KINETIC BEHAVIOR OF THE RADIOLYSIS PRODUCTS OF WATER

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I. Introduction

Radiation chemistry is the study of the chemical changes observable in materials exposed to ionizing radiations.* These changes are produced as the result of a series of intermediate steps following the initial absorption of energy. Before studying the chemical phenomena occurring in irradiated aqueous solutions it is well, therefore, first to recall briefly how this energy absorption by matter comes about.

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* For a more detailed analysis of this topic reference may usefully be made to numerous publications and reviews (*3, 17, 21, 22, 42, 43, 45, 49, 50, 57, 65, 76, 100, 102, 103, 104*).

A. PRIMARY ACTION OF IONIZING RADIATIONS

1. Electromagnetic Radiation

Gamma- or X-rays are absorbed in matter by various processes, the chief of which are, for energies usually employed in radiation chemistry, the photoelectric effect and the Compton effect. In the photoelectric effect a peripheral electron in the bombarded atom captures all the energy of the incident photon and is thus removed from its surroundings while acquiring energy $E = h\nu - I$, where I is the ionization energy corresponding to the level in which the electron is situated.

The Compton effect is an elastic collision between a photon and an electron, after which the electron carries only a fraction of the energy of the photon; the magnitude of this fraction varies with the angle of scattering.

The ratio between photoelectrons and Compton electrons depends on the wavelength of the incident radiation and the atomic number of the substance irradiated. In the case of the γ-rays from Co^{60}, the number of photoelectrons produced in water is very small in relation to that of Compton electrons. Summarizing, we may say that irradiation by γ- and X-rays produces electrons of varied energies. One is thus led to study the action of charged particles on matter.

2. Charged Particles

Charged particles (electrons, photoelectrons, Compton electrons, protons, deuterons, helium ions, etc.) can bring about excitation or ionization, either directly or by the intermediate action of secondary electrons. In the case of excitation, the whole molecule absorbs a certain amount of energy, which is a function of its electronic structure, but always less than its ionization energy. On the other hand, in the case of ionization, the energy is transmitted to a single electron, which may acquire sufficient velocity to cause, in its turn, ionization and excitation.

The spatial distribution of these phenomena in the irradiated medium depends on the nature and the energy of the particles: for the same energy, the density of ionization becomes greater as the particles become heavier. A radiation is often characterized by its linear energy transfer (L.E.T.), i.e., the energy transmitted to the irradiated material per unit length of trajectory $[dE/dx]$. Thus the mean L.E.T. of the α-rays of Po^{210} is equal to 146 kev/μ, while that of the Compton electrons produced by the γ-rays of Co^{60} is less than 1 kev/μ.

B. NATURE OF CHEMICAL CHANGES IN IRRADIATED AQUEOUS SOLUTIONS

The most commonly observed effects in solutions of inorganic substances are either oxidations or reductions, depending on the oxidation-reduction potential of the irradiated system in the aqueous medium under consideration. Thus, for oxidation-reduction couples with a normal potential of less than 1 volt, oxidations are usually observed, while reduction invariably occurs for those with a potential above 1 volt. When the solution to be irradiated has been previously degassed one can readily measure the gas produced, which always consists of hydrogen, sometimes admixed with oxygen.

When a dilute solution of sulfuric acid in the presence of air, or a solution whose components do not react with hydrogen peroxide, is irradiated, accumulation of the latter product is observed. If H_2O_2 reacts slowly with the solute, this may continue even after the irradiation is ended. All such reactions which occur in this way after irradiation are called "after effects," whether they are brought about by hydrogen peroxide or by any other intermediate product.

Because of the covalent character of bonds in organic substances, electron transfer rarely occurs when they are irradiated in dilute solution: usually atom transfer occurs, leading to dehydrogenation, hydroxylation, and the formation of degradation or condensation products.

In order to be able to estimate conveniently the chemical utilization of the energy absorbed, the yield, or G value, has been introduced. This is defined as the ratio of the number of molecules, ions, or free radicals formed or decomposed to the number of hundreds of electron volts absorbed in the solution. To give some idea of its order of magnitude it may be mentioned, for example, that tetravalent cerium in 0.8 N H_2SO_4 is reduced to trivalent cerium under the action of γ-radiation from Co^{60} with a yield, $G = 2.4$ (*46*, *92*). In the presence of air, ferrous ions in the same medium are oxidized with a yield $G(Fe^{3+}) = G(-Fe^{2+}) = 15.6$ mol/100 ev. (This value is taken as a reference standard in the dosimetry of γ-rays of Co^{60}, see reference *72*). The yield for the formation of hydrogen peroxide by the α-rays from Po in 0.8 N H_2SO_4 in absence of air is given by $G(H_2O_2) = 0.95$ mol/100 ev (*9*). This reaction is accompanied by evolution of hydrogen [$G(H_2) = 1.7$ mol/100 ev] and oxygen [$G(O_2) = 0.40$ mol/100 ev]. Many other yields have been determined, as well as their dependence on various factors (concentration of the solute, radiation intensity (dosage rate), dose absorbed, nature and energy of the radiation, and the presence of other solutes).

C. MECHANISM OF THE RADIOLYSIS OF WATER

In order to establish the connection between the primary physical effects (ionization and excitation) and the chemical effects which can ultimately be measured in irradiated aqueous solutions, three fundamental concepts must be introduced. These are the idea of indirect action and the hypotheses of radical and of molecular products. Historically, these have forced themselves successively on experimenters.

1. Indirect Action

It has been recognized for a long time (*27, 28, 39, 40*) that energy given up by radiation to aqueous solutions is not captured directly by the solute, when the molarity of the latter is of the order of 0.1, but is stored up by the irradiated water, giving it oxidation-reduction properties capable later of changing compounds in solution. The reality of this concept of "activation" of water is shown mainly by the fact that yields are for the most part constant when the concentration of the dissolved substance is varied within certain limits. It is only when the concentration becomes much higher (0.5–1 *M*) that direct effects, due to absorption of radiation by the solute, and proportional to its electronic concentration, can be observed.

2. Radical Hypothesis

As early as 1914 Debierne (*30*) suggested that activation of water by radiation could be attributed to the formation of H atoms and free OH radicals. This hypothesis was subsequently put forward several times (*63, 83*), but only when the existence of radical processes in irradiated gases was demonstrated (*18, 58, 90*), was it made more precise (*98*) and utilized.

It is assumed that OH radicals are formed from positive ions according to the equation $H_2O^+ \rightarrow H^+ + OH$, or perhaps by a molecule-ion interaction: $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$, while H atoms arise from the action on water of the ejected electron, perhaps after its solvation:

$$H_2O + e \rightarrow OH^- + H.$$

It is also considered (*32, 85*) that the electron may recombine with the H_2O^+ ion, forming an excited water molecule ($H_2O^+ + e \rightarrow H_2O^*$). This water molecule will decompose subsequently into an H atom and an OH radical ($H_2O^* \rightarrow H + OH$). Whatever the process envisaged, the stoichiometric result is the same.

These reactions involving the transformation of ions into radicals are very fast, and it appears that they occur before the solute is able to intervene in the primary phenomena of radiolysis. The main proofs of the existence of free OH or H radicals in irradiated aqueous solutions are as follows.

(*a*) Radiolysis yields often depend on the presence of oxygen in the solutions. Thus the yield for the oxidation of ferrous ions by γ-rays is practically doubled by the presence of oxygen dissolved at atmospheric pressure. This cannot be explained by a purely ionic hypothesis. On the other hand, with a radical hypothesis it will be seen that H atoms become HO_2 radicals, which are capable of oxidizing three ion-equivalents according to the reactions:

$$HO_2 + Fe^{++} \rightarrow Fe^{3+} + HO_2^-$$
$$HO_2^- + H^+ \rightarrow H_2O_2$$
$$H_2O_2 + Fe^{++} \rightarrow Fe^{3+} + OH + OH^-$$
$$OH + Fe^{++} \rightarrow Fe^{3+} + OH^-.$$

(*b*) Polymerization of acrylonitrile in an irradiated aqueous solution has been observed (*25*), although it is known that this reaction can be initiated only by free radicals.

(*c*) The existence of OH radicals during the irradiation of solid water has been detected directly by paramagnetic resonance (*70*).

In spite of this, the single hypothesis of the formation of H and OH radicals in the irradiation of water does not suffice for the kinetic interpretation of all the results obtained, and this has led to the formulation of the following hypothesis.

3. Molecular Products Hypothesis. Allen (*1*, *2*, *4*) has been led to think that, in addition to H and OH radicals, the two other radiolytic products, H_2 and H_2O_2, are also formed before the solute is able to intervene, at least when the solution is sufficiently dilute. Indeed, for a certain number of systems, the yields of hydrogen and hydrogen peroxide, whether measured directly or determined from the kinetics, are independent of the nature and concentration of the solute. Everything occurs as if the molecular products are formed in preferred sites, which can only be in the immediate neighborhoods of the trajectories of the secondary electrons, and which are called *spurs*.

The energy of these electrons is very low and, as a result, the ionization phenomena which they produce are very localized. Dyne and Kennedy (*35*) consider that the average spur corresponds to an energy exchange of 65 ev and contains about six pairs of radicals arising either from excitation or from ionization of water molecules. These radicals may combine to form molecular products

$$H + H \rightarrow H_2,$$
$$OH + OH \rightarrow H_2O_2,$$

or may recombine

$$H + OH \rightarrow H_2O.$$

These three reactions are favored by the high local radical concentration, but a certain fraction of the radicals diffuse toward the outside of the spur, where reaction with the solute can occur. The further the radical moves from the spur, the greater is the probability that it will react with the solute and the smaller the chance that it will encounter another radical derived from the same spur. Several calculations on the heterogeneous kinetics have been made (*37*, *38*, *60*, *73*). They show, particularly, that, as a first approximation, the solution at any instant can be divided into two zones. One of these is formed by all the spurs, where the radical and molecular products are built up. The other consists of the bulk of the solution where the four species H, OH, H_2, and H_2O_2 may be considered as appearing at a constant rate which is independent of the nature of the solute and, to a certain extent, of its concentration. The classical kinetic laws are valid in this zone.

