2G_{H_2O_2} + 2G_{HO_2}, \qquad (12)$$

the reformation of H_2O in reaction (10) being taken into account. It will be noted that Burton's convention for writing these yields is now more convenient than those of Allen, Hart and Dainton, who write their *G*-values in terms of individual equations for the decomposition of water, such as $H_2O \rightarrow H + OH$, $2H_2O \rightarrow H_2 + H_2O_2$, etc. The inclusion of an equation involving HO_2 in such a scheme would be an unwarranted complication.

Using γ-rays, G_{HO_2} is small (from Hart's work, $G^{\gamma}_{HO_2} = 0{\cdot}026$),[2] and can ordinarily be neglected. We submit, however, that with α-radiation G_{HO_2} cannot from the evidence just presented be regarded as negligible.

On the basis of the mechanism given in the introduction, amended by the inclusion of reaction (10), the yield of hydrogen $G^{Fe-Cu}_{H_2}$ for the solutions in 1 N and 0·01 N acid with $[Cu^{2+}] = 10$ mM and $[Fe^{2+}] \leqslant 1{\cdot}6$ mM should be equal to the G_{H_2} of eqn. (12). It is in fact in agreement within experimental error with the value of G_{H_2} obtained by Miller and Wilkinson[4] with ferrous sulphate solutions. Values of the remaining quantities in eqn. (12) can be obtained using in addition the yield of ferric ion with α-particles from dissolved polonium in aerated solution.[8] Here the H atoms react exclusively according to (4) and (7), these processes being followed by (8), (2) and (3), and the following relationships are derived:

$$G^{Fe}_{Fe^{3+}} = 3G_H + G_{OH} + 2G_{H_2O_2} + 3G_{HO_2} = 6{\cdot}2,$$

$$G^{Fe-Cu}_{Fe^{3+}} = -G_H + G_{OH} + 2G_{H_2O_2} - G_{HO_2} = 2{\cdot}1,$$

$$2G_{H_2} = -G_H + G_{OH} + 2G_{H_2O_2} + 3G_{HO_2} = 3{\cdot}1.$$

The solution of these three simultaneous equations leads to the values for the yields quoted in table 1.

The calculated value for G_{HO_2} (0·25) in table 1 agrees within experimental error with the yield of oxygen from solutions 1 mM in $[Fe^{2+}]$, 10 mM in $[Cu^{2+}]$ and

10 mN in H_2SO_4 ($G_{O_2} = 0{\cdot}23$). It should be borne in mind that these figures are not to be regarded as constants but are subject to small variations depending on the concentration of solutes, as will be seen in more detail shortly.

TABLE 1.—APPROXIMATE YIELDS OF PRIMARY PRODUCTS OF THE α-RAY IRRADIATION OF SOLUTIONS BETWEEN 0·01 N AND 1 N IN H_2SO_4

$G_H = 0{\cdot}77$, $G_{HO_2} = 0{\cdot}25$,

$G_{H_2} = 1{\cdot}55$, $G_{OH} + 2G_{H_2O_2} = 3{\cdot}12$, $-G_{H_2O} = 3{\cdot}62$.

The products of the α-irradiation of water and dilute H_2SO_4 containing no Fe^{2+} or Cu^{2+}, with their approximate yields, have been found to be: $G_{H_2} = 1{\cdot}8$, $G_{H_2O_2} = 0{\cdot}9$, $G_{O_2} = 0{\cdot}42$.[10] The higher oxygen yield in the absence of Fe^{2+} can be attributed to a short-chain decomposition of H_2O_2 largely initiated by reaction (10) within the tracks, and involving the intermediates OH and HO_2 which react readily with Fe^{2+} when this is present. No O_2 is evolved from airfree solutions containing Fe^{2+} only.

We now pass on to consider the remainder of fig. 3, which presents the results of experiments in which a tenfold excess of [Cu^{2+}] over [Fe^{2+}] is maintained, but both are increased while the acidity of the solution remains constant. Under these conditions, as already described, $k_7[Fe^{2+}]$ is negligible in comparison with $k_5[Cu^{2+}]$, and $k_9[Cu^{2+}]$ rises with respect to $k_4[O_2]$. Here G_{H_2} is seen to fall from 1·55 at 1 mM [Fe^{2+}], 10 mM [Cu^{2+}] to 1·05 at 10 mM [Fe^{2+}], 100 mM [Cu^{2+}]. Our explanation of this effect is that, as [Cu^{2+}] rises, reaction (9) becomes predominant in the removal of H atoms, and is even able to penetrate into the zones where the "molecular" hydrogen is being formed, suppressing reaction (11). In agreement with this view, we have found that when the ferrous concentration is increased from 1 to 10 mM without a simultaneous increase in the concentration of [Cu^{2+}] the G_{H_2} remains constant at 1·55. There is some evidence from work with ^{60}Co γ-rays that (9) prevails over (4) in aerated solution even when [Cu^{2+}] is as low as 10 mM. We have found the ratio of ferric yields in aerated and airfree solutions containing 1 mM Fe^{2+}, 10 mM Cu^{2+} and 10 mN H_2SO_4 with this radiation to be 1·00, in fair agreement with Hart, who found it to be 1·03. The calculated figure using G_H for γ-rays of 3·77,[8] and the experimental one of k_5/k_7 would be 1·18 if (4) were predominant, whereas in the event of (9) prevailing it would be unity.

