INORGANIC FREE RADICALS IN SOLUTION

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I. INTRODUCTION

Evidence for the occurrence of free radicals in solution rests mainly on kinetic studies. During the last twenty years the number of kinetic investigations in solution which have been interpreted on the basis of reaction schemes involving atoms, free radicals, or radical-ions has been steadily increasing. The monographs of Steacie (282) and Waters (314) are mainly concerned with organic free radicals. In this review those reactions are dealt with which involve inorganic ions or radicals in the primary steps. The subjects discussed include the catalytic decomposition of hydrogen peroxide, the energetics of free radicals in solution, reactions with Fenton's reagent, the initiation of polymerization, the photochemical formation of inorganic free radicals in solution, their subsequent reactions, and their significance in the process of photosynthesis, and, finally, the production of free radicals by ionizing radiations (x-rays, α-rays, etc.); the last topic is described only briefly, as other reviews dealing with the subject have been published recently. The literature survey covers mainly the period from 1930 to July, 1951, although a few references to later papers were added in the galley proofs.

II. THE HABER–WEISS MECHANISM FOR THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

The major pioneering work introducing the concept of inorganic free radicals (OH and HO_2) into the field of reaction kinetics in solution was that of Haber and Weiss (177, 178). Haber and Willstätter (179) had already vaguely suggested that OH and HO_2 are chain carriers in the catalytic decomposition of hydrogen peroxide. Their investigation was preceded by the work of Franck and Haber (146), who postulated the formation of OH radicals in the irradiation of aqueous solutions of halide and sulfite ions. They also suggested that the autoöxidation of sulfite ions is a chain reaction involving the SO_3^- (or HSO_3) and OH radicals as chain carriers. A start was also made toward gaining insight into the energetics of free-radical reactions in solution. Thus, Franck and Haber introduced radically new ideas into the field of reaction kinetics. The existence of the OH and HO_2 radicals, notably in the gas phase, had previously been suggested. Bonhoeffer and Haber (51), Farkas, Goldfinger, and Haber (126), and Haber (175) postulated the OH radical in the reaction between hydrogen and oxygen. In the decomposition of water vapor its occurrence was assumed by Bonhoeffer and Reichardt (52). Urey, Dawsey, and Rice (297) postulated the OH radical in a study of the absorption spectrum of hydrogen peroxide in the gas phase and in solution. The HO_2 radical was first suggested by Taylor (295) and later suggested by Urey, Dawsey, and Rice (297).

It should be pointed out that early in this century the disproportionation equilibrium

$$3H_2O_2 \rightleftharpoons 2HO_2 + 2H_2O$$

was postulated. Although recently applied in a kinetic study (167), it is incompatible with modern ideas; no simple mechanism for such a disproportionation can be devised and the heats of formation of H_2O_2, H_2O, and HO_2 would not favor it thermodynamically. If the first step towards the formation of this equilibrium is assumed to be $H_2O_2 \rightarrow 2OH$ (168), it would be endothermic to an extent of $\sim$55 kcal.

The work of Haber and Weiss (178) was the first in which a complete reaction mechanism was based on OH and HO_2 radicals in solution as intermediate entities. The original Haber and Weiss scheme for the reaction of ferrous ion and hydrogen peroxide is as follows:

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^- + OH \tag{1}$$

$$\rightarrow OH + H_2O_2 \longrightarrow HO_2 + H_2O \tag{2}$$

$$HO_2 + H_2O_2 \longrightarrow O_2 + H_2O + \underline{OH} \tag{3}$$

$$Fe^{+2} + OH \longrightarrow Fe^{+3} + OH^- \tag{4}$$

The catalytic decomposition of hydrogen peroxide is thus a chain reaction, with OH and HO_2 radicals as chain carriers, accompanied by the oxidation of ferrous ion. On the basis of this scheme the authors could explain why the stoichiometric ratio $\Delta H_2O_2/\Delta Fe^{2+}$ was dependent on the mixing condition ("jet" experiments, "pouring" experiments, and "centrifugal" experiments), as, on the one hand, a local excess of ferrous ion would favor chain termination and, on the other hand, a local excess of hydrogen peroxide would favor chain propagation. In the ferric-ion catalysis the primary step suggested by Haver and Weiss is

$$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + HO_2 \tag{5}$$

Long ago it had been observed that the rate constant was proportional to the concentration of ferric ion and hydrogen peroxide and inversely proportional to the acidity, an observation which would be in agreement with the assumption that the HO_2^- ion was the reactive entity. Subsequently, a chain reaction, as in the ferrous-ion catalysis or a reaction of ferric ion with the HO_2 radical, i.e.,

$$Fe^{+3} + HO_2 \rightarrow Fe^{+2} + O_2 + H^+$$

would lead to evolution of oxygen. Kuhn and Wasserman (221) had observed that the rate of production of oxygen from hydrogen peroxide catalyzed by the brown ferric α,α'-dipyridyl complex was about one hundred times more rapid than the evolution of oxygen in the reaction catalyzed by ferric ion. This phenomenon, termed by its discovers "Katalasestoss," which seemed at first incompatible with our general knowledge of reaction kinetics, is considered by Haber and Weiss (178) as one of the best pieces of evidence in favor of their mechanism, for α,α'-dipyridyl forms a very stable complex with ferrous ion and would thus be expected to decrease the concentration of the latter, so that ferrous ion ceases to be an effective chain terminator by reaction 4. The authors also deem it feasible to apply the scheme to the heterogeneous catalysis of hydrogen peroxide, its photochemical decomposition, its reaction with ozone, and also the promoting action of cupric ion in the ferric-ion catalysis first studied by Bohnson and Robertson (48). While the reaction of cupric ion with hydrogen peroxide is assumed to be similar to that of ferric ion, the promoting effect in the presence of ferric ion would be based on the reaction:

$$Cu^{+} + Fe^{+3} \rightarrow Cu^{+2} + Fe^{+2}$$

While the kinetic detail and thermodynamic data had to be revised in later years, this work was the basic inspiration to many researches, particularly in recent years when its concepts were applied to radiation chemistry, and it would therefore be fitting to quote the authors' own summarizing conclusion:

> "The simple basic idea inherent in the foregoing theory is that the hydrogen peroxide molecule is never simultaneously attacked by two monovalent reagents nor by a bivalent reagent, whether the material is oxidized to oxygen or reduced to water; instead there is a monovalent change transforming the peroxide into one of the radicals HO_2 or OH. This is true of the chemical, photochemical or electrochemical processes."

This conclusion is clearly recognized today, and the monovalent changes are classified into bond-breaking and electron-transfer reactions. The question as to whether in some special cases a two-electron transfer process can occur is still speculative.

III. MODIFICATION OF THE ORIGINAL HABER–WEISS SCHEME AND INVESTIGATION OF THE PROPERTIES OF OH AND HO_2 RADICALS

Recognizing the importance of this new free-radical mechanism, Weiss has, since 1935, tried to fill in the gaps of the original scheme and to learn more about the properties of OH and HO_2 radicals. The first modification was introduced (315, 316) in 1935, in a postulate that the HO_2 radical is dissociated (assuming a dissociation constant $K = \sim 10^{-6}$ at 20°C.) into H^+ and O_2^- radical-ions. The suggestion was made that it is the O_2^- radical-ion which reacts with the hydrogen peroxide rather than the HO_2 radical. This idea is doubtless partially based on the concepts put forward by Franck and Haber (146). Weiss (316) also made the first attempt to evaluate quantitatively the electron affinities of the OH and HO_2 radicals and the O_2 molecule in the gas phase and in solution, as it was clear that these were essential for an understanding of the reactions of these entities. He obtained the following results: $E_{OH} = 85$ kcal., $S_{OH^-} = 88$ kcal., $E_{HO_2} = 55$ kcal., $S_{HO_2^-} = 106$ kcal., $E_{O_2} = 62$ kcal., $S_{O_2^-} = 55$ kcal. These data were recently revised by Evans and Uri (112) and will be discussed in a later section of this review 383).

The decomposition of ozone in aqueous solution was studied by Weiss (315). It was shown that this can be accounted for by a chain reaction catalyzed by OH^- ion:

$$\begin{array}{ll}
O_3 + OH^- \rightarrow O_2^- + HO_2 & \text{initiating step} \\
\left.\begin{array}{l} O_3 + HO_2 \rightarrow 2O_2 + OH \\ O_3 + OH \rightarrow O_2 + HO_2 \end{array}\right\} & \text{chain propagation} \\
\left.\begin{array}{l} HO_2 + OH \rightarrow O_2 + H_2O \\ HO_2 + HO_2 \rightarrow O_2 + H_2O_2 \end{array}\right\} & \text{termination}
\end{array}$$

Further, the reaction between ozone and hydrogen peroxide was explained quantitatively on this basis. In addition, Weiss (317) investigated the decomposition of hydrogen peroxide on metal surfaces (such as platinum, gold, palladium, silver, and zinc) and postulated the general scheme:

$$\text{(a)}\quad H_2O_2 + M \rightarrow OH^- + OH + M^+$$

$$\text{(b)}\quad M^+ + HO_2^- \rightarrow M + HO_2$$

The first stage of this early work is concluded by Weiss's review (318), in which some further applications of the univalent electron-transfer processes in chemical kinetics are indicated, such as the oxidation of water by cobaltic ion *via* the process

$$Co^{+3} + OH^- \rightarrow Co^{+2} + OH$$

(Recent studies of this reaction have been carried out by Baxendale and Hargrave (36) and by Bawn and White (27).) It was also suggested that the autooxidation of ferrous ion proceeds *via* the primary step

$$Fe^{+2} + O_2 \rightarrow Fe^{+3} + O_2^-$$

The aerobic oxidation of hydroquinone and the quenching of the fluorescence of dyes are also assumed to involve free-radical intermediates.