The appearance of products coming from the spurs may be represented by the following equation:

$$G_{-H_2O}H_2O \overset{100\text{ev}}{\rightsquigarrow} G_{H}H + G_{OH}OH + G_{H_2}H_2 + G_{H_2O_2}H_2O_2, \tag{I}$$

where G_{-H_2O} represents the number of molecules of water decomposed per 100 ev of energy absorbed, G_H the number of H atoms appearing, and so on. These values of the yields G_{-H_2O}, G_H, G_{OH}, G_{H_2}, and $G_{H_2O_2}$ are linked by the relationships expressing the stiochiometric balance of Eq. (I)

$$G_{-H_2O} = G_H + 2G_{H_2} = G_{OH} + 2G_{H_2O_2}.$$

Equation (I) allows us to treat a large number of chemical reactions in irradiated water quantitatively, at least within certain concentration limits. When the solute concentration is high it is able to interfere in the spurs and modify the radical and molecular yields, for example, by capturing some of the OH radicals and H atoms and thus partially preventing their dimerization to molecular products. This interaction will be considered later.

Application of Eq. (I) to the action of α-rays on aqueous solutions has presented certain difficulties. Various authors have finally been led to postulate that reactions between radical and molecular products would take place in the track (*33*, *49*, *77*):

$$OH + H_2O_2 \rightarrow H_2O + HO_2$$
$$OH + H_2 \rightarrow H + H_2O$$
$$H + H_2O_2 \rightarrow OH + H_2O.$$

These reactions will, however, be suppressed or reduced in extent by solutes which capture radicals readily, and molecular and radical yields might thus, to a certain extent, depend on the nature and concentration of the solute (*78*, *80*).

The radical HO_2 appears as a primary product of radiolysis of water, and Eq. (I) must be written for α-rays in the form:

$$G_{-H_2O}H_2O \rightsquigarrow G_{H}H + G_{OH}OH + G_{HO_2}HO_2 + G_{H_2}H_2 + G_{H_2O_2}H_2O_2 \tag{I'}$$

with the equation of balance

$$G_{-H_2O} = G_H + 2G_{H_2} - G_{HO_2} = G_{OH} + 2G_{H_2O_2} + 2G_{HO_2}.$$

D. Rates of Formation of Radical and Molecular Products

Numerical values of the coefficients in Eqs. (I) and (I′) may be calculated in certain simple cases where the nature of the chemical action of the radicals with the solute being studied is well known. For example, for the γ-rays from Co^{60} it is possible to deduce (*4*) the rates of appearance of H, OH, H_2O_2, and H_2 from the yields of three radiolytic effects: the reduction of Ce(IV), the evolution of hydrogen which accompanies it, and the oxidation of ferrous sulfate in the presence of air. It is assumed that H atoms reduce Ce(IV) while OH radicals oxidize Ce(III). The reducing action of hydrogen peroxide on Ce(IV) is well known and consequently we may write*

$$G[-\text{Ce(IV)}] = G_H - G_{OH} + 2G_{H_2O_2}. \tag{1}$$

Since hydrogen does not react with the products present it is evolved in the free state:

$$G(H_2) = G_{H_2}. \tag{2}$$

Ferrous ions in presence of air are oxidized by OH and HO_2 radicals and by hydrogen peroxide according to the reactions:

$$OH + Fe^{++} \rightarrow Fe^{3+} + OH^-$$
$$H_2O_2 + Fe^{++} \rightarrow OH + OH^- + Fe^{3+}$$
$$HO_2 + Fe^{++} \rightarrow Fe^{3+} + HO_2^-.$$

The oxidation yield is then equal to:

$$G(Fe^{3+}) = G_{OH} + 3G_H + 2G_{H_2O_2}. \tag{3}$$

Equations (1), (2), and (3), together with the equation of balance,

$$2G_{H_2} + G_H = G_{OH} + 2G_{H_2O_2},$$

allow the radical and molecular yields to be calculated. Various analogous determinations have been carried out with other solutes (see, for example, *36*, *53*, *79*, *96*). Thus, irradiations of dilute vanadium solutions with γ-rays from Co^{60} under various conditions have given for a medium consisting of 0.8 N H_2SO_4 the following values: $G_H = 3.7$; $G_{OH} = 2.8$; $G_{H_2} = 0.45$; $G_{H_2O_2} = 0.9$; $G_{-H_2O} = 4.6$ (*79*). For the radiolysis of solutions of hydroxylamine in a neutral medium it is found (*96*) that $G_H = 2.7$; $G_{OH} = 2.1$;

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* G(X) denotes the measured yields and G_x those defined by Eq. (I) for the appearance of radical and molecular products.

$G_{H_2O_2} = 0.72$; $G_{H_2} = 0.42$; $G_{-H_2O} = 3.54$. These two series of values are in satisfactory agreement with other determinations. The fact that, for a given acidity, these values are independent of the system studied thus constitutes an excellent confirmation of the initial hypothesis. It is possible, therefore, within certain limits, to consider irradiated water as a homogeneous solution of the species H, OH, H_2, and H_2O_2.

E. The Nature of the Chemical Action of Radical and Molecular Products

The radicals H and OH react rapidly, from the instant of their formation, either with the solute or with molecular products. Their stationary states are established in times which are of the order of a microsecond and correspond with very low radical concentrations. The determination of the nature of these reactions is one of the tasks in the interpretation of radiation chemistry: research in this direction is guided by certain criteria, the first of which is involved with the establishment of the thermodynamic balance. Table I, which summarizes the oxidation-reduction potentials at pH 0 of various systems which occur in irradiated water, is based on Latimer's data *(62)*.

TABLE I

Normal Potentials of Various Systems Present in Irradiated Water

Eq. No.	Reactions	E_0 in volts (European convention)
(4)	$H_2O \leftrightharpoons H^+ + OH + e$	2.8
(5)	$H_2 \leftrightharpoons H + H^+ + e$	2.1
(6)	$2H_2O \leftrightharpoons H_2O_2 + 2H^+ + 2e$	1.77
(7)	$H_2O_2 \leftrightharpoons H^+ + HO_2 + e$	1.5
(8)	$OH + H_2O \leftrightharpoons H_2O_2 + H^+ + e$	0.72
(9)	$H_2O_2 \leftrightharpoons 2H^+ + O_2 + 2e$	0.68
(10)	$HO_2 \leftrightharpoons H^+ + O_2 + e$	−0.13
(11)	$H \leftrightharpoons H^+ + e$	−2.10

Examination of this table shows the following points: *(a)* radical and molecular products cannot react with solvent water; *(b)* they can, on the other hand, react among themselves by radical-radical or radical-molecular reaction. For example, the reactions given below are thermodynamically possible:

(10)–(7) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

(7)–(4) $OH + H_2O_2 \rightarrow HO_2 + H_2O$

(5)–(4) $OH + H_2 \rightarrow H + H_2O$

(11)–(8) $H + H_2O_2 \rightarrow OH + H_2O$

(10)–(8) $HO_2 + H_2O_2 \rightarrow H_2O + OH + O_2$.

These reactions can take place in the absence of a solute, or when the concentration of the latter is insufficient to enable it to capture radical or molecular products completely. There is thus often a competition between reactions, and the rate constants then determine the course of events.

The oxidation-reduction potential of the solute may be compared with the potentials given in Table I. It will then be seen that the radical and molecular products are often able, on the basis of thermodynamics, to react as oxidizing or reducing agents toward one or other of the valence states of the solute (Table II). Here again it is the relative rates of these reactions which is determinative. Thermodynamic considerations are not, then, sufficient for the prediction of reactions occurring in irradiated aqueous solutions. A knowledge of the rates of radical reactions brings more coherence and precision to the formulation of reaction schemes.