Simultaneously with this fall in $G_{H_2}^{Fe-Cu}$ there is a fall in $G_{O_2}^{Fe-Cu}$. This we believe to be due to a competition between reactions (3) and (10) for OH radicals within the tracks, reaction (3) being favoured with increasing [Fe^{2+}]. The effect of increasing [Fe^{2+}] is assigned to reaction (3) rather than the Fenton reaction (2) as the latter is very slow by comparison. In solutions in which the [Fe^{2+}] alone is increased to 10 mM, while the [Cu^{2+}] remains constant at 10 mM, we have observed the oxygen yield to fall to $G_{O_2}^{Fe-Cu} = 0{\cdot}11 \pm 0{\cdot}02$ in confirmation of this postulate. A reduction in oxygen yield is to be anticipated in any event due to the increase in reaction (7) relative to (5) involving HO_2 radicals, but the fall is much greater than would have been predicted using the experimental ratio of k_5/k_7 obtained by Barb *et al.*, viz. from $G_{O_2}^{Fe-Cu} = 0{\cdot}23$ to $G_{O_2}^{Fe-Cu} = 0{\cdot}215$. The replacement of reaction (10) by (3) leads not only to the oxidation of ferrous ion by one OH, but also by one H_2O_2, so that the ferric ion yield should increase markedly as (3) begins to compete with (10), other features of the process remaining constant. The rise in ferric ion yield on the right-hand side of fig. 2 is entirely in accord with this prediction, and is once again much greater than can be attributed to the increase in reaction (7) relative to (5), viz. at [Fe^{2+}] = 10 mM, the observed value of $G_{Fe^{3+}}^{Fe-Cu}$ is 2·91, whereas calculated using the experimental ratio k_5/k_7, it should be only 2·34.

In the face of this evidence, let us accept at least for the moment the principle that the intra-track reaction (10) takes place, and pass on to consider other analogous reactions such as the following:

$$H + H_2O_2 \rightarrow OH + H_2O \qquad (13)$$

$$OH + H_2 \rightarrow H_2O + H. \qquad (14)$$

Both these reactions are known from homogeneous kinetics to be rapid. Reaction (13) is known to be almost as fast as (4) at room temperature,[11] and is thus one of the fastest known reactions involving H atoms in aqueous solution, while reaction (14) takes place at a speed comparable with reaction (3),[12] and is thus in a similar category regarding OH radicals.

At a very early stage in the expansion of the tracks, both these reactions may take place to a small extent so rapidly as to escape detection, the only effect being a decrease in the $-G_{H_2O}$ of eqn. (12), and corresponding changes in the G-values of the individual products. Even at a somewhat later stage, (13) may continue to be favoured for a while over (4) when dissolved oxygen is present, but ultimately reaction (4) will dominate the situation for the H atoms remaining. In airfree solution, (13) may remain predominant to a greater extent over the alternative reactions removing the H atoms, viz. (11) and (15):

$$H + H^+ \rightarrow H_2^+. \qquad (15)$$

Miller and Wilkinson have shown that the observed ferric ion yield in airfree solution is rather lower than can be accounted for by (11) or (15) or any combination of the two occurring simultaneously.[4] An explanation of this discrepancy is possible if reaction (13) is invoked as just described, but it is by no means the only one. We intend to carry out experiments to obtain further information on this matter.

Concerning reaction (14), the little relevant evidence is mostly negative. Lefort has irradiated with α-particles solutions 0·75 M in acrylonitrile, which reacts extremely rapidly with OH radicals, and found a yield of molecular hydrogen from the solution very similar to that observed in the absence of this solute.[10]

The extent to which intra-track reactions such as (10), (13) and (14) take place will clearly be governed by the entropies of activation of the reactions involved, the relative diffusion rates of the species and the effective temperatures of the zones in which they react. It would be premature to pursue the matter further, other than to note that the terms " concentration " and " temperature " must be used with reserve in respect of a system in which the spatial distribution of reactants is non-uniform and equipartition cannot necessarily be assumed between the electronic, vibrational and other modes of the species involved.

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