As stated above, the first modification of the Haber–Weiss mechanism was the suggestion that the HO_2 radical should be substituted for by the O_2^- radical-ion. This question has not yet been decided unequivocally. Evans, Hush, and Uri (108) suggested a pK value of $\sim$2 for the dissociation of HO_2; this means that in slightly acid solutions both species, HO_2 and O_2^-, will be present. HO_2 reacts as an oxidizing agent,

$$Fe^{+2} + HO_2 \rightarrow Fe^{+3} + HO_2^-$$

and O_2^- as a reducing agent (the oxidation product being O_2).

$$O_2^- + H_2O_2 \rightarrow O_2 + OH^- + OH$$

Both these reactions are exothermic. The reaction of $O_2^- + H_2O_2$ is also to be preferred to the reaction $HO_2 + H_2O_2$ for a different reason: whereas the latter involves a complicated rearrangements of atoms, the former can be interpreted as the breaking of the HO···OH bond accompanied by electron transfer from O_2^- to OH by analogy with the primary step of the Haber–Weiss mechanism, the reaction of ferrous ion and hydrogen peroxide. Uri (300) has shown in a kinetic study of the catalytic decomposition of hydrogen peroxide by pertungstic and permolybdic acids in the presence of cupric ion and various copper complexes that the Haber–Weiss mechanism has some wider application. An alternative chain mechanism was suggested by Bray and Gorin (62), who assumed the formation of ferryl ion (tetravalent iron):

$$Fe^{+2} + H_2O_2 \rightarrow FeO^{+2} + H_2O$$

$$FeO^{+2} + H_2O_2 \rightarrow Fe^{+2} + H_2O + O_2$$

Although this mechanism was revived by Medalia and Kolthoff (241), this reviewer considers it unlikely on the principle that reactions for which no simple mechanism involving only bond-breaking and electron transfer can be devised are less probable. The formation of ferryl ion by a different mechanism was suggested by Barb, Baxendale, George, and Hargrave (20, 21),

$$Fe^{+3} + OH \rightarrow FeO^{+2} + H^+$$

but these authors are not convinced that the experimental evidence for its occurrence is conclusive.

Abel (2) tried recently to revise the Haber–Weiss mechanism, assuming that the reactions occurring in the system are only the following:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH$$

$$Fe^{+2} + OH \rightarrow Fe^{+3} + OH^-$$

$$Fe^{+3} + HO_2^- \rightarrow Fe^{+2} + HO_2$$

$$Fe^{+3} + HO_2 \rightarrow Fe^{+2} + O_2 + H^+$$

He has, however, overlooked the fact that the reactions which he omitted are considerably exothermic, and this simple mechanism cannot account for the "burst" of oxygen observed on mixing ferrous ion and hydrogen peroxide solutions. Abel realizes that his scheme is at variance with the experimental facts and suggests that inhomogeneous conditions may be responsible for the observation of the oxygen "burst." As the writer of this review is closely acquainted with the sound experimental technique used by some of the investigators, he considers Abel's suggestion very unlikely indeed.

George (166) investigated the dissolution of KO_2 (recognized as the salt of the free radical HO_2) in hydrogen peroxide solutions and did not observe any chain reaction even with 99 per cent hydrogen peroxide. This seemed to indicate that there was no reaction of the HO_2 radical (or the O_2^- ion) with H_2O_2, as postulated by Haber and Weiss (178). Agar and Dainton (5) consider that no valid conclusions can be drawn from George's work on the reaction in the solution phase, as in the alkaline layer in the vicinity of the KO_2 crystals the concentrations of

OH^- and HO_2^- are very large and O_2^- ion could disappear by a different mechanism before its diffusion into the bulk of the solution.

An important modification of the original Haber–Weiss mechanism was put foward almost simultaneously by Barb, Baxendale, George, and Hargrave (19), by Weiss and Humphrey (334), and by Medalia and Kolthoff (241). It was recognized by these authors that the main step leading to oxygen evolution is the reaction:

$$Fe^{+3} + O_2^- \rightarrow Fe^{+2} + O_2$$

This applies not only to the slow decomposition of hydrogen peroxide by ferric ions, where Haber and Weiss have already suggested the reaction

$$Fe^{+3} + HO_2 \rightarrow Fe^{+2} + H^+ + O_2$$

but also to the oxygen burst in the reaction of ferrous ion and hydrogen peroxide. Medalia and Kolthoff arrived at it from a theoretical analysis of the reaction kinetics. Weiss and Humphrey (334) and Barb, Baxendale, George, and Hargrave (19) based their view on experimental results, particularly on the effect of ferric-ion concentration on the oxygen burst, which can be reduced to a minimum by addition of fluoride ion to form a complex with the ferric ions produced in the course of the reaction. The latter research workers have carried out a very detailed and thorough kinetic study of the iron–hydrogen peroxide system (20, 21) which allowed them to evaluate various rate constants and constant ratios (which are summarized in Section IX) and have thus contributed very much to the quantitative basis of the concepts underlying the Haber–Weiss mechanism. In a careful experimental study Andersen (9) observed recently an interesting deviation from the kinetic equation in the catalytic decomposition of hydrogen peroxide:

$$-\frac{d[H_2O_2]}{dt} = k_r \frac{[Fe^{+3}][H_2O_2]}{[H^+]}$$

Log a/x plotted against time (a = initial concentration of hydrogen peroxide and x its concentration at the time t) was no longer a linear function at low concentrations of hydrogen peroxide, as would be expected from a first-order rate equation. The following mechanism was suggested:

$$Fe^{+3} + HO_2^- \rightarrow FeOOH^{+2}$$

$$FeOOH^{+2} \rightarrow FeOH^{+2} + O$$

$$O + HO_2^- \rightarrow O_2 + OH^-$$

Andersen and Christiansen (10) revised this scheme and postulated instead:

$$Fe^{+3} + HO_2^- \rightarrow FeOOH^{+2}$$

$$FeOOH^{+2} \rightarrow Fe^{+3} + HO_2^{-*}$$

$$HO_2^{-*} + H_2O \rightarrow O + H_2O + OH^-$$

It should be pointed out that these mechanism are not probable. The formation of an excited HO_2^{-*} ion in a thermal reaction seems far fetched, and the formation of oxygen atoms in the reaction of ferric ion and HO_2^- ion is impossible from an energetic point of view.

Barb, Baxendale, George, and Hargrave (20, 21) show that the deviation from the first-order decomposition can be explained by assuming that the catalytic decomposition of hydrogen peroxide by ferric ion is a chain reaction produced by the small but measurable stationary concentration of ferrous ion. (Simon, Haufe, Reetz, and Preissler (279) had previously made qualitative observations to this effect.) Stationary-state kinetics would lead to the rate equation:

$$-\frac{d[H_2O_2]}{dt} = 2k_1[Fe^{+2}]_s[H_2O_2]$$

$[Fe^{+2}]_s$ is the stationary ferrous-ion concentration, which is proportional to the ferric-ion concentration and inversely proportional to the hydrogen-ion concentration. Their treatment of systems with low concentrations of hydrogen peroxide leads to a rate equation of the form:

$$-\frac{d[H_2O_2]}{dt} = K\frac{[Fe^{+3}]^{1/2}}{[H^+]}[H_2O_2]^{3/2}$$

While a $\frac{3}{2}$ power of $[H_2O_2]$ could be derived from Andersen's results, a square-root dependence on [ferric ion] was never observed. Using different methods of approximation, Weiss (330) shows that Andersen's empirical equation can be accounted for by assuming, like Barb, Baxendale, George, and Hargrave, a chain mechanism based on the stationary ferrous-ion concentration. Uri (302) considers that an important reaction in the Haber–Weiss mechanism has been overlooked: *viz.*,

$$Fe^{+3}OH^- + OH \xrightarrow{k_1'} Fe^{+2} + H_2O_2$$

This is the back-reaction of the primary step of the Haber–Weiss mechanism, which is exothermic to an extent of 5–10 kcal. The reaction $Ce^{+4}OH^- + OH$ was postulated by Haissinsky and Lefort (182) in the radiation chemistry of ceric salt solutions (not involving, however, the ion-pair) and by Evans and Uri (115) in the photoöxidation of water by ceric ions. The forward reaction has not been formulated by Haber and Weiss as

$$Fe^{+2} + H_2O_2 \xrightarrow{k_1} Fe^{+3}OH^- + OH$$

but as

$$Fe^{+2} + H_2O_2 \xrightarrow{k_1} Fe^{+3} + OH^- + OH$$

The formation of an ion-pair complex equilibrium

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

was not visualized, so that the back-reaction would have involved termolecular collisions. The importance of ion-pairs in reaction kinetics has only recently been fully recognized and this is the most likely reason for the omission of the reaction of $Fe^{+3}OH^-$ with OH radicals. Obviously this reaction will be more pronounced at a large ratio of ferric ion to hydrogen peroxide. In the catalytic decomposition of hydrogen peroxide by ferric ion the equation arrived at by Barb, Baxendale, George, and Hargrave (20, 21) and by Weiss (330) should be revised. Stationary-state kinetics of the revised system would lead to the rate equation

$$-\frac{d[H_2O_2]}{dt} = 2k_1[Fe^{+2}]_s[H_2O_2] - 2k_1'[Fe^{+3}OH^-][OH]_s$$

where $[Fe^{+2}]_s$ and $[OH]_s$ denote stationary-state concentrations. The integration of this equation leads to

$$\log\frac{a - (b/K)}{x - (b/K)} = kt$$

where $K = 2k_1[Fe^{+2}]_s$ and $b = 2k_1'[Fe^{+3}OH^-][OH]_s$. $[Fe^{+2}]_s$ and $[OH]_s$ are independent of $[H_2O_2]$ within a large range of concentrations. Andersen (9) has plotted log (a/x) against time and failed to obtain a straight line. If Andersen's results are used for a plot of

$$\log\frac{a - (b/K)}{x - (b/K)}$$

against time, where $K = 7 \times 10^{-4}$ and $b = 1.24 \times 10^{-6}$, a perfectly straight line has been obtained by omitting the experiment at the lowest hydrogen peroxide concentration, where the experimental error is considerable (303).