TABLE II
THERMODYNAMICALLY POSSIBLE REACTIONS IN WATER IRRADIATED AT pH 0 FOR A SYSTEM AT THE NORMAL POTENTIAL E_0

E_0	Reduction by	Oxidation by
$2.8 > E_0 > 2.1$	H,HO_2,OH,H_2O_2,H_2	OH
$2.1 > E_0 > 1.77$	H,HO_2,OH,H_2O_2	OH,H
$1.77 > E_0 > 1.5$	H,HO_2,OH,H_2O_2	$OH,H,H_2O_2 + OH$
$1.5 > E_0 > 0.77$	$H,HO_2,OH,H_2O_2 + HO_2$	$OH,H,H_2O_2 + OH,HO_2$
$0.72 > E_0 > 0.68$	$H,HO_2,H_2O_2 + HO_2$	OH,H,H_2O_2,HO_2
$0.68 > E_0 > -0.13$	H,HO_2	OH,H,H_2O_2,HO_2
$-0.13 > E_0 > -2.10$	H	OH,H,H_2O_2,HO_2

F. RATES OF CHEMICAL REACTIONS OF RADICAL PRODUCTS

The absolute measurement of the rates of radical reactions presents great difficulties, which, however, are resolved in the case of chain reactions. The rotating sector method enables the chain length to be measured and the rate of the chain-terminating reaction to be calculated. Its application in radiation chemistry is, however, not easy, and absolute rate measurements are very few in number. It is far more frequently possible to determine the ratio of two kinetic constants. To do this it is necessary that two products present in the solution compete for the same radical. Thus, for example, the case of two reactions of the OH radical may be considered:

$$\mathrm{OH} + \mathrm{A} \rightarrow \mathrm{A}' \tag{12}$$

$$\mathrm{OH} + \mathrm{B} \rightarrow \mathrm{B}' \tag{13}$$

The equation of the stationary state is:

$$\frac{d(\mathrm{OH})}{dt} = G_{\mathrm{OH}}I - k_{12}(\mathrm{A})(\mathrm{OH}) - k_{13}(\mathrm{B})(\mathrm{OH}) = 0$$

where I is the radiation intensity in hundreds of electron volts per unit volume and per unit time. The yield for the formation of A′, $G(A')$, is given at each instant by:

$$G(A') = \frac{k_{12}(\mathrm{OH})(\mathrm{A})}{I} = \frac{G_{\mathrm{OH}}}{1 + [k_{13}(\mathrm{B})/k_{12}(\mathrm{A})]}.$$

The ratio k_{13}/k_{12} may then be determined if the rate of appearance of OH radicals is known

$$\frac{k_{13}}{k_{12}} = \left[\frac{G_{\mathrm{OH}}}{G(A')} - 1\right]\frac{(\mathrm{A})}{(\mathrm{B})}.$$

In practice the expression giving k_{13}/k_{12} is not often so simple, for H atoms are able to react with one or several species A, B, A′, B′, or, in the presence of air, with O_2, to give the radical HO_2. These reactions, and also those of hydrogen peroxide, must be taken into consideration in the kinetic calculation. The determination of this ratio is then often linked with a knowledge of all the reactions which occur in the irradiated solution. Nevertheless, however complicated the final equation may be, the rate of appearance of A′ will always be a function of k_{13}/k_{12}.

Another difficulty arises from the fact that, to obtain sufficient precision, the ratio of concentrations of A and B must be chosen so that competition between the reactions described in Eqs. (12) and (13) is fully effective. A simple calculation shows that the ratio $[k_{12}(\mathrm{A})]/[k_{13}(\mathrm{B})]$ should be of the order of unity for maximum precision. It is also of interest to vary the ratio (A)/(B) in order to verify the constancy of the ratio of constant rates and hence the corrections of the reaction scheme. Now fixing the concentrations initially or varying them over wide limits may introduce complications. In practice, besides influencing the competing reactions, the concentration variation may modify the phenomena in three different ways.

(1) As has been seen, when the solution is dilute the solute may no longer capture all the radicals, which will then react either with molecular products or with one another. These reactions will then modify the kinetic scheme. The study of these concentration ranges corresponding to *incomplete capture* will therefore be of interest in determining the ratio of kinetic constants.

(2) If, on the other hand, the concentration is increased the solute may react in the spurs and partially prevent the formation of H_2 and H_2O_2 by capturing their parent radicals. This implies a change in the radical or molecular yields. The study of this interaction can no longer be treated by the classical methods of kinetics.

(3) Finally, for high concentrations, *the direct effect* of the radiation is no longer negligible.

The exact ranges of concentrations corresponding to these effects depend on the nature of the solute and are difficult to predict. However, for a certain number of solutions with concentrations between 10^{-1} and $10^{-3}M$ none of the three phenomena mentioned above occurs to a noticeable extent.

Even if it is often difficult to obtain kinetic data in radiation chemistry, several ratios of constants have been determined and it is proposed to collect these values in order to see if it is possible to classify radical reactions according to their rates. To do this, results obtained with techniques for producing radicals other than ionizing radiations, such as, for example, the photochemical decomposition of H_2O_2 or Fenton's reagent, are also considered.

II. Rates of Reactions of the OH Radical

We will attempt to calculate from the data in the literature the value of the ratio of the kinetic constants in the expression

$$\frac{k_{\mathrm{OH+S}}}{k_{\mathrm{OH+H_2O_2}}} = \mathcal{R}_{\mathrm{OH,S}}$$

for various solutes S. The choice of the reaction

$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$

as a reference is governed by the important role played in the radiolysis of aqueous solutions by hydrogen peroxide, produced both in the decomposition of water and by the combination of two HO_2 radicals:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2.$$

A. Direct Determinations of $\mathcal{R}_{\mathrm{OH,S}}$

This quantity may be derived directly from the results of irradiation of mixtures of hydrogen peroxide with the solute, provided that these two products do not interact rapidly. A determination of this sort has been made for four compounds: benzene, hydrogen, formic acid, and nitrites.

$\underline{\mathcal{R}_{\mathrm{OH,C_6H_6}}}$

Phung and Burton (*75*) have irradiated aqueous solutions of benzene with the γ-rays from Co^{60} and have measured the yields of phenol, diphenyl, and hydrogen peroxide as a function of various parameters. The authors interpret their results on aerated 0.8 N sulfuric acid solutions by the following scheme:

$$\mathrm{H + C_6H_6 \rightarrow C_6H_7 \rightarrow polymer} \tag{14}$$
$$\mathrm{OH + C_6H_6 \rightarrow C_6H_5 + H_2O} \tag{15}$$
$$\mathrm{OH + H_2O_2 \rightarrow H_2O + HO_2} \tag{16}$$
$$\mathrm{H + O_2 \rightarrow HO_2} \tag{17}$$
$$\mathrm{C_6H_5 + O_2 \rightarrow C_6H_5O_2} \tag{18}$$
$$\mathrm{HO_2 + HO_2 \rightarrow H_2O_2 + O_2} \tag{19}$$
$$\mathrm{C_6H_5O_2 + H_2O \rightarrow C_6H_5OH + HO_2} \tag{20}$$
$$\mathrm{C_6H_5O_2 + C_6H_6 \rightarrow oxygenated\ products + OH} \tag{21}$$

The rate of appearance of phenol is determined by two pairs of competing reactions; that of water and benzene for the $C_6H_5O_2$ radical and that of benzene and hydrogen peroxide for the OH radical. The yield of phenol is given by the following equation:

$$G(\mathrm{C_6H_5OH}) = \frac{G_{\mathrm{OH}}}{1 + \left[1 + \dfrac{k_{21}(\mathrm{C_6H_6})}{k_{20}(\mathrm{H_2O})}\right] \dfrac{k_{16}(\mathrm{H_2O_2})}{k_{15}(\mathrm{C_6H_6})}}.$$

The authors have determined k_{21}/k_{20} from the consumption of oxygen. From the preceding equation they calculate $\mathcal{R}_{\mathrm{OH,C_6H_6}} = 0.47 \pm 0.08$.

$\mathcal{R}_{\mathrm{OH,H_2}}$

The determination of $\mathcal{R}_{\mathrm{OH,H_2}}$ is very important, as H_2 and H_2O_2 are the two molecular products of the decomposition of water. It was carried out in 1952 by Hochanadel (*55*), who studied the radiolysis by $\mathrm{Co^{60}}$ γ-rays of deaerated solutions of H_2 and H_2O_2 in a pH range 2.5–7. The author postulated the following mechanism:

$$\mathrm{H_2O_2 + H \rightarrow H_2O + OH}$$
$$\mathrm{H_2 + OH \rightarrow H_2O + H}$$
$$\mathrm{H_2O_2 + OH \rightarrow H_2O + HO_2}$$
$$\mathrm{H + HO_2 \rightarrow H_2O_2}$$

The fact that H_2O_2 competes with H_2 for the capture of OH radicals decreases the chain length:

$$G(-\mathrm{H_2O_2}) = \frac{G_{\mathrm{H}} + G_{\mathrm{OH}}}{2} \frac{k_{\mathrm{OH+H_2}}(\mathrm{H_2})}{k_{\mathrm{OH+H_2O_2}}(\mathrm{H_2O_2})} - G_{\mathrm{H_2}}.$$

Hochanadel measured the initial decomposition rates of H_2O_2 for various values of the ratio $(\mathrm{H_2})/(\mathrm{H_2O_2})$. From his results it is possible to calculate (*8*) that $\mathcal{R}_{\mathrm{OH,H_2}} = 1.02$ if the more recent value of $(G_{\mathrm{H}} + G_{\mathrm{OH}})/2$ of 2.51 is taken instead of that used by the author (i.e., 2.74).

Hart, McDonnel, and Gordon (*51*) give $\mathcal{R}_{\mathrm{OH,H_2}}$ as 0.98. Although the value 3.13 has also been quoted (*56*), Allen and Schwarz (*8*) have concluded that a value of 1 should be retained for $\mathcal{R}_{\mathrm{OH,H_2}}$ between pH 2 and 7, and this will be adopted in this article. Unfortunately no determination of this quantity has been made for 0.8 N H_2SO_4. This fact is the more regrettable, as according to Sworski (*92*) the rate of the reaction

$$OH + H_2 \rightarrow H + H_2O$$

depends on the sulfuric acid concentration. We will discuss later the influence of H_2SO_4 on the rates of reactions of the OH radical.

$\mathcal{R}_{OH,HCOOH}$

This quantity has been measured by Weeks and Matheson (*97*) in the course of a photochemical investigation in which they studied the decomposition of formic acid in a chain reaction in the presence of H_2O_2 and absence of air and attributed it to the following reactions:

$$\begin{gathered} H_2O_2 \xrightarrow{h\nu} 2OH \\ OH + HCOOH \rightarrow H_2O + HCOO \\ HCOO + H_2O_2 \rightarrow H_2O + CO_2 + OH \\ OH + H_2O_2 \rightarrow HO_2 + H_2O \text{ (chain breaking).} \end{gathered}$$

This mechanism had already been established by Hart (*47*) in connection with the study of the action of γ-rays from Co^{60} on similar solutions. From measurements of the rate of formation of CO_2, Weeks and Matheson calculated $\mathcal{R}_{OH,HCOOH} = 5.4$ for $10^{-3}N$ H_2SO_4, which is in agreement with Hart's results.

$\mathcal{R}_{OH,NO_2^-}$

Schwarz and Allen (*87*) have studied the action of the γ-rays from Co^{60} on neutral deaerated solutions of nitrites, containing, initially, hydrogen peroxide. The OH radical leads to the oxidation of nitrites:

$$\begin{gathered} OH + NO_2^- \rightarrow NO_2 + OH^- \\ 2NO_2 + H_2O \rightarrow HNO_2 + H^+ + NO_3^-. \end{gathered}$$

Hydrogen peroxide prevents it from playing this role by reacting according to the following scheme:

$$\begin{gathered} OH + H_2O_2 \rightarrow HO_2 + H_2O \\ HO_2 + NO_2 \rightarrow HNO_2 + O_2. \end{gathered}$$

From the variation in the oxidation yield as a function of the H_2O_2 concentration, Schwarz and Allen calculate that in a neutral medium $\mathcal{R}_{OH,NO_2^-} = 55 \pm 20$. The four values of $\mathcal{R}_{OH,S}$ determined separately by a direct method now enables us to calculate other values indirectly.

B. VALUE OF $\mathcal{R}_{OH,S}$ CALCULATED FROM $\mathcal{R}_{OH,C_6H_6}$

$\mathcal{R}_{OH,C_6H_5OH}$

Kurien, Phung, and Burton (*61*) studied the effect of small quantities of benzene and phenol on the yield for the oxidation of ferrous ions by the γ-rays from Co^{60} in the presence of air. For the concentrations studied the increase in yield is due, according to the authors, to the following reactions:

$$RH + OH \rightarrow R + H_2O$$
$$R + O_2 \rightarrow RO_2.$$

The RO_2 radical, like HO_2, will oxidize three ferrous ions, whereas, when OH reacts according to the equation

$$OH + Fe^{++} \rightarrow Fe^{3+} + OH^-,$$

it oxidizes only one.

Comparing the concentrations of benzene and phenol needed to obtain the same increase in the oxidation yield of Fe^{2+}, the authors conclude that $k_{OH+C_6H_6}/k_{OH+C_6H_5OH} = 12$ in 0.8 N H_2SO_4. Since $\mathcal{R}_{OH,C_6H_6} = 0.47$, it will be seen that in this medium $\mathcal{R}_{OH,C_6H_5OH} = 0.039$.

C. VALUES OF $\mathcal{R}_{OH,S}$ CALCULATED FROM $\mathcal{R}_{OH,H_2}$

The determination of $\mathcal{R}_{OH,H_2}$ previously mentioned allows the rate of reaction of OH radicals with Fe^{++} ions to be evaluated and this, in turn, makes possible a comparison of the rates of the reaction of OH radicals with D_2, CO, Sn^{++}, acrylamide, and various organic compounds.

$\mathcal{R}_{OH,Fe^{++}}$

The value of $k_{OH+Fe^{++}}/k_{OH+H_2}$ has been determined by Dainton, Hardwick *et al.* (*16*, *23*) from a study of the influence of hydrogen on Fenton's reagent. In an aerated solution H_2 reacts with OH according to the equations

$$H_2 + OH \rightarrow H + H_2O$$
$$H + O_2 \rightarrow HO_2.$$

Formation of the HO_2 radical from OH increases the rate of oxidation of Fe^{++}. From the variation of this rate as a function of the hydrogen concentration, Dainton and Hardwick calculated $k_{OH+Fe^{++}}/k_{OH+H_2} = 7.1$ in 0.1 N $HClO_4$. Another determination of the same ratio was made by Rothschild and Allen (*84*), who irradiated sulfuric acid solutions of Fe^{++} with γ-rays from Co^{60} in the absence of air and in the presence of hydrogen. In this case H_2 again converts OH radicals into H atoms. These two species do not always react in the same way with Fe^{++}, for OH radicals oxidize ferrous ions irrespective of the acidity, whereas H atoms can either reduce

$$H + Fe^{3+} \rightarrow Fe^{++} + H^+$$

or, in an acid medium, oxidize, by a reaction whose nature is still under discussion and to which we will return.

Irrespective of the nature of this reaction, the authors calculate from the decrease in the oxidation yield of Fe^{++} as a function of hydrogen concentration that $k_{OH+Fe^{++}}/k_{OH+H_2} = 5.7$ at pH 2.10 and 7.1 at pH 1.57, in agreement with the preceding results. Bearing in mind the accuracy of the determinations the mean value 6.4 will be adopted for a pH of about 2. Between pH 2 and 7 $\mathcal{R}_{OH,H_2} = 1$, from which a value of $\mathcal{R}_{OH,Fe^{++}} = 6.4$ may be calculated.

$\mathcal{R}_{OH,D_2}$

Using the first of the two preceding methods, the same authors (*16*) determined the ratio $k_{OH+D_2}/k_{OH+Fe^{++}} = 0.050$ in 0.1 N $HClO_4$, from which $\mathcal{R}_{OH,D_2} = 0.32$.

$\mathcal{R}_{OH,CO}$

Dainton and Hardwick (*23*) measured the rate of the reaction

$$OH + CO \rightarrow CO_2 + H,$$

which also converts OH into H, and found $k_{OH+CO}/k_{OH+Fe^{++}} = 2.6$ in 0.2 N $HClO_4$ and 2.14 in 0.8 N H_2SO_4. We will adopt the value 2.6 obtained in absence of HSO_4^- ions, since, according to Sworski (*92*), these influence the rate of reaction of OH with H_2 and thus the ratio found. Using the value of $\mathcal{R}_{OH,Fe^{++}}$, we find $\mathcal{R}_{OH,CO} = 16.6$.

$\mathcal{R}_{OH,Sn^{++}}$

Boyle, Weiner, and Hochanadel (*15*) studied the reduction of Fe^{3+} by Sn^{++} under the influence of the γ-rays of Co^{60}

$$2Fe^{3+} + Sn^{++} = Sn^{4+} + 2Fe^{++}. \tag{22}$$

They assume that OH radicals oxidize Sn^{++}:

$$OH + Sn^{++} \rightarrow Sn^{3+} + OH^-.$$

This reaction is followed by:

$$Sn^{3+} + Fe^{3+} \rightarrow Sn^{4+} + Fe^{++}$$

If there is a sufficient concentration of ferrous ions, the reaction

$$OH + Fe^{++} \rightarrow Fe^{3+} + OH^-$$

decreases the over-all yield (22). One can calculate in this way that $k_{\mathrm{Sn}^{++}+\mathrm{OH}}/k_{\mathrm{Fe}^{++}+\mathrm{OH}} = 7.0$ in 0.8 N H_2SO_4. We have seen that $\mathcal{R}_{\mathrm{OH,Fe}^{++}} = 6.4$ and we therefore deduce that $\mathcal{R}_{\mathrm{OH,Sn}^{++}} = 44.8$. However, since ratios have been compared which have not been measured for the same acidity, a more direct confirmation of this result is necessary.

$\mathcal{R}_{\mathrm{OH,RH}}$

The value of $\mathcal{R}_{\mathrm{OH,Fe}^{++}}$ allows us to obtain further results. Thus, in the case of organic products, Dainton and Hardwick (*24*) found that the reaction

$$\mathrm{OH} + \mathrm{CH_2{=}CH{-}CONH_2} \rightarrow \mathrm{OH{-}CH_2{-}CH{-}CONH_2}$$

is fifty times more rapid than $\mathrm{Fe}^{++} + \mathrm{OH} \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^-$. It follows that $\mathcal{R}_{\mathrm{OH,acrylamide}} = 320$. Moreover, Merz and Waters (*71*), using OH radicals produced by Fenton's reagent, determined the values of $k_{\mathrm{OH+RH}}/k_{\mathrm{OH+Fe}^{++}}$ in 0.1 N H_2SO_4 for a certain number of organic solutes which give a radical R by the action of OH

$$\mathrm{OH} + \mathrm{RH} \rightarrow \mathrm{R} + \mathrm{H_2O}.$$

Taking the value of $\mathcal{R}_{\mathrm{OH,Fe}^{++}}$ which has already been calculated, we have obtained the values given in Table III for $\mathcal{R}_{\mathrm{OH,RH}}$.

TABLE III

$\mathcal{R}_{\mathrm{OH,RH}}$ VALUES

Solute	$\dfrac{k_{\mathrm{OH+RH}}}{k_{\mathrm{OH+Fe}^{++}}}$	$\mathcal{R}_{\mathrm{OH,RH}}$
Benzoic acid	7	44.8
Benzylamine	6.6	42.2
Dimethyl aniline	6.6	42.2
Diethyl ether	6.4	40.9
Phenylacetic acid	4.8	30.7
Benzene sulfonic acid	4.7	30
Chloral hydrate	4.7	30
Ethyl alcohol	3.8	24.3
Benzene	3.2	20.5
Isopropyl alcohol	3	19.2
Nitrobenzene	2.9	18.5
Acetaldehyde	2.2	14
Ethyl acetate	1.1	7.0
Butyl alcohol	0.65	4.1
Diethylamine sulfate	0.4	2.5

D. VALUES OF $\mathcal{R}_{OH,S}$ CALCULATED FROM $\mathcal{R}_{OH,HCOOH}$

$\mathcal{R}_{OH,Ce(III)}$

Several studies of the reduction of Ce(IV) by irradiation of its solutions lead us to suppose that the OH radical is able to oxidize Ce(III):

$$Ce(III) + OH \rightarrow Ce(IV) + OH^- \tag{23}$$

Sworski (*94*) irradiated mixtures of formic acid, Ce(IV), and Ce(III) in 0.8 *N* H_2SO_4. The reduction yield is increased because reaction (23) is replaced by the reduction of Ce(IV).

$$\begin{aligned} OH + HCOOH &\rightarrow HCOO + H_2O \\ HCOO + Ce(IV) &\rightarrow Ce(III) + H^+ + CO_2 \end{aligned} \tag{24}$$

From the competition between reactions (23) and (24) Sworski was able to calculate $k_{OH+Ce(III)}/k_{OH+HCOOH} = 1.7$ in 0.8 *N* H_2SO_4. Comparison of this value with $\mathcal{R}_{OH,HCOOH} = 5.4$ leads to $\mathcal{R}_{OH,Ce(III)} = 9.2$.