IV. ENERGETICS OF INORGANIC FREE RADICALS

A closer understanding of chemical kinetics involving free radicals is not possible without data on such quantities as electron affinities, heats and entropies of solvation, bond-dissociation energies, ionization potentials, etc.

A. THE OH RADICAL

The $O\cdots H$ bond-dissociation energy was evaluated by Dwyer and Oldenberg (98) from spectroscopic measurements in the gas phase as 100.1 kcal. This value is now generally accepted and is certainly accurate to the extent of ±2 kcal. Dwyer and Oldenberg postulate a value of 118.2 kcal. for the heat of dissociation of water into H atoms and OH radicals. The average bond energy of $O\cdots H$ in water is thus 109 kcal.[2] With the data of Evans and Uri (112) (also applied in

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[2] The values of Dwyer and Oldenberg (98) must be revised, as these investigators have used in their calculations out-of-date values for the dissociation energy and the heat of formation of water from its atoms (i.e., 102.5 kcal. and 218.3 kcal. instead of 104.1 kcal. and 220.7 kcal., respectively). The best approximate estimate of the heats of dissociation for the hydrogen atoms in water vapor would be 120 kcal. for the first one and 100 kcal. for the second.

recent work by Evans, Hush, and Uri (108)) on the energetics of reactions involving hydrogen peroxide, its radicals, and its ions, the average bond energy of $O\cdots H$ in water is 110.6 kcal. (±1 kcal.). (The relationship between bond-dissociation energy and average bond energy has been discussed recently by Szwarc (292).)

The dissociation energy of hydrogen peroxide into two OH radicals can be evaluated from the following cycle (in the gas phase):

$$\begin{tikzcd}
H_2 \arrow[d, "-D_{H_2}"'] & + & O_2 \arrow[d, "-D_{O_2}"] \arrow[r, "Q_f"] & H_2O_2 \\
2H & + & 2O \arrow[r, "2D_{OH}"'] & 2OH \arrow[u, "D_{HO\cdots OH}"']
\end{tikzcd}$$

With $D_{H_2} = 104.1$ kcal., $D_{O_2} = 118.2$ kcal., and $Q_f = 33.6$ kcal., $D_{HO\cdots OH}$ is evaluated as 55.6 kcal. This is the bond-dissociation energy in the gas phase. If we assume that the heat of solution of OH radicals is similar to the heat of condensation of water, the bond-dissociation energy of $HO\cdots OH$ in aqueous solutions becomes 46.7 kcal. (the heat of condensation of hydrogen peroxide being 11.6 kcal. and its heat of dilution in accordance with the measurements of Evans, Baxendale, and Uri (106) being 0.7 kcal.).

The heat of the reaction

$$OH(g) + e \rightarrow OH^-(aq)$$

which is the sum of the electron affinity of the OH radical in the gas phase (E_{OH}) and the hydration energy of OH^- ions (S_{OH^-}), can be evaluated from the thermodynamic cycle given below (earlier results of Weiss (316) and Baughan, Evans, and Polanyi (25) were revised by Evans and Uri (112)).

$$\begin{tikzcd}
(H_2O)(g) \arrow[r, "-120.7", "-D_{HO\cdots H}"'] & H + OH \arrow[r, "-312 + E_{OH}", "-I_H + E_{OH}"'] & H^+ \arrow[d, "+282"', "S_{H^+}"] & + & OH^- \arrow[d, "S_{OH^-}"] \\
(H_2O) \arrow[u, "-10.6", "-\lambda_{H_2O}"'] \arrow[rr, "-13.7", "Q"'] & & H^+(aq) & + & OH^-(aq)
\end{tikzcd}$$

This leads to a value of 147.6 kcal. for $E_{OH} + S_{OH^-}$. In reactions in which the OH radical is formed, we assume for the sum $E_{OH} + S_{OH^-}$, denoted by E^S_{OH}, the value of 136 kcal.

The occurrence of OH^+ was postulated by Derbyshire and Waters (93) in the oxidation of mesitylene by acid hydrogen peroxide solutions. No estimate has yet been made of the ionization potential of OH radicals. It is not certain whether this work allows a distinction to be drawn between OH^+ ions and the perhydrated proton, $H_3O_2^+$. The latter was postulated by Evans and Uri (112), Weiss (326), and particularly in electrochemical investigations of the dissociation of acids in hydrogen peroxide by Wynne-Jones (344). The equilibrium OH +

$H^+ \rightleftharpoons H_2O^+$ has been suggested by Weiss (326), but no quantitative data relating to this equilibrium are available. It has been suggested that H_2O^+ may be a precursor in the anodic formation of molecular oxygen in electrolysis (Weiss (326); Walker and Weiss (308)).

The energetics of the OH radical put forward by Evans and Uri (112) are in agreement with the considerations of Skinner (280), who has shown that Pauling's data (257) must be revised. It should be emphasized that in this review *"bond-dissociation energy"* is used in the sense defined by Szwarc and not in the sense in which "bond energy" has been used by Glockler and Matlack (170) or by Walsh (309).

B. THE HO_2 RADICAL

Divergent estimates were recently made on the bond-dissociation energy $H\cdots O_2$ of the HO_2 radical. Walsh (309) suggests a value as high as 67 kcal. Earlier estimates by Bodenstein and Schenk (47), Haber and Weiss (178), and Bray (61) were all in the range of 40–50 kcal. Evidence cited by Walsh is based mainly (*a*) on theoretical considerations of the electronic structure of the HO_2 radical and the stabilizing effect of the three-electron bond; (*b*) the interatomic $O\cdots O$ distances based on x-ray work by Kassatochkin (204), who quoted 1.20 Å. for O_2, 1.27 Å. for O_2^-, and 1.35 Å. for O_2^{-2}; hence Walsh assumes that the $O\cdots O$ bond energy in the HO_2 radicals is by first approximation the mean of those in oxygen and hydrogen peroxide, which would lead to the value of 67 kcal. for the bond dissociation energy $H\cdots O_2$ in the HO_2 radical; and (*c*) kinetic evidence from the sensitization by oxygen of addition of hydrogen bromide to hydrocarbons and chain propagation in the oxidation of hydrocarbons (Bolland and Gee (49)). Walsh's evidence is, in the reviewer's mind, not conclusive. The theoretical treatment does not appear to be unequivocal; it may be argued that, while qualitative agreement is not excluded, a quantitative comparison cannot be made of the O_2^- ion in the crystal lattice with the properties of the HO_2 radical in the gas phase or solution; the interatomic distances quoted included O_2 in the gas phase, on the one hand, and O_2^- ion in the crystal lattice on the other. The mechanism of O_2-sensitized addition of hydrogen bromide to olefins has not been established and in the oxidation of hydrocarbons rather than the chain propagation, it is the activation energy of the primary step $R\cdots H + O_2 \rightarrow R + HO_2$ which is really indicative of the $H\cdots O_2$ bond-dissociation energy.

Evans, Hush, and Uri approach the problem of the $H\cdots O_2$ bond-dissociation energy from a different angle. This quantity can be evaluated from the $HO_2\cdots H$ bond-dissociation energy. It is estimated from the following cycle:

$$\begin{tikzcd}
(H_2O_2)(g) \arrow[r, "-D_{HO_2\cdots H}"] & H \arrow[d, "(-I_H + S_{H^+})"'] & + & HO_2 \arrow[d, "E_{HO_2} + S_{HO_2^-}"] \\
(H_2O_2)(aq) \arrow[u, "-(\lambda + S)_{H_2O_2}"] \arrow[r, "-Q"'] & H^+(aq) & + & HO_2^-(aq)
\end{tikzcd}$$

$$D_{HO_2\cdots H} = -Q - (\lambda + S)_{H_2O_2} + (-I_H + S_{H^+}) + (E_{HO_2} + S_{HO_2^-})$$

The value of Q has been measured by Evans and Uri (112); $(\lambda + S)_{H_2O_2} = 11.6 + 0.7 = 12.3$ kcal.; the ionization potential and heat of solvation of the proton are well established. The unknown quantity is the sum of the electron affinity of the HO_2 radical and the solvation energy of the HO_2^- ion. Evans, Hush, and Uri (108) and Evans and Uri (116) have shown that a linear function is obtained when the energy values of the absorption maxima of various ferric-ion pairs, which are interpreted as electron-transfer spectra, are plotted against the electron affinity in solution of corresponding anions. By interpolation one obtains $E_{HO_2} + S_{HO_2^-} = 136$ kcal. This leads to a value of 102 kcal. for the $HO_2\cdots H$ bond-dissociation energy. In obtaining heat values for the solution phase Evans and Uri (112) and Evans, Hush, and Uri (108) have identified the heat of solution of HO_2 with that of hydrogen peroxide.