$\mathcal{R}_{OH,Tl^+}$

Univalent thallium ions play the same role in the reduction of Ce(IV) as HCOOH by the operation of the following reactions (*93*):

$$\begin{aligned} OH + Tl(I) &\rightarrow Tl(II) + OH^- \\ Ce(IV) + Tl(II) &\rightarrow Tl(III) + Ce(III). \end{aligned}$$

In this way one can calculate that $k_{OH+Ce(III)}/k_{OH+Tl(I)} = 0.026$ in 0.8 *N* H_2SO_4, in agreement with the value 0.024, determined from a photochemical study of the same mixture (*95*); thence one obtains $\mathcal{R}_{OH,Tl(I)} = 354$.

$\mathcal{R}_{OH,H_2SO_4}$

Sworski (*94*) found from the preceding work that $G(-Ce(IV))$ does not remain constant when (Ce(III)) + (HCOOH) is varied while keeping the ratio $(Ce^{3+})/(HCOOH)$ constant. This fact is incompatible with the hypothesis of a simple competition of Ce(III) and Tl(I) for the capture of OH radicals. Sworski explained it by supposing that the third solute, sulfuric acid, also competes for OH radicals,

$$H_2SO_4 + OH \rightarrow HSO_4 + H_2O \tag{25}$$

and that the HSO_4 radical formed in this way does not react with HCOOH. This reaction has been invoked several times (*4*, *5*, *29*, *59*, *74*, *91*, *101*) in radiation chemistry to explain the influence of the sulfuric acid concentration. On the basis of this hypothesis Sworski calculated that

$k_{\mathrm{OHHCOOH+}}/k_{\mathrm{OH+H_2SO_4}} = 380$, leading to $\mathcal{R}_{\mathrm{OH,H_2SO_4}} = 1.4 \times 10^{-2}$. The rate constant of reaction (24) is then relatively low but the concentration of H_2SO_4 for 0.4*M* solutions suffices for competition with the solute to be possible in some cases. In order to define this possibility more exactly we have calculated the percentage (*F*) of OH radicals which will react in 0.4 *M* H_2SO_4 through the intermediary of HSO_4 radicals for the solutes which have been studied, at three solute concentrations (Table IV). The quantity *F* is given by the expression

$$F = \frac{\mathcal{R}_{\mathrm{OH,H_2SO_4}}(\mathrm{H_2SO_4})}{\mathcal{R}_{\mathrm{OH,S}}(\mathrm{S}) + \mathcal{R}_{\mathrm{OH,H_2SO_4}}(\mathrm{H_2SO_4})} \times 100$$

If the reactions of HSO_4 and OH radicals with the solute are equivalent and no competition for these two radicals intervenes, the yield for the transformation of solute does not vary appreciably with the concentration of H_2SO_4. If, however, there is a reaction which competes for one or other of these radicals, or for both, the final yield should vary with (H_2SO_4), for there is no reason why the reaction rate constants of these radicals with the same compound should be equal. If the values in Table IV are to be of use it is necessary that the preceding determination of $\mathcal{R}_{\mathrm{OH,S}}$ in 0.4 *M* H_2SO_4 should involve OH radicals and not HSO_4. It is for this reason that rates calculated in 0.4 *M* H_2SO_4 have been placed in a separate column in Table V. The results marked with an asterisk are those for which we have been obliged to combine results obtained for different acidities.

TABLE IV

PERCENTAGE OF OH RADICALS REACTING THROUGH THE INTERMEDIARY OF HSO_4 IN 0.4 *M* H_2SO_4

Solute S	(S) = 10^{-2} *M*	(S) = 10^{-3} *M*	(S) = 10^{-4} *M*
Tl^{+}	0	1.5	13.4
Acrylamide	0	1.7	15
NO_2^{-}	1	9.2	50
Sn^{++}	1.2	11.2	56
CO	3.3	26.5	77
Ce^{3+}	5.7	38	86
Fe^{3+}	8.1	47	90
HCOOH	9.4	51	91
H_2 and H_2O_2	36	85	98

Table V shows that, in general, reactions involving an electron transfer are the most rapid, a fact whose importance in radiation chemistry has already been emphasized by Haïssinsky (*44*). The rather low rate of capture of OH radicals by benzene in 0.8 *N* H_2SO_4 given in Table V seems uncertain. Benzene has been thought to capture free OH radicals efficiently

TABLE V
RATES OF REACTIONS OF OH RADICALS

Solute, S	$\mathcal{R}_{OH,S} = \frac{k_{OH+S}}{k_{OH+H_2O_2}}$ 0.4 M H_2SO_4	 Other media
Tl^+	354*	—
Acrylamide	—	320
NO_2^-	—	55
Sn^{++}	44.8*	—
Benzoic acid	—	44.8
Benzylamine	—	42.2
Dimethylaniline	—	42.2
Diethyl ether	—	40.9
Phenylacetic acid	—	30.7
Benzenesulfonic acid	—	30
Chloral hydrate	—	30
Isopropyl alcohol	—	19.2
Nitrobenzene	—	18.5
CO	—	16.6
Acetaldehyde	—	14
Ce^{3+}	9.2*	—
Ethyl acetate	—	7.0
Fe^{++}	—	6.4
Formic acid	—	5.4
Butyl alcohol	—	4.1
Diethylamine sulfate	—	2.5
H_2O_2 and H_2	—	1
Benzene	0.47	20.5
D_2	—	0.32
Ethyl alcohol	—	24.3
Phenol	0.039	—
H_2SO_4	0.014	—

(*64*) in certain reduction processes. In the same table it will be seen that the reaction

$$OH + H_2 \rightarrow H + H_2O \tag{25a}$$

is also not rapid.* It is consequently not possible to conclude that, when bubbling hydrogen through the solution has no influence on the yields, the H and OH radicals play the same role. It is also necessary that competition between solute and H_2 with respect to free OH radicals should be clearly in favor of (25a).

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* *Note added in proof:* The absolute value of the rate constant of $OH + H_2 \rightarrow H + H_2O$ has recently been determined by Schwarz (private communication), to be 4.4×10^7 M^{-1} sec^{-1} in neutral medium. This value permits the calculation of the rate constants of the reactions of Table V.

III. Rates of Reactions of H Atoms

We will attempt to make an analogous classification of the rates of certain reactions of H atoms which occur in radiation chemistry. It will not be appropriate to compare them with the reaction

$$H + H_2O_2 \rightarrow OH + H_2O,$$

since various authors (*8, 75*) agree in considering its rate as pH-dependent. We choose for reference purposes the reaction

$$H + O_2 \rightarrow HO_2$$

the rate of which is probably independent of pH (*84*). We will then calculate for various solutes, S, the relationships:

$$\mathcal{R}_{H,S} = \frac{k_{H+S}}{k_{H+O}}$$

A. DIRECT DETERMINATIONS OF $\mathcal{R}_{H,S}$

There are five direct determinations of $\mathcal{R}_{H,S}$ in the literature. They relate to hydrogen peroxide, benzene, formic acid, and ferrous and ferric ions.

$\underline{\mathcal{R}_{H,H_2O_2}}$

This relationship has been calculated by Allen and Schwarz (*8*) from the decomposition yields of hydrogen peroxide in water containing known quantities of oxygen. The reactions which occur are:

$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$
$$H + H_2O_2 \rightarrow OH + H_2O \qquad (26)$$
$$H + O_2 \rightarrow HO_2 \qquad (27)$$
$$2HO_2 \rightarrow H_2O_2 + O_2$$

It is then possible, because of the competition between (26) and (27), to determine $\mathcal{R}_{H,H_2O_2}$ as equal to 0.54 in pure water, a value which will be adopted. According to the authors this relationship does not involve H atoms produced by

$$OH + H_2 \rightarrow H' + H_2O.$$

These, indeed, will react much more rapidly with oxygen than with hydrogen peroxide. This hypothesis has been put forward to explain why traces of oxygen inhibit the chain decomposition of hydrogen in irradiated aqueous solutions:

$$OH + H_2 \rightarrow H' + H_2O$$
$$H' + H_2O_2 \rightarrow OH + H_2O.$$

It must then be conceded that $\mathcal{R}_{H,H_2O_2}$ is very small and certainly smaller than the value 0.54 found for H atoms coming from spurs. The fact that the reaction

$$H + H_2O_2 \rightarrow OH + H_2O$$

is slower in an acid medium led Schwarz and Allen to postulate that H′ is a more acidic form of the H atom. The entities H and H′ may be, respectively, either the solvated electron and the H radical or the H radical and the radical ion, H_2^+, the existence of which has already been postulated. The possibility has, however, been discussed (*16*) that H_2^+ could be formed by electron transfer:

$$OH + H_2 \rightarrow H_2^+ + OH^-.$$

Phung and Burton (*75*) have found quite a different value for $\mathcal{R}_{H,H_2O_2}$. They believe it to be between 1.5 and 2.5 for solutions of benzene in pure water and very close to zero when 0.8 *N* H_2SO_4 is the medium.