The bond-dissociation energy $D_{H\cdots O_2}$ is then evaluated from the cycle:

$$\begin{tikzcd}
(H_2O_2) \arrow[r, "-D_{HO_2\cdots H}"] & H + HO_2 \\
H_2 + O_2 \arrow[u, "Q_f"] \arrow[r, "-D_{H_2}"] & H + \overbrace{H + O_2} \arrow[u, "D_{H\cdots O_2}"']
\end{tikzcd}$$

$$D_{H\cdots O_2} = -D_{HO_2\cdots H} + Q_f - D_{H_2} = 36 \text{ kcal.}$$

The value obtained is much lower than that cited by Walsh (236). There is considerable chemical evidence (cited in Section IV, C) to support this value of $D_{H\cdots O_2}$.

C. THE O_2^- RADICAL-ION

The O_2^- ion is the anion of the free radical HO_2. Potassium superoxide, which was originally given the structure M_2O_4, is paramagnetic, and the x-ray study of its crystal structure by Helms and Klemm (188) revealed that the correct formula was MO_2 (M = potassium, rubidium, or cesium). This was confirmed more recently by Kassatochkin (204), who with Kotov (205) had previously suggested the structure MO_2. Evans and Uri evaluated the sum of the electron affinity of O_2 and the solvation energy of O_2^- from the cycle:

$$\begin{tikzcd}
(M)(g) \arrow[r, "-I_M + E_{O_2}"] & M^+ + O_2^- \arrow[d, "U_s"'] \\
(M)(sol) + O_2 \arrow[u, "-\lambda_M"] \arrow[r, "Q"] & (M^+O_2^-)_s
\end{tikzcd}$$

where λ_M is the latent heat of vaporization of the metal M, I_M is the ionization potential of the metal, and Q is the heat of formation of $(M^+O_2^-)$. Using the interionic distances provided by the work of Helms and Klemm (188), the lattice energies of KO_2, RbO_2, and CsO_2 were calculated by Evans and Uri (112) and an average value for the first electron affinity of oxygen (E_{O_2}), defined by O_2 +

$e \rightarrow O_2^- + E_{O_2}$, of 15.8 kcal. was estimated. The same authors suggested a value of 70.0 kcal. for the solvation energy of O_2^- (O_2^{-2} does not occur in aqueous solution as the reaction

$$O_2^{-2} + HOH \rightarrow HO_2^- + OH^-$$

is exothermic to the extent of 90 kcal.; the gas-phase reaction $O_2 + 2e \rightarrow O_2^{-2}$ is endothermic to the extent of 112 kcal.). Evans, Hush, and Uri have revised the value obtained by Evans and Uri for the electron affinity of oxygen in aqueous solution and suggest the slightly different value of 79 kcal. for the sum of the first electron affinity of O_2 in the gas phase and the heat of solvation of the O_2^- ion. In aqueous solution the HO_2 radical is dissociated into H^+ and O_2^-, though the value of the dissociation constant has not yet been established with certainty. Evans, Hush, and Uri suggest a pK value of 2. This is in agreement with the chemical evidence obtained recently by Barb, Baxendale, George, and Hargrave (20, 21). Kinetic evidence for a similar pK value has been previously reported by Taube (293a).

If it is assumed that the heat of the reaction $H + O_2 \rightarrow HO_2$ is as high as 65 kcal., the dissociation of HO_2 in aqueous solution would be endothermic to an extent of ~30 kcal., a result which is very unlikely in view of the kinetic data obtained by Barb, Baxendale, George, and Hargrave (20).

Further evidence for a heat value of $H + O_2 \rightarrow HO_2$ in the range of 40 kcal. is obtained from a consideration of the primary step of the oxidation of hydrocarbons. Szwarc (290) has shown that as a result of the large resonance energy stabilization of the benzyl radical the $R \cdots H$ bond-dissociation energy is reduced from ~100 kcal. for the $H \cdots CH_3$ bond to ~75 kcal. for the $H \cdots CH_2C_6H_5$ bond. Accordingly, in the oxidation of toluene by oxygen the endothermicity of the reaction $RH + O_2 \rightarrow R + HO_2$ is $(75 - D_{HO_2})$ kcal. No oxidation to any measurable extent is, however, observed below 600°C. (Sehon and Szwarc (276)). Finally, a value of the $H \cdots O_2$ bond-dissociation energy in the range of 40 kcal. is supported by the activation energy of the reaction

$$Fe^{+3} + HO_2^- \rightarrow Fe^{+2} + HO_2$$

which was determined by Barb, Baxendale, George, and Hargrave (21) as 28 kcal. (if it is assumed that the endothermicity of this reaction is similar to its activation energy). It confirms the electron affinity in solution of HO_2 as 123 kcal. and thus indirectly the $H \cdots O_2$ bond-dissociation energy as 36 kcal.

V. SUMMARY OF HEATS OF REACTION

From the above data the heats given in table 1 are obtained for reactions involving atoms, radicals, and molecules composed of hydrogen and oxygen. The heats of solution of OH and HO_2 radicals are assumed to be similar to those of water and hydrogen peroxide, respectively. The following heats of solution were used in the calculations: 1.4 kcal. for H_2; 5 kcal. for H; 3.9 kcal. for O_2; 5 kcal. for O.[3]

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[3] It is assumed that H and O atoms have a slightly larger affinity towards the water molecules than H_2 and O_2.

VI. ENERGETICS OF RADICAL–ION TRANSFER

It has frequently been observed (e.g., in recent work by Barb, Baxendale, George, and Hargrave (20, 21), Kolthoff and Medalia (211, 212), Taube and Bray (294), and Allen (7)) that chloride ions inhibit reactions of OH radicals. This effect is based on radical–ion transfer of the type $OH + X^- \rightarrow OH^- + X$. The relevant energy data are summarized in table 2. These are based on data

TABLE 1

Summary of heats of bond-breaking reactions involving atoms, radicals, and molecules derived from oxygen and hydrogen

REACTION	HEAT
	kcal.
(*a*) *Reactions in the gas phase:*	
$OH + H_2O_2 \rightarrow H_2O + HO_2$	+19
$OH + HO_2 \rightarrow H_2O + O_2$	+85
$HO_2 + H_2O_2 \rightarrow H_2O + OH + O_2$	+30
$HO_2 + HO_2 \rightarrow O_2 + H_2O_2$	+67
$OH + O_2 \rightarrow HO_2 + O$	−65
$HO_2 + H_2 \rightarrow H_2O_2 + H$	−2
$HO_2 \rightarrow H + O_2$	−36
$H_2O_2 \rightarrow H + HO_2$	−102
$OH + OH \rightarrow H_2O_2$	+56
$OH + OH \rightarrow H_2O + O$	+21
$OH + H_2 \rightarrow H_2O + H$	+17
$H + H_2O_2 \rightarrow HOH + OH$	+65
(*b*) *Reactions in aqueous solution:*	
$OH + H_2O_2 \rightarrow H_2O + HO_2$	+19
$OH + HO_2 \rightarrow H_2O + O_2$	+77
$HO_2 + H_2O_2 \rightarrow H_2O + OH + O_2$	+30
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	+58
$OH + OH \rightarrow H_2O_2$	+47
$OH + OH \rightarrow H_2O + O$	+15
$OH + H_2 \rightarrow H_2O + H$	+22
$H + H_2O_2 \rightarrow H_2O + OH$	+69

TABLE 2

Thermodynamic data relating to radical–ion transfer of the type $OH + X^- \rightarrow OH^- + X$

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
$OH + F^- \rightarrow OH^- + F$	+34	−6	+36
$OH + Cl^- \rightarrow OH^- + Cl$	+3	−21	+9
$OH + Br^- \rightarrow OH^- + Br$	−10	−24	−3
$OH + I^- \rightarrow OH^- + I$	−27	−29	−18
$OH + SH^- \rightarrow OH^- + SH$	−30	−10	−27
$OH + HO_2^- \rightarrow OH^- + HO_2$	−13	−3	−12
$OH + O_2^- \rightarrow OH^- + O_2$	−62	−5	−61

adopted by Evans and Uri (112), Evans, Warhurst, and Whittle (118) (for electron affinities of halogen atoms), and Latimer (223) (entropies of solvation) and were compiled and revised by Evans, Hush, and Uri (108). Such values will make it possible to judge equilibria and rates of radical–ion transfer reactions from a quantitative point of view. Table 3 contains thermodynamic data for the reactions of halogen atoms with water, producing OH radicals. Only with fluorine atoms is the reaction with water exothermic; it has, however, been shown by Bates, Evans, and Uri (23) that it nevertheless requires an activation energy of 5–10 kcal. Table 4 presents data on the reaction of halogen atoms with hydrogen peroxide. Thermodynamic data on such reactions as those between O_2 or HO_2 and halide ions can be calculated from combinations of the data in table 2. Table 5 gives further data on reactions involving species composed of oxygen and hydrogen, including ions.

TABLE 3

Thermodynamic data relating to the oxidation of water by halogen atoms

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
$F + H_2O \rightarrow F^- + H^+ + OH$...	−21	−20	−15
$Cl + H_2O \rightarrow Cl^- + H^+ + OH$...	+10	−5	+11
$Br + H_2O \rightarrow Br^- + H^+ + OH$...	+23	−2	+24
$I + H_2O \rightarrow I^- + H^+ + OH$...	+40	+3	+39

TABLE 4

Thermodynamic data relating to the oxidation of hydrogen peroxide by halogen atoms

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
$F + H_2O_2 \rightarrow F^- + H^+ + HO_2$..	−39	−23	−32
$Cl + H_2O_2 \rightarrow Cl^- + H^+ + HO_2$..	−8	−8	−6
$Br + H_2O_2 \rightarrow Br^- + H^+ + HO_2$..	+5	−5	+6
$I + H_2O_2 \rightarrow I^- + H^+ + HO_2$...	+22	0	+22

TABLE 5

Thermodynamic data relating to reactions of species composed of oxygen and hydrogen, including ions in aqueous solution

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
$\frac{1}{2}H_2 + HO_2 \rightarrow HO_2^- + H^+$........................	−42	−24	−35
$HO_2 \rightarrow H^+ + O_2^-$................................	−3	−18	+3
$\frac{1}{2}H_2 + OH \rightarrow OH^- + H^+$........................	−55	−28	−47
$\frac{1}{2}H_2 + O_2 \rightarrow O_2^- + H^+$...........................	+7	−22	+14
$HO_2^- + H_2O_2 \rightarrow HO_2 + OH + OH^-$..............	+36	+5	+35
$O_2^- + H_2O_2 \rightarrow O_2 + OH + OH^-$..................	−13	+3	−14
$\frac{1}{2}H_2 + H_2O_2 \rightarrow H^+ + OH + OH^-$................	−7	−21	−1

TABLE 6

Thermodynamic data relating to the oxidation of metal ions and some metal complexes by the OH *radical*

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
$Co^{+2} + OH \rightarrow Co^{+3} + OH^-$	−21	−59	−3
$Fe^{+2} + OH \rightarrow Fe^{+3} + OH^-$	−44	−59	−26
$V^{+2} + OH \rightarrow V^{+3} + OH^-$	−68	−59	−50
$Cr^{+2} + OH \rightarrow Cr^{+3} + OH^-$	−72	−59	−56
$Cu^+ + OH \rightarrow Cu^{+2} + OH^-$	−60	−65	−42
$Fe(CN)_6^{-4} + OH \rightarrow Fe(CN)_6^{-3} + OH^-$	−30	+19	−36
$Ag^+ + OH \rightarrow Ag^{+2} + OH^-$	−19	−66	+1
$Ce^{+3} + OH \rightarrow Ce^{+4} + OH^-$	−24	−52	−8
$Mn^{+2} + OH \rightarrow Mn^{+3} + OH^-$	−28	−59	−10
$Fe(C_{12}H_8N_2)_3^{+2} + OH \rightarrow Fe(C_{12}H_8N_2)_3^{+3} + OH^-$	-	-	−19
$Mo(CN)_6^{-4} + OH \rightarrow Mo(CN)_6^{-3} + OH^-$	−22	+19	−28
$Mn(CN)_6^{-4} + OH \rightarrow Mn(CN)_6^{-3} + OH^-$	−44	+19	−50
$MnO_4^{-2} + OH \rightarrow MnO_4^- + OH^-$	-	-	−32
$Co(CN)_6^{-4} + OH \rightarrow Co(CN)_6^{-3} + OH^-$	−58	19	−64

TABLE 7

Thermodynamic data relating to the oxidation of water

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
$Co^{+3} + H_2O \rightarrow Co^{+2} + OH + H^+$	+34	+33	+24
$Fe^{+3} + H_2O \rightarrow Fe^{+2} + OH + H^+$	+57	+33	+47
$V^{+3} + H_2O \rightarrow V^{+2} + OH + H^+$	+81	+33	+71
$Cr^{+3} + H_2O \rightarrow Cr^{+2} + OH + H^+$	+85	+33	+75
$Cu^{+2} + H_2O \rightarrow Cu^+ + OH + H^+$	+73	+39	+61
$Fe(CN)_6^{-3} + H_2O \rightarrow Fe(CN)_6^{-4} + OH + H^+$	+43	−45	+56

TABLE 8

Thermodynamic data relating to the oxidation of hydrogen peroxide

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
$Co^{+3} + H_2O_2 \rightarrow Co^{+2} + HO_2 + H^+$	+16	+30	+7
$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2 + H^+$	+39	+30	+30
$V^{+3} + H_2O_2 \rightarrow V^{+2} + HO_2 + H^+$	+63	+30	+54
$Cr^{+3} + H_2O_2 \rightarrow Cr^{+2} + HO_2 + H^+$	+67	+30	+58
$Cu^{+2} + H_2O_2 \rightarrow Cu^+ + HO_2 + H^+$	+55	+36	+46
$Fe(CN)_6^{-3} + H_2O_2 \rightarrow Fe(CN)_6^{-4} + HO_2 + H^+$	+25	−48	+40

VII. Ionic Reactions Involving Metal Ions

In addition to electron affinities and bond-dissociation energies, these reactions involve also ionization potentials of the corresponding metal ions in aqueous solutions.

Tables 6 to 9 summarize the data obtained by Evans, Hush, and Uri (108).

VIII. Ion-Pair Complex Formation

In view of the role which the formation of ion-pairs may play in the energetics of the transition state of reactions involving oppositely charged ions, it is important to gain more knowledge on the equilibria of ion-pair complexes in solution. The author has repeated part of the important work of Rabinowitch and Stockmayer (264) and investigated some further ferric-ion pairs. These results, together with those of other workers, are summarized in table 10.

TABLE 9

Thermodynamic data relating to the reduction of hydrogen peroxide

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
$Co^{+2} + H_2O_2 \rightarrow Co^{+3} + OH + OH^-$	+28	−50	+43
$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH + OH^-$	+5	−50	+20
$V^{+2} + H_2O_2 \rightarrow V^{+3} + OH + OH^-$	−19	−50	−4
$Cr^{+2} + H_2O_2 \rightarrow Cr^{+3} + OH + OH^-$	−23	−50	−8
$Cu^{+} + H_2O_2 \rightarrow Cu^{+2} + OH + OH^-$	−11	−56	+6
$Fe(CN)_6^{-4} + H_2O_2 \rightarrow Fe(CN)_6^{-3} + OH + OH^-$	+19	+28	11

TABLE 10

Ion-pair formation in aqueous solution

REACTION	$K_{association}$	ΔG^0	ΔH^0	ΔS^0	REFERENCES
		kcal./mole	*kcal./mole*	*e.s.u.*	
$Fe^{+3} + OH^- \rightleftharpoons Fe^{+3}OH^-$	5×10^{11}	−16	−1.2	+50	(117, 264)
$Fe^{+3} + O_2H^- \rightleftharpoons Fe^{+3}O_2H^-$	2×10^{9}	−12.5	+1.8	+49	(107)
$Fe^{+3} + F^- \rightleftharpoons Fe^{+3}F^-$	8×10^{4}	−6.9	+7.5	+49	(117)
$Fe^{+3} + Cl^- \rightleftharpoons Fe^{+3}Cl^-$	30	−2.0	+8.5	+35	(264)
$Fe^{+3} + Br^- \rightleftharpoons Fe^{+3}Br^-$	4	−0.8	+6.1	+23	(264)
$Fe^{+3} + N_3^- \rightleftharpoons Fe^{+3}N_3^-$	1.3×10^{4}	−5.7	−4.3	+5	(117)
$Fe^{+3} + C_2O_4^{-2} \rightleftharpoons Fe^{+3}C_2O_4^{-2}$	3×10^{9}	−13.2	−0.3	+43	(117)
$V^{+3} + OH^- \rightleftharpoons V^{+3}OH^-$	4×10^{12}	−17.2	−3.7	+45.5	(159)
$Ce^{+3} + SO_4^{-2} \rightleftharpoons Ce^{+3}SO_4^{-2}$	60	−2.5	-	-	(76)
$Ce^{+3} + NO_3^- \rightleftharpoons Ce^{+3}NO_3^-$	2.5	−0.6	-	-	(76)
$Ce^{+3} + F^- \rightleftharpoons Ce^{+3}F^-$	1×10^{4}	−5.6	-	-	(239)
$Cu^{+2} + Cl^- \rightleftharpoons Cu^{+2}Cl^-$	1.30	−0.15	+0.65	+2.5	(240)
$Pb^{+2} + Cl^- \rightleftharpoons Pb^{+2}Cl^-$	0.08	+1.5	-	-	(158)
$Cd^{+2} + Cl^- \rightleftharpoons Cd^{+2}Cl^-$	30	−1.9	+0.6	+8.5	(210)
$Sn^{+2} + Cl^- \rightleftharpoons Sn^{+2}Cl^-$	13	−1.5	-	-	(96)
$Sn^{+2} + Br^- \rightleftharpoons Sn^{+2}Br^-$	2.7	−0.6	-	-	(96)
$Ca^{+2} + OH^- \rightleftharpoons Ca^{+2}OH^-$	9.1	−1.3	-	-	(39)
$Ba^{+2} + OH^- \rightleftharpoons Ba^{+2}OH^-$	2.3	−0.5	-	-	(39)
$Ba^{+2} + S_2O_3^{-2} \rightleftharpoons Ba^{+2}S_2O_3^{-2}$	1.9×10^{2}	−3.0	+2.6	+19	(343)
$Th^{+4} + F^- \rightleftharpoons Th^{+4}F^-$	6×10^{7}	−10.8	-	-	(90)
$Th^{+4} + Cl^- \rightleftharpoons Th^{+4}Cl^-$	1.76	−0.35	-	-	(90)
$Th^{+4} + NO_3^- \rightleftharpoons Th^{+4}NO_3$	4.73	−0.95	-	-	(90)

The entropy changes in the formation of ferric-ion pairs can be compared with Latimer's data (223) on entropies of solvation of the corresponding negative ions. The latter entropy changes are negative; the former, which involve a process of desolvation, are positive. If $\Delta S_{ass.}$ (of ion-pair formations) is plotted against $-\Delta S_{sol.}$ (of solvation of the negative ion) a roughly linear function is obtained. It is noteworthy that there is no such regularity when the entropies of the formation of ion-pair complexes of the same anion with cations of different valency are being compared with the entropy change for the reaction:

$$e + M^{+n}(aq) \rightarrow M^{+(n-1)}(aq)$$

This fact is very significant in some phenomena of homogeneous catalysis (*cf.* page 395 of this review).