$\mathcal{R}_{H,C_6H_6}$

Phung and Burton (*75*) have studied also the competition between the reactions

$$H + C_6H_6 \rightarrow C_6H_7$$

and

$$H + O_2 \rightarrow HO_2.$$

The last reaction leads to formation of hydrogen peroxide:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2.$$

From the variation in the rate of its formation as a function of the ratio $(C_6H_6)/(O_2)$ the authors find $\mathcal{R}_{H,C_6H_6} = 6 \times 10^{-3}$. This result is valid for solutions in both pure water and 0.8 *N* H_2SO_4.

$\mathcal{R}_{H,HCOOH}$

Using γ-rays from Co^{60} to irradiate formic acid solutions containing limited quantities of oxygen, Hart (*48*) has been able to calculate the value of $\mathcal{R}_{H,HCOOH}$. In effect, hydrogen atoms bring about the liberation of hydrogen by reacting with HCOOH, while the HO_2 radicals combine to form hydrogen peroxide:

$$H + HCOOH \rightarrow H_2 + COOH$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2.$$

Hart found in this way that, for pH 1–3, $\mathcal{R}_{H,HCOOH} = 2 \times 10^{-3}$.

$\mathcal{R}_{H,Fe^{++}}$ and $\mathcal{R}_{H,Fe^{3+}}$

A knowledge of the rates of reactions of H atoms with ferrous and ferric ions is particularly interesting because it leads to precise information on the much-debated mechanisms of the reactions leading to the oxidation of ferrous ions in sulfuric acid solution by γ-rays.

The experimental facts to be explained may be recalled briefly. The oxidation yield of Fe^{++} in 0.8 N H_2SO_4 in the absence of air equals 8.3. This yield is decreased by the presence of ferric ions, the influence of which increases with the pH. In order to interpret the results it is necessary to assume that H atoms oxidize ferrous ions in an acid medium, the value 8.3 being equal to $G_H + G_{OH} + 2G_{H_2O_2}$. This reaction may be written:

$$H + H^+ + Fe^{++} \rightarrow Fe^{3+} + H_2.$$

It is thermodynamically possible, but seems not to be very rapid, for it requires a three-body collision and there is also an electrostatic repulsion between H^+ and Fe^{++}. It has been suggested (*99*) that the oxidation is facilitated by formation of the radical ion $H_2^+(H + H^+ \rightarrow H_2^+)$, followed by electron transfer

$$H_2^+ + Fe^{++} \rightarrow H_2 + Fe^{3+}.$$

The variation of the rates of oxidation and reduction of Fe^{++} and Fe^{3+} by H atoms as a function of pH has been the subject of controversy (*19, 20, 54a, 67, 82*). These rates were measured by Allen and Rothschild (*7*), who studied the oxidation of Fe^{++} by the γ-rays from Co^{60} in the presence of limited quantities of oxygen. They determined the rates of the two reactions of oxidation and reduction by H as a function of the rate of $H + O_2 \rightarrow HO_2$ and found $\mathcal{R}_{H,Fe^{++}} = 7.7 \times 10^{-4}$. This value is constant between pH 0.4 and 2.10. On the other hand (*6*), the rate of reduction by H atoms will depend on the pH; the authors give the following values for $\mathcal{R}_{H,Fe^{3+}}$

6.1×10^{-4}	in	0.8N H_2SO_4
0.007	at	pH 2.10
0.1	at	pH 2.7

The fact that the rate of oxidation of ferrous ions by H atoms does not vary when the H^+ concentration is increased by a factor of 50 does not appear to confirm the reaction

$$H + H^+ + Fe^{++} \rightarrow H_2 + Fe^{3+}.$$

On the other hand, it can be compatible with the hypothesis of the preliminary formation of H_2^+ radical ions only on two conditions. First, it is necessary, as Allen and Rothschild pointed out, to suppose that all the H atoms are in the state H_2^+, at least up to pH 2, the pK of the radical ion being then greater than 2. Moreover it is also necessary to suppose that the rate of formation of H_2^+ is so great that the ferric ions cannot pick up H atoms and so introduce a competing reaction which would inevitably result in a dependence of $\mathcal{R}_{H,Fe^{++}}$ on pH.

Some information on the rate of the reaction $H + H^+ \rightarrow H_2^+$ is available. Friedman and Zeltman (*41*) have studied the exchange reaction between H_2 and D_2 induced by radiation in aqueous acid solution. The preceding reaction should contribute to this exchange. The authors concluded that this rate was low and of the order of 200 liters mole^{-1} sec^{-1}, a value which agrees with that given by Czapski, Jortner, and Stein (*19*) in connection with the oxidation of I^- ions in solution by atomic hydrogen produced by a high-frequency discharge.

A higher value of 2×10^4 liters mole^{-1} sec^{-1} has been reported (*89*) in work on the oxidation of ferrous ions by the γ-rays from Co^{60} with hydrogen under pressure. At all events it will be seen (Table VII) that these rates are very small in relation to those of other reactions of H atoms. It is necessary, then, that the rate of the reaction

$$H + Fe^{3+} \rightarrow Fe^{++} + H^+$$

should be exceptionally low if it is not to compete in capturing H atoms, reduction taking place only by the process

$$Fe^{3+} + H_2^+ \rightarrow Fe^{++} + 2H^+.$$

Lefort and Douzou's hypothesis (*67*), put forward at the conclusion of photochemical experiments, seems more likely. They assume that the reaction involving oxidation by H takes place as a result of the rupture of the H—OH bond in a molecule of water forming part of the environment of the ferrous ion:

$$Fe^{++}(H_2O) + H \rightarrow FeOH^{++} + H_2.$$

The rate of this reaction would be independent of pH and, moreover, could be sufficiently great because of the absence of electrostatic repulsion. However, such a mechanism would be difficult to envisage for I^- ions, for which oxidation by H has also been invoked, and where, moreover, the rate would depend on the acidity (*19*). To explain the fact that, on the contrary, the reduction rate does depend on the acidity, it has been suggested (*7*) that various forms of the ferric ion react at different rates with H. In a sulfuric acid medium the predominating species will be $FeSO_4^+$, reduction of which by H will be slower than oxidation since the $SO_4^=$ ion is protecting Fe^{3+}. This protection will not exist in a less acid medium, where the partially hydrolyzed forms $Fe(OH)_2^+$ and $Fe(OH)^{++}$ will react with H atoms more rapidly.

B. VALUE OF $\mathcal{R}_{H,S}$ CALCULATED FROM $\mathcal{R}_{H,C_6H_6}$

$\underline{\mathcal{R}_{H,C_6H_5OH}}$

In comparing the effectiveness of C_6H_5OH and C_6H_6 in preventing the oxidation of ferrous ions in deaerated 0.8 *N* sulfuric acid solution when irradiated with γ-rays from Co^{60}, Kurien, Phung, and Burton (*61*) have calculated:

$$\frac{k_{H+C_6H_5OH}}{k_{H+C_6H_6}} = 2.$$

From the value of $\mathcal{R}_{H,C_6H_6}$, the value of $\mathcal{R}_{H,C_6H_5OH}$ may be calculated as 1.2×10^{-2}.

C. VALUE OF $\mathcal{R}_{H,S}$ CALCULATED FROM $\mathcal{R}_{H,HCOOH}$

Baxendale and Smithies (*12*) with 200 kev X-rays, irradiated deaerated sulfuric acid solutions of pH 1 containing an organic compound and Fe^{++} ions. By measuring the hydrogen evolved they were able to compare the effectiveness of various organic solutes in the competing reactions

$$RH + H \rightarrow R + H_2$$
$$Fe^{3+} + H \rightarrow Fe^{++} + H^+.$$

In this way they were able to classify various solutes in relation to formic acid. These authors have also measured in the same way the ratio of the rates of the reactions

$$H + HCOOH \rightarrow H_2 + HCOO$$
$$Cu^{++} + H \rightarrow H^+ + Cu^+.$$

These results are collected in Table VI, which includes the derived values of $\mathcal{R}_{H,S}$. Donaldson and Miller (*34*) measured the ratio $k_{H+Cu^{++}}/k_{H+HCOOH}$

TABLE VI
$\mathcal{R}_{H,S}$ VALUES

S	$\frac{k_{H+S}}{k_{H+HCOOH}}$	$\mathcal{R}_{H,S}$
Acetic acid	0.1	2×10^{-4}
Acetone	0.34	6.8×10^{-4}
Ethyl acetate	0.56	1.1×10^{-3}
Methyl alcohol	1.5	3.0×10^{-3}
Formaldehyde	4.7	9.4×10^{-3}
Deuterated formic acid	6.8	1.3×10^{-2}
Ethyl alcohol	14	2.8×10^{-2}
Sucrose	35	7×10^{-2}
Cu^{++}	56	0.11
Benzoquinone	3000	6

by an analogous method and found it to vary with the acidity. They found the following values: 0.1 *N* H_2SO_4, 50; 0.01 *N* H_2SO_4, 24; 0.001 *N* H_2SO_4, 11. The first of these agrees well with the value of Baxendale and Smithies.