IX. THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY FERROUS ION AND FERRIC ION IN VIEW OF RECENT ENERGETIC DATA

From recent work compiled in the previous section it can be concluded that the following reactions occur in the system ferrous ion–ferric ion–hydrogen peroxide in aqueous solution:

REACTION	HEAT
	kcal.
(1) $Fe^{+2} + H_2O_2 \xrightarrow{k_1} Fe^{+3}OH^- + OH$	−(5 to 7)
(2) $OH + H_2O_2 \xrightarrow{k_2} H_2O + HO_2$	+19
(3) $O_2^- + H_2O_2 \xrightarrow{k_3} O_2 + OH^- + OH$	+(13 to 15)
(4) $Fe^{+2} + OH \xrightarrow{k_4} Fe^{+3} + OH^-$	+42
(5) $Fe^{+3} + HO_2^- \xrightarrow{k_5} Fe^{2+} + HO_2$	−29
(6) $Fe^{+3} + O_2^- \xrightarrow{k_6} Fe^{+2} + O_2$	+20
(7) $Fe^{+2} + HO_2 \xrightarrow{k_7} Fe^{+3} + HO_2^-$	+29
(8) $Fe^{+3}OH^- + OH \xrightarrow{k_8} Fe^{+2} + H_2O_2$	+(5 to 7)

The accuracy of these heats is about ±2 kcal. Within these limits the values summarized in this review are self-consistent. The estimate of the accuracy of the heats is an optimistic one, not taking into account possible but unrecognized sources of error.

It should be noted that reactions 1 to 7 of this scheme (HO_2, however, being considered as undissociated radical) were contained in the original Haber–Weiss publication (178). Reaction 8 is postulated by the author of this review. As HO_2 appears to be an acid of medium strength ($pK \sim 2$), both HO_2 and O_2^- are present in dilute aqueous solution. HO_2 is an oxidizing species and O_2^- ion a reducing one. Thus the oxidation of ferrous ion by HO_2 and the reduction of ferric ion by O_2^- are both exothermic reactions. It is also seen that the reaction $Fe^{+3}OH^- + OH$ is exothermic to an extent of 6 kcal. The entropy change is approximately zero. The following constants and constant ratios were evaluated by Barb, Baxendale, George, and Hargrave (20, 21):

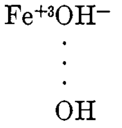
$$\begin{aligned} k_1([\text{mole/l.}]^{-1}[\text{sec.}]^{-1}) \text{ at } 0°\text{C.}&: 12.6 \pm 0.15 \\ \text{at } 14.6°\text{C.}&: 31.6 \pm 0.5 \\ \text{at } 24.6°\text{C.}&: 53.0 \pm 0.7 \end{aligned}$$

The temperature-independent factor of k_1 was determined as 4.45×10^8 and the activation energy as 9.4 kcal. In view of the scrupulous experimentation the values of k_1 should be considered as well established (within ±2 per cent). Earlier estimates of k_1 were made by Baxendale, Evans, and Park (34) ($k_1 = 1.78 \times 10^9 \exp.(-10{,}100/RT)$ (mole/l.)$^{-1}$(sec.)$^{-1}$) and by Haber and Weiss (178) ($4.0 \times 10^7 \exp.(-8500/RT)$ (mole/l.)$^{-1}$(sec.)$^{-1}$). The ratio k_2/k_4 is much less certain. Different experimental methods lead to divergent results, albeit of similar order. The results of the above authors show that the value of this ratio is of the order of 10 to 100 (20, 21). k_5 was found to be $1.1 \times 10^{24} \exp.(-28{,}000/RT)$ (mole/l.)$^{-1}$(sec.)$^{-1}$. The uncertainty in this activation energy is ±8 kcal. k_6/k_7 was evaluated at $7 \times 10^{-3}/K_{HO_2}$, where K_{HO_2} is the dissociation constant of HO_2 in aqueous solution. k_6/k_9 (where k_9 is the rate constant of $Cu^{+2} + O_2^- \rightarrow Cu^+ + O_2$, a reaction which will be referred to in Section XI of this review) was approximately 1:20. The activation energy of all the exothermic electron-transfer reactions, which do not involve bond breaking, is of the order of 0–5 kcal.

Baxendale, Evans, and Park (34) have already discussed the theoretical basis of the abnormally low temperature-independent factor k_1. Some numerical data should, however, be revised. The total entropy change in the reaction

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3}OH^- + OH$$

is zero, as the formation of the ion-pair $Fe^{+3} + OH^- \rightarrow Fe^{+3}OH^-$ has a positive entropy change of 50 E.S.U. It is, however, not unlikely that $\Delta S^{\ddagger}$ for the formation of the transition state



$$\begin{array}{c} Fe^{+3}OH^- \\ \vdots \\ OH \end{array}$$

is of the order of -15 E.S.U. ($e^{\Delta S/R} = 5 \times 10^{-4}$) corresponding to the temperature-independent factor of $\sim 4.5 \times 10^8$. The activation energy of reaction 8 should be the difference between the activation energy and the endothermicity of reaction 1. This value is 4 ± 2 kcal. (dependent on the various estimates of the endothermicity of reaction 1). In view of the net entropy change of zero in reaction 1 the entropy of activation of the back-reaction (reaction 8) should be the same as in the forward reaction. A rough estimate for k_8 at 25°C. is $\sim 5 \times 10^5$ (mole/l.)$^{-1}$sec.$^{-1}$

X. THE TRANSITION STATE AND ITS SIGNIFICANCE IN THE KINETICS OF FREE-RADICAL REACTIONS

The general theory of the transition state in chemical reactions developed by Pelzer and Wigner (258), Eyring (120), Wynne-Jones and Eyring (345), and Evans and Polanyi (109, 110) can well be applied to the kinetics of free-radical reactions. Evans (104) was the first to point out the similarity of the Haber–Weiss reaction

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH$$

and the sodium flame reaction

$$Na + RCl \rightarrow Na^+ + Cl^- + R$$

the thorough study of which by Polanyi and his school was one of the main pillars in the development of the transition-state theory. The frequency factor of the Haber–Weiss reaction has already been discussed in Section IX. We owe also to Evans (104) the basic recognition that for all simple electron-transfer reactions the activation energy changes in the same direction as the corresponding values of the oxidation–reduction potentials. We must distinguish clearly between endothermic and exothermic electron-transfer reactions. In the former the activation energy is roughly equal to the endothermicity; in the latter it is usually less than 5 kcal. If, however, the reaction involves also the breaking of a bond, the activation energy may be larger, as in the case of

$$F + H_2O \rightarrow H^+ + F^- + OH$$

in which the activation energy, according to Bates, Evans, and Uri (23), is of the order of 5–10 kcal. Entropy changes will affect the temperature-independent factor for bimolecular reactions in aqueous solution, which is normally of the order of 10^{12}, and will be increased or reduced by the factor $e^{\Delta S^{\ddagger}/R}$. Baxendale, Evans, and Parks (34) have already pointed out that in case of a negative overall entropy change the formation of the transition state might well be accompanied by a fraction only of the overall negative entropy change. In some cases, as in the reaction

$$Fe^{+2} + OH \rightarrow Fe^{+3} + OH^-$$

(see Section XIV, B, 1, (c), page 417, on the photoöxidation of water) the knowledge of the thermodynamics of the formation of the ion-pair $Fe^{+3}OH^-$ makes it possible to estimate this fraction, at least approximately.

In the case of a positive entropy change the frequency factor will be considerably larger than 10^{12}. The value of the latter for the reaction

$$Fe^{+3} + HO_2^- \rightarrow Fe^{+2} + HO_2$$

is 10^{24}. This is in striking agreement with the positive entropy change of 55 E.S.U.; accordingly the factor $e^{\Delta S^{\ddagger}/R}$ is both theoretically and experimentally 10^{12}.

XI. Catalysis and Promotion

In the light of these new findings on the heat and entropy changes in reactions involving ions and radicals, some phenomena of catalysis and promotion can be accounted for by making use of the transition-state theory. Bohnson and Robertson (48) investigated the catalytic decomposition of hydrogen peroxide by a mixture of ferric and cupric ions. Cupric ion itself is a very weak catalyst. In the presence of ferric ion it acts as a promoter (or additional catalyst). Bohnson and Robertson attributed this phenomenon to the formation of ferrate ion, FeO_4^{-2}, and its subsequent decomposition. Evans and Uri (112) found no evidence for the formation of ferrate ion and thought it not unlikely that the observations of a violet-colored compound by Bohnson and Robertson (48) were due to traces of salicylic acid frequently added as a stabilizer. The principle of a much more satisfactory explanation was first indicated by Haber and Weiss

(178) and worked out from a quantitative point of view by Barb, Baxendale, George, and Hargrave (21). The first step is

$$M^{+n} + HO_2^- \rightarrow M^{+(n-1)} + HO_2$$

With cupric ion this reaction is endothermic to a considerably larger extent (~15 kcal.) than with ferric ion. Assuming an activation energy similar to the endothermicity, this would mean a reduction of the rate of the primary step by about ten powers of 10, which is sufficient to explain why cupric ion by itself is almost inactive. The HO_2 radical produced in the primary step dissociates into H^+ and O_2^-. The second step, leading to oxygen evolution, i.e.,

$$M^{+n} + O_2^- \rightarrow M^{+(n-1)} + O_2$$

is exothermic for both ferric ion and cupric ion. The decisive factor will be $e^{\Delta S/R}$ and this is twenty times larger for cupric ion than for ferric ion. It is also proof that a mere consideration of the ionic charges which would favor the reaction with ferric ion is insufficient for the explanation of the abnormal temperature-independent factor. Cuprous ion formed, would be, of course, instantaneously reoxidized by ferric ion. This scheme may be of much more general application than is realized. In any system of two consecutive oxidation–reduction reactions in which the first step is endothermic and the second step exothermic, a similar effect by the coupled action of ferric ion and cupric ion could be expected. It has also been found that the joint action of ferric ion and cupric ion as catalysts in the oxidation of hydrocarbons (with peroxides as intermediate products) is not merely additive (66).

An interesting case is the reaction of ferric ion and thiosulfate. A deep violet unstable complex is formed, which in aqueous solution is mainly $Fe^{+3}S_2O_3^{-2}$ (274). This ion-pair would decompose into ferrous ion and the free-radical ion $S_2O_3^-$, which would dimerize, producing the tetrathionate ion. The decomposition of this complex is catalyzed by cupric ion, to the extent that traces of cupric ion can be determined chronometrically. Feigl (130) suggested as the underlying mechanism that cupric ion is reduced by a fast reaction. The cuprous ion thus produced reduces the ferric thiosulfate complex. In this case both the reduction of ferric ion and that of cupric ion are exothermic, as in the case of the reaction with the O_2^- ion. The ratio of the reaction rates is, however, much larger than 20. The reviewer considers that the explanation for this discrepancy is that the positive entropy change in the reaction

$$Fe^{+3}(aq) + e \rightarrow Fe^{+2}(aq)$$

is at least partially consumed in ion-pair formation, and it can be seen from table 10 that the positive entropy change accompanying the formation of ferric ion-pairs is considerably larger than that for ion-pairs of divalent cations.

The same basic idea can be applied to the reaction of sulfite ion with ferric or cupric ion, which was first critically studied by Franck and Haber (146). With cupric ion a fast electron-transfer reaction is observed, while with ferric ion the reaction is very slow and accompanied by the formation of an ion-pair complex.

The reviewer considers that the reason for the slow reduction of ferric ion (by itself) lies in the fact that the positive entropy change accompanying the eleciron-transfer reaction is almost entirely consumed by the formation of the ton-pair complex.

XII. INITIATION OF POLYMERIZATION OF VINYL COMPOUNDS

Baxendale, Evans, and Park (34) have shown that free radicals produced in the Haber–Weiss reaction initiate the polymerization of vinyl compounds. This work was preceded by investigations by Bacon (15) and Morgan (249) on "reduction activation," a term used for the first time by Bacon. The system contained potassium persulfate as oxidizing agent and various reducing agents such as sodium bisulfite, sodium sulfite, sodium thiosulfate, sodium sulfide, hydrogen sulfide, thioglycolic acid, hydroxylamine, hydrazine, ferrous sulfate, stannous chloride, titanous sulfate, cuprous chloride, silver nitrate, metallic iron, hydroquinone, etc. In the presence of acrylonitrile or styrene, polymerization occurred, which was initiated by an intermediate product formed in the reduction of persulfate ions. Bisulfite, hydrosulfite, ferrous, and silver ions were the most active reduction activators. Bacon (15) also studied reduction activation with various oxidizing agents such as ceric sulfate, hydrogen peroxide, and sodium hypochlorite, with sodium bisulfite as reduction activator. These were, however, less active than the persulfate ion. The mechanism of the persulfate "redox polymerization" (a term introduced recently by Medalia and Kolthoff (241)) was investigated by Morgan (249). It was shown that the polymerization was initiated by an intermediate product formed in the oxidation–reduction process. At the same time Baxendale, Evans, and Park (34) established the theoretical basis of redox polymerization with the relatively simpler system ferrous ion–hydrogen peroxide–vinyl monomer. Their reaction scheme is

(a) $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH$

(b) $OH + Fe^{+2} \xrightarrow{k_b} Fe^{+3} + OH^-$

(c) $OH + H_2O_2 \rightarrow H_2O + HO_2$

(d) $OH + CH_2{=}CHX \xrightarrow{k_d} HO{-}CH_2{-}CHX{-}$

(e) $HO{-}CH_2{-}CHX{-} + CH_2{=}CHX \rightarrow HO{-}CH_2{-}CHX{-}CH_2{-}CHX{-}$

It was shown that both reactions (b) and (c) are suppressed in the presence of excess vinyl monomer. Only 1 mole of ferrous ion is being oxidized per mole of hydrogen peroxide disappearing, whereas in the absence of monomer and a large excess of hydrogen peroxide, the value $\Delta H_2O_2/\Delta Fe^{+2} = 0.5$. Conditions could, however, be altered by addition of ferrous ion, so that both ferrous ion and monomer would compete for OH radicals. The monomers used were acrylonitrile, methyl acrylate, and methacrylic acid. The polymers formed precipitated from the aqueous solution. By measuring the changes in the stoichiometry of the ferrous ion–hydrogen peroxide reaction, the rates of reactions (b) and

(d) could be compared. The values obtained for the ratio k_b/k_d vary from 0.03 to 0.25 with methyl acrylate as monomer. Evans, Santappa, and Uri (111) obtained results with acrylonitrile and methyl methacrylate which led to a value of the order of 10^4 for the same ratio. It is not unlikely that in the case of methyl acrylate there is partial oxidation in addition to polymerization. The discrepancy in these observations is considerable. Some supporting evidence for the larger value of the ratio is obtained from recent observations made by Barb, Baxendale, George, and Hargrave (19, 20) that polymerization in the ferrous ion–hydrogen peroxide system can be completely suppressed in solutions containing 1.0 *M* hydrogen peroxide and *M*/5 acrylonitrile (the reaction of OH with hydrogen peroxide is at least ten times slower than the reaction of OH with ferrous ion and yet under the above conditions no polymerization occurs) and also from data obtained by Baxendale and Fearnley (35). The great practical importance of this new method of polymerization was immediately recognized by Dainton (82). Its main advantage lies in the low activation energy of the primary step, by which free radicals are produced, which allows low-temperature polymerization and is thus favorable to the production of synthetic rubber. The inhibition of the polymerization by oxygen was considered to be due to the formation of a per compound of the active polymer ending with O_2 of the formula $HO(CH_2CHX)_nCH_2CHX—O—O\cdot$, which would react with ferrous ion to give $Fe^{+3}OH^-$ and $HO(CH_2CHX)_nCH_2CX{=}O$ and thus terminate the chain. Bunn (67) showed that the mechanism of the persulfate redox polymerization can be put into the same general picture as those with Fenton's reagent (see page 400). The redox system was persulfate ion–thiosulfate and the monomer was methylacrylamide, which does not react with thiosulfate ion at pH 7. The following mechanism was suggested:

$S_2O_8^{-2} + S_2O_3^{-2} \rightarrow SO_4^{-2} + SO_4^- + S_2O_3^-$	formation of radical ions
$SO_4^- + S_2O_3^{-2} \rightarrow SO_4^{-2} + S_2O_3^-$ $SO_4^- + HOH \rightarrow HSO_4^- + OH$ $OH + S_2O_3^{-2} \rightarrow OH^- + S_2O_3^-$	radical–ion transfer
$2S_2O_3^- \rightarrow S_4O_6^{-2}$	termination (in the absence of monomer)
$SO_4^- + M \rightarrow —M—SO_4^-$ $OH + M \rightarrow —M—OH$ $S_2O_3^- + M \rightarrow —M—S_2O_3^-$	initiation of polymerization with vinyl monomer (M)

Apart from its intrinsic importance in polymerization reactions this new method of redox polymerization afforded a new and sensitive method for detecting free radicals. Its value lies in the fact that one free radical gives rise to a large polymer chain (the observed chain length is generally above 200), which would precipitate from aqueous solution. The further development of this method is described in the following paragraphs. Its application in photochemical reactions is discussed in the corresponding sections dealing with photochemical methods of the production of free radicals.

Baxendale, Evans, and Kilham (32, 33) have shown that a similar mechanism of redox polymerization is obtained with aqueous emulsions, using cetyltrimethylammonium bromide as emulsifying agent for methyl methacrylate. It was also shown that termination occurs by the interaction of two active polymer chains. The activation energy of polymerization (if termination is considered to occur with zero activation energy) would, in accordance with the results of Baxendale, Evans, and Kilham, amount to 5 kcal. An interesting aspect of this study of polymerization in aqueous emulsions (33) is the formation of highly swollen micelles by growing polymer chains with dead polymer molecules and monomers. Thus dead polymer acts as an inhibitor on chain termination and catalyzes indirectly the propagation of polymerization.