D. VALUES OF $\mathcal{R}_{H,S}$ CALCULATED FROM $\mathcal{R}_{H,H_2O_2}$

$\mathcal{R}_{H,NO_2^-}$ and $\mathcal{R}_{H,NO_3^-}$

Schwarz and Salzman (*88*) studied the oxidation of nitrites in dilute solution at their natural pH (7–8). According to the scheme proposed by these authors, H atoms will be subject to three competing processes:

$$H + NO_2^- \rightarrow NO + OH^-$$
$$H + H_2O_2 \rightarrow OH + H_2O$$
$$H + NO_3^- \rightarrow NO_2 + OH^-.$$

The OH radicals will likewise form NO_2($OH + NO_2^- \rightarrow NO_2 + OH^-$). Nitric oxide will be destroyed by the reverse reaction

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

and NO_2 in excess will lead to formation of NO_3^-

$$2NO_2 + H_2O \rightarrow HNO_2 + H^+ + NO_3^-$$

From the yields of H_2O_2 and NO_3^- the following values are calculated,

$$\frac{k_{H+NO_2^-}}{k_{H+H_2O_2}} = 0.3; \qquad \frac{k_{H+NO_3^-}}{k_{H+H_2O_2}} = 1.$$

Taking $\mathcal{R}_{H,H_2O_2} = 0.54$, one finds for neutral solutions that $\mathcal{R}_{H,NO_2^-} = 0.16$ and $\mathcal{R}_{H,NO_3^-} = 0.54$.

$\mathcal{R}_{H,NH_3OH^+}$

The value of $\mathcal{R}_{H,NO_2^-}$ enables $\mathcal{R}_{H,NH_3OH^+}$ to be calculated. Tarrago (*96*) has determined the ratio $k_{H+NO_2^-}/k_{H+NH_3OH^+}$ as equal to 2. This result was deduced from the yield for the disappearance of hydroxylamine in the irradiation with γ-rays from Co^{60} of solutions at pH 4.4 containing both nitrites and hydroxylamine. The value of $\mathcal{R}_{H,NH_3OH^+}$ is then readily obtained as 0.08.

$\mathcal{R}_{H,N_2H_5^+}$

Dewhurst and Burton (*31*), in order to interpret their results on the radiolysis of solutions of hydrazine in the absence of air, suggest that H atoms and free OH radicals form the same radical $N_2H_4^+$:

$$H + N_2H_5^+ \rightarrow H_2 + N_2H_4^+$$
$$OH + N_2H_5^+ \rightarrow H_2O + N_2H_4^+.$$

This subsequently gives NH_3 by the reactions:

$$N_2H_4^+ \rightarrow N_2H_3 + H^+$$
$$2N_2H_3 \rightarrow N_4H_6 \rightarrow N_2 + 2NH_3.$$

In the presence of hydrogen peroxide, formation of ammonia is diminished by the reaction

$$N_4H_6 + H_2O_2 \rightarrow N_2 + N_2H_4 + H_2O,$$

which competes with the reaction

$$H + H_2O_2 \rightarrow H_2O + OH$$

From the values for the ammonia yield as a function of the concentrations of hydrazine and hydrogen peroxide the authors calculate that, for pH 2,

$$\frac{k_{H+N_2H_5^+}}{k_{H+H_2O_2}} = 0.5 \times 10^{-3}.$$

Adoption of a slightly different mechanism proposed by Lefort and Haïssinsky (*66*) leads to the same result. If the value of $\mathcal{R}_{H,H_2O_2}$ of 0.54, determined for pure water, is accepted, at this pH then $\mathcal{R}_{H,N_2H_5^+} = 2.7 \times 10^{-4}$. This is an upper limit since, as has been seen, $\mathcal{R}_{H,H_2O_2}$ decreases with the pH.

E. Values of $\mathcal{R}_{H,S}$ Calculated from $\dfrac{\mathcal{R}_{H,Fe^{3+}}}{\mathcal{R}_{H,D_2}}$

Riesz and Hart (*81*) measured the yields of HD and H_2 liberated by a solution of ferric sulfate and D_2 irradiated by the γ-rays of Co^{60} and have calculated, for pH 2, the ratio $k_{H+Fe^{3+}}/k_{H+D_2} = 120$, whence $\mathcal{R}_{H,D_2} = 4 \times 10^{-5}$.

The rate constant of the reaction $H + D_2 \rightarrow HD + H$ has been measured (*13*) when this takes place in the gas phase, and found equal to $k = 0.4 \times 10^5$ liters mole^{-1} sec^{-1}. Riesz and Hart assumed that the rate of this reaction is substantially the same in the gaseous and liquid phases. They think that the error involved in this assumption is probably less than a factor of 2. Indeed the reacting molecules undergo little solvation. From this value and results in the literature, they have calculated the absolute values of the rate constants of the reactions of H atoms with D_2, Fe^{3+}, Fe^{++}, O_2, Cu^{++}, HCOOH, CH_3COOH, CH_3COCH_3, CH_3OH, C_2H_5OH, and benzoquinone. These values are given in Table VII with the rate constants which we have calculated in the same way and the yields $\mathcal{R}_{H,S}$.

F. Discussion

1. The results in Table VII allow us to find the order of magnitude of the concentration of the free radicals at the stationary state. If, for example,

TABLE VII
Rates of Reactions of H Atoms

Solute, S	$\mathcal{R}_{H,S} = \frac{k_{H+S}}{k_{H+O_2}}$		Absolute rates (liters mole^{-1} sec^{-1})
	pH ≤ 2	pH > 2	
Benzoquinone	6		6×10^9
O_2	1	1	10^9
H_2O_2		0.54	5.4×10^8
NO_3^-		0.54	5.4×10^8
NO_2^-		0.16	1.6×10^8
Cu^{++}	0.11		10^8
Fe^{3+} (pH 2.7)		0.10	10^8
NH_3OH^+		8×10^{-2}	8×10^7
Sucrose	7×10^{-2}		7×10^7
Ethyl alcohol	2.8×10^{-2}		2.8×10^7
Deuterated formic acid	1.3×10^{-2}		1.3×10^7
Phenol	1.2×10^{-2}		1.2×10^7
Formaldehyde	9.4×10^{-3}		9.4×10^6
Benzene	6×10^{-3}	6×10^{-3}	6×10^6
Methyl alcohol	3×10^{-3}		3×10^6
Formic acid	2×10^{-3}		2×10^6
Ethylacetate	1.1×10^{-3}		1.1×10^6
Fe^{++}	7.7×10^{-4}		7.7×10^5
Acetone	6.8×10^{-4}		6.8×10^5
Fe^{3+} (0.8N H_2SO_4)	6.1×10^{-4}		6.1×10^5
$N_2H_5^+$	2.7×10^{-4}		2.7×10^5
Acetic acid	2×10^{-4}		2×10^5
D_2	4×10^{-5}		4×10^4

we take a solution which is 0.1 N in sulfuric acid and 10^{-3} M in Cu^{++} and suppose that the only reaction occurring in absence of air is

$$H + Cu^{++} \rightarrow Cu^+ + H^+;$$

the rate of appearance of H atoms in this solution is given by

$$\frac{d(H)}{dt} = G_H I - k(H)(Cu^{++}).$$

The concentration of these H atoms as a function of time is

$$(H) = \frac{G_H I}{k(Cu^{++})} \{1 - \exp[-k(Cu^{++})t]\}.$$

The concentration at the stationary state is

$$(H) = \frac{G_H \cdot I}{k(Cu^{++})}$$

Taking $I = 10^{15}$ ev/cm$^3 \cdot$ sec, $G_H = 3.7$ and $k = 10^8$ liters mole^{-1} sec^{-1}, the value of (H) at the stationary state is 6.2×10^{-13} M. Half this concentration accumulates after a period T given by $T = 0.69/k(\text{Cu}^{++})$ and equal to 0.69×10^{-5} sec. At the end of 5×10^{-5} sec, corresponding to seven such periods, the stationary state is reached to within 1%.

2. From Table VII it is seen that, in agreement with what is generally accepted, the reaction $H + O_2 \rightarrow HO_2$ is very rapid. It must not be assumed, however, that in a solution saturated with air the reaction involves all the H atoms irrespective of the nature of the solute and its concentration. Table VIII shows the percentage of H atoms which react in solutions saturated with air with solutes which capture H atoms readily (as shown by Table VII) with the HO_2 radical as an intermediary. It is seen that this percentage is 100 only for solutes whose rates of reaction with H are less than 6×10^6 liters mole^{-1} sec^{-1}.

TABLE VIII
PERCENTAGE OF H ATOMS REACTING THROUGH THE INTERMEDIARY OF HO_2 IN SOLUTIONS SATURATED WITH AIR

Solute, S	(S) = $10^{-2}M$	(S) = $10^{-3}M$	(S) = $10^{-4}M$
Benzoquinone	0.36	3.6	27
H_2O_2	4.1	30	80
NO_3^-	4.1	30	80
NO_2^-	12.2	57	93.5
Cu^{++}	16.6	66.6	95
Fe^{3+} (pH 2.7)	18	69	95.5
NH_3OH^+	21.5	73	97
Sucrose	23.8	76	97
Ethyl alcohol	44.5	87	98.8
Deuterated formic acid	63	94.5	99.5
Phenol	64.5	95	100
Formaldehyde	70	96	100
Benzene	79	97	100

It would also be of interest to compare the rates for the HO_2 radical, as has been done for H atoms and free OH radicals. Unfortunately data at present available (see, for example, *11, 26, 33, 52, 84, 97*) are too fragmentary for such comparisons to be possible. This is the more regretable, as it would enable us to know quantitatively the effect of dissociation of the HO_2 radical which interferes at about pH 2, the kinetic importance of which has already been stressed (*44*).

IV. Heterogeneous Kinetics in Radiation Chemistry

The kinetic data in the preceding sections are not very precise. It would be necessary to increase the number of experiments both to reduce the uncertainty about the influence of acidity and to decide between various values on which the correctness of the reaction schemes used depends. In addition, all the rates that have been considered have been determined at ambient temperatures, which have not in general been controlled. It is therefore impossible to know if an activation energy is involved. It is felt, nevertheless, that these results have a certain interest apart from their application to the assessing of the probability of reactions between the products of radiolysis of water and various dissolved substances. We have already seen that, above a certain concentration, solutes are able to interfere in the special zones in which radical and molecular products are formed —spurs for γ-rays and tracks for α-particles.

It is difficult to compare reaction rates in the bulk of the solution and in these special zones because of the uncertainties which have just been mentioned. On the one hand, phenomena which occur in the spurs depend on the H_2SO_4 concentrations, since the radical and molecular yields are a function of this concentration, though it is not possible, at present, to state exactly the origin of this effect. On the other hand, products which are formed in the spurs may initially have a certain kinetic or excitation energy. As a result, reactions which have an activation energy may be accelerated. It is even possible that some reactions that do not take place in the bulk of the solution will play a considerable role in the spurs. This may be so for the reaction $OH + OH \rightarrow H_2O_2$, which has an activation energy in the gas phase (*14*).

A. GAMMA RAYS

The characteristics of a spur, and particularly the proportion of products which emerge from it, depend essentially on three factors.

1. The initial distribution of radicals. It is thought in general to be gaussian, but comparison of distributions between H and OH depends to a certain extent on the hypotheses put forward for the transformation of ions into radicals (See Section I).

2. The rates of diffusion of H and OH. It is taken in calculations that they are inversely proportional to the square roots of the masses.

3. The rate constants of reactions of radicals with one another:

$$OH + OH \rightarrow H_2O_2 \qquad (29)$$

$$H + H \rightarrow H_2 \qquad (30)$$

$$H + OH \rightarrow H_2O \qquad (31)$$

It is usual in these three cases to consider all collisions as effective (*35*, *38*), which may not always be correct. The rate constants are then:

$$k_{29} = 1.5 \times 10^8 M^{-1}\mathrm{sec}^{-1}$$

$$k_{30} = 2 \times 10^8 M^{-1}\mathrm{sec}^{-1}$$

$$k_{31} = 5 \times 10^8 M^{-1}\mathrm{sec}^{-1}$$

It is possible that the reduction in the rates of formation of molecular products when the concentration of certain solutes is increased is due to the fact that these solutes capture OH radicals or H atoms in the spur itself. This interaction will depend on one of the two ratios:

$$\frac{k_{\mathrm{OH+S}}}{k_{\mathrm{OH+OH}}} \quad \text{and} \quad \frac{k_{\mathrm{H+S}}}{k_{\mathrm{H+H}}}$$

It should then be possible to classify various solutes according to the rates of these reactions in the spurs. Schwarz (*86*) and other authors have drawn curves giving the reduction of the molecular yields, $G_{\mathrm{H_2}}$ and $G_{\mathrm{H_2O_2}}$, as a function of the logarithm of concentration for a certain number of solutes. In each case the interaction in the spurs may be represented for γ-rays by an equation of the form

$$G'_{\mathrm{H_2}} = G_{\mathrm{H_2}} - A \times C^{1/3},$$

where C is the solute concentration and A is a constant which is characteristic of it.

These curves are then superposable with a normalization factor. From Schwarz's calculations this factor is proportional to the rate constant of the reaction of the solute with H atoms or free OH radicals. It seemed to us interesting to compare these two parameters using the rates previously calculated. Tables IX and X, where the different rates are referred to those of nitrites, summarize this comparison. The values for the capture of H atoms in the spurs by NO_2^-, Cu^{++}, H_2O_2, O_2, and HCOOH and for the capture of OH by Br^- and Cl^- were calculated by Schwarz from his own results and those of other authors. We have added the normalization factor for acrylamide given by Armstrong *et al.* (*10*) and those which we have calculated for the reactions of H atoms with Ce(IV) (*68*), Fe^{3+} (*86a*), and

TABLE IX

RATES OF REACTIONS OF H ATOMS IN SPURS AND IN SOLUTION

Solute, S	$\frac{k_{\mathrm{H+S}}}{k_{\mathrm{H+NO_2^-}}}$ (spur)	$\frac{k_{\mathrm{H+S}}}{k_{\mathrm{H+NO_2^-}}}$ (solution)
HCOOH	$<8 \times 10^{-2}$	1.3×10^{-2}
NO_3^-	0.13	3.4
Ce(IV)	0.20	—
NO_2^-	1	1
H_2O_2 (neutral medium)	1.9	3.4
O_2	2	6.3
Acrylamide	5.7	—
Cu^{++}	9.3	0.63
Fe^{3+} (HCl 0.4 M)	6.7	1.25

NO_3^- (*69*) as well as for the reactions of OH radicals with Ce^{3+} (*94*) and NO_2^- (*88*).

The scanty results make conclusions difficult. Nevertheless, certain anomalies may be noted: for example, Cu^{++} ions react with H atoms in the spurs more rapidly than do NO_2^- ions, whereas they react more slowly in the bulk of the solution. Likewise NO_3^- acts on H atoms in spurs much more slowly than hydrogen peroxide, whereas the rates of these reactions differ little in solution. It will also be seen that the reaction of Ce^{3+} with OH radicals in spurs is slower than in solution.

TABLE X

RATES OF REACTIONS OF OH RADICALS IN SPURS AND IN SOLUTION

Solute, S	$\frac{k_{OH+S}}{k_{OH+NO_2^-}}$ (spur)	$\frac{k_{OH+S}}{k_{OH+NO_2^-}}$ (solution)
Ce(III)	6.3×10^{-2}	0.17
Cl^- (pH 2)	7.4×10^{-2}	
Cl^- (0.8 N H_2SO_4)	0.78	
NO_2^-	1	1
Br^- (neutral medium)	2.2	
Br^- (0.8 N H_2SO_4)	3	

If the differences in rate between the bulk of the solution and the spurs were confirmed, they could be explained by supposing that the dissolved substances do not always react with the chemical species H and OH but that they are able to capture the precursors of free OH radicals (H_2O^+) or of H atoms (H_2O^- or the solvated electron) in the spurs. The anomalies cited above appear to favor such a hypothesis since, for the reactions shown below, electrostatic attraction and repulsion between ions could explain the effects observed: acceleration for Cu^{++}; retardation for NO_3^-, NO_2^-, and Ce^{3+}

$$Cu^{++} + H_2O^- \rightarrow Cu^+ + H_2O$$
$$NO_2^- + H_2O^- \rightarrow NO + 2OH^-$$
$$NO_3^- + H_2O^- \rightarrow NO_2 + 2OH^-$$
$$Ce(III) + H_2O^+ \rightarrow Ce(IV) + H_2O.$$

The very fact that it is sometimes necessary to postulate rates in the spurs which are less than those in the homogeneous phase would seem to indicate that: (i) these rate changes cannot be explained by the need for an energy of activation which is supplied to the radicals in the spurs; (ii) it is the precursors of the radicals, and not the radicals themselves, which form the molecular products directly.

Capture of the precursors of the radicals in the spurs by the solute molecules has already been invoked (*10*, *54*) and will also explain two other anomalies which are apparent in comparing directly reactions in the spurs and in the bulk of the solution. Thus, if it is accepted that molecular products result from the dimerization of radicals, it is difficult to see how the solute can capture radicals in the spurs, when, at the same concentration, it is unable to prevent reaction of these radicals with molecular products in the bulk of the solution. Now this has been established for acrylamide (*10*), where the solute will prevent H atoms from being dimerized in the spurs, while it will not prevent them from undergoing the reaction

$$H + H_2O_2 \rightarrow OH + H_2O$$

in the bulk of the solution. This seems also to be the case with chlorides in the formation of H_2O_2 (*59*). Nevertheless, further systematic experiments are necessary to justify such conclusions.

B. Alpha Rays

We have seen that, to interpret results on the radiolysis of dilute solutions by α-rays, it is necessary to assume that a second heterogeneous zone exists around the tracks in which the following three reactions occur:

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \qquad \text{(a)}$$

$$OH + H_2 \rightarrow H + H_2O \qquad \text{(b)}$$

$$H + H_2O_2 \rightarrow OH + H_2O. \qquad \text{(c)}$$

One or more of these reactions could be suppressed or diminished in extent by solutes which capture OH, H, or H_2O_2 readily and are able to compete in this zone. One can attempt the comparison of the assumptions concerning the scavenging properties of a solute in these zones and the kinetic data which have been calculated in Sections II and III. It is found in this way that Ce(IV) and Cu^{++} capture H atoms readily (*80*), which does not contradict the results in Table VII. Phosphite, on the other hand, captures H atoms poorly, but there are, unfortunately, no precise kinetic data for this ion in solution. In the case of iron, ferrous ions, like ferric ions, capture H atoms poorly according to results obtained in absence of air (*80*). Ce^{3+} ions are considered to capture OH radicals readily, in agreement with Table V. Ferrous ions, from results obtained in the absence—as well as in the presence—of air, occupy an intermediate position for the capture of OH radicals. The interpretation of the oxidation of Fe^{++} in solution by α-rays is, however, still under discussion (see reference *78*). Here further experiments will again be useful and, in particular, will perhaps allow us to see, as in the case of γ-rays, if the molecular products are destroyed by the radicals according to reactions a, b, and c, or if it is the precursors of the radical products which bring about this decomposition, as has been suggested (*78*).

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