A very pronounced effect of heterogeneous catalysis was recently observed by Bengough and Norrish (40, 41) in the photopolymerization of vinyl chloride. Possibly these two observations have a very different origin. Bengough and Norrish suggest, on the basis of a very detailed and thorough experimental study, that the co-catalytic effect of dead polymer in the presence of free radicals is due to accumulation of stabilized centers of polymer growth on the surface of solid polymer. This effect of "dead" polymer catalysis in free-radical polymerization reactions may be of considerable practical importance.

Baxendale, Cowling, and Evans (105) investigated the systems ferrous ion–chlorine–monomer, ferrous ion–bromine–monomer, and ferrous ion–hypobromous acid–monomer. The primary step in the systems involving halogens is

$$Fe^{+2} + Hal_2 \rightarrow Fe^{+3} + Hal^- + Hal$$

(Hal atom initiating polymerization). In the case of hypobromous acid both the reaction

$$Fe^{+2} + HOBr \rightarrow Fe^{+3} + Br^- + OH$$

and the reaction

$$Fe^{+2} + HOBr \rightarrow Fe^{+3} + OH^- + Br$$

are feasible. In view of the larger electron affinity of the OH radical, the second step will predominate.

Davies, Evans, and Higginson (89) recently investigated the system titanous ion–hydroxylamine–vinyl monomer in acid solution. The primary step could be

$$Ti^{+3} + H_2N{-}OH \rightarrow Ti^{+4} + NH_2^- + OH$$

and

$$Ti^{+3} + H_2N{-}OH \rightarrow Ti^{+4} + OH^- + NH_2$$

It was shown that the latter step is predominant and that it is the NH_2 radical which initiates polymerization. This is in accordance with expectation, in view of the larger electron affinity of the OH radical. Titanous ion was the most active among the reduction activators of hydroxylamine. Chromous, vanadous, and molybdic ions were less active. Ferrous ion shows hardly any activity, as its ionization potential is too large. In fact, the ferric ion is reduced by hydroxylamine in acid solution. It is interesting that even $[FeF_6]^{-4}$ and $[Fe(CN)_6]^{-4}$ were practically inactive, notwithstanding the lowering of the oxidation–reduction potential by $\sim$0.5 v.

Weiss suggested in 1935 that decomposition reactions catalyzed by metal surfaces proceed *via* free radicals (317). It is, therefore, noteworthy that Parravano (253, 254) obtained polymerization with methyl methacrylate solutions induced by the decomposition of hydrazine on surfaces of palladium black. It is not unlikely that the primary step is

$$M + H_2N{-}NH_2 \rightarrow M^+ + NH_2^- + NH_2$$

The NH_2 radical would lead to the initiation of polymerization. Parravano also studied the system formic acid–oxygen–vinyl monomer on catalytic surfaces such as palladium, platinum, silver, and charcoal. This polymerization would also belong to the category of redox polymerization, and it is not surprising that oxygen at higher concentrations acts as an inhibitor, in view of the results obtained by Baxendale, Evans, and Park (34). Moreover, it was shown by Parravano (255, 256) that polymerization of vinyl compounds can be initiated by free radicals produced in enzymic systems and by hydrogen atoms formed in the course of electrolysis (this was also reported by Wilson (342)). The enzymic systems chosen were *B. coli* in formic acid and xanthine oxidase in formaldehyde. On the other hand, according to Dainton (86), the system catalase–hydrogen peroxide does not initiate polymerization.

Recent developments in the field of emulsion polymerization, using redox systems as initiators, have been described by Kolthoff and Medalia (214), who recently made considerable contributions to the field of redox polymerization and the kinetics of free-radical reactions in solution as a whole. The system used by Medalia and Kolthoff (241) for the copolymerization of butadiene and styrene was cumene hydroperoxide, a soluble iron phosphate complex, and a reducing sugar. The emulsifying agent used was potassium myristate. It was shown that the reaction of ferrous ion with cumene hydroperoxide leading to the production of free radicals, as in the Haber–Weiss mechanism, takes place in the aqueous phase; in the presence of sufficient soap the free radicals diffuse into the organic phase and initiate polymerization.

Bovey and Kolthoff (53, 54) studied the aqueous-phase polymerization of styrene (at a concentration of 0.02 M) in a detergent solution. These authors also suggested that the thermal polymerization of styrene in aqueous potassium oleate solutions, studied by Frillette and Hohenstein (157), might have been, in fact, a redox polymerization initiated by free radicals. Kolthoff and Youse (217) have shown that not only with iron–cumene hydroperoxide but also with iron–benzoyl peroxide systems the locus of initiation in an emulsion polymerization recipe is in the aqueous phase. Apart from mentioning these major features it would be beyond the scope of this review to describe in greater detail the work of Kolthoff and his school in the field of emulsion polymerization.[4] It would not appear unlikely that polymerization, thought to be initiated by the thermal decomposition of cumene hydroperoxide (136), might have been partially a wall-catalyzed redox initiation of polymerization (perhaps caused by impurities). The main reason for this suggestion is that it would appear to this reviewer that the observed activation energy (20–31 kcal.) is too low for the breaking of the —O···O— bond.

XIII. Oxidation by Fenton's Reagent

The mixture ferrous ion–hydrogen peroxide, termed Fenton's reagent, is one of the most powerful inorganic oxidizing reagents. Its action is based on the formation of OH radicals by the Haber–Weiss reaction:

$$Fe^{+2} + HO{:}OH \rightarrow Fe^{+3}OH^- + OH$$

The strength of the OH radical as oxidizing reagent lies in (*a*) the bond-dissociation energy of 120 kcal. for H···OH and (*b*) the large electron affinity (in solution) of the OH radical (∼136 kcal.).

With the exception of hydrogen fluoride there is no larger R···H bond-dissociation energy, R denoting any radical. A reaction of the type $R \cdots H + OH \rightarrow R + HOH$ ($R \neq F$) will be considerably exothermic. All organic compounds containing hydrogen are oxidized by OH radicals and hence by Fenton's reagent. The R···H bond-dissociation energy in hydrocarbons, aldehydes, alcohols, etc. is in the range 75–105 kcal. This indicates that the heat of the step $R \cdots H + OH \rightarrow R + HOH$ will be 15–45 kcal. R thus formed could react with a further OH radical, with oxygen, with itself, with ferric ion, or with hydrogen peroxide. The large electron affinity (in solution) of the OH radical (∼136 kcal.) is approximately equalled by the chlorine atom and exceeded only by the fluorine atom and radicals of strong oxy acids such as perchloric acid. Therefore, practically every X^- ion would react with the OH radical to yield OH^- ion and X radical as the first step of the oxidation of the X^- ion. The second step could vary as indicated in case (*a*). These fundamental energetic considerations were not conceived till recently. As a result, the important investigations by the discoverer (131) of the reagent and the very extensive studies by Wieland and Franke (341) were not understood. Their concept of a complex between ferrous ion and the substrate is unfounded.

The system ferric ion–hydrogen peroxide as oxidizing agent is much weaker than the system ferrous ion–hydrogen peroxide. As, however, OH radicals are produced in this system, too, it is similar in principle. It differs from the ferrous ion–hydrogen peroxide system in that (*a*) the stationary OH radical concentration is much smaller, (*b*) the HO_2 radical is produced in the primary step, which could lead to different reactions from those occurring with OH radicals, (*c*)

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[4] Attention should be drawn to the Symposium on Low Temperature Rubber (Ind. Eng. Chem. **41**, 1553–1616 (1949)) in which the important industrial applications of redox recipes in polymerization processes are described. Cumene hydroperoxide redox recipes have also been described by Vandenberg and Hulse (304).

the O_2 formed by the reaction $Fe^{+3} + O_2^- \rightarrow Fe^{+2} + O_2$ can act as inhibitor of chain reactions.

Uri (298), slightly modifying a proposal made by Weiss (324), suggested a division of ferrous ion–hydrogen peroxide substrate reactions into three groups:

(*a*) The substrate is oxidized by both the ferrous ion–hydrogen peroxide system and the ferric ion–hydrogen peroxide system but neither by ferric ion nor by hydrogen peroxide alone. Most substrates belong to this group, like alcohols, hydroxy acids, benzene, and many benzene derivatives, etc.

(*b*) The substrate is also oxidized by ferric ion but not by hydrogen peroxide alone. Hydroquinone, hydroxylamine, and hydrazine are typical examples. In this group the oxidation of the substrate by ferric ion is accompanied by a large positive entropy change and very greatly increased temperature-independent factors of the rate constant.

(*c*) The substrate is oxidized by the ferrous ion–hydrogen peroxide system but not by the ferric ion–hydrogen peroxide mixture. This is the case in chain oxidation reactions, in which oxygen, formed *via* the HO_2 radical, acts as inhibitor. A typical example of this group is oxalic acid.

Recent studies of oxidations by Fenton's reagent, in which the principle of the mechanism and energetic factors were clearly recognized, are relatively few. They include investigations by Weiss (323), Merz and Waters (245, 246), Loebl, Stein, and Weiss (234), Barb, Baxendale, George, and Hargrave (20), Kolthoff and Medalia (211, 212), and Baxendale and Magee (38).

Weiss (323) studied the system ferrous ion–hydrogen peroxide–oxalic acid. It was shown that the so-called "active oxalic acid" is in fact the radical $C_2O_4^-$, the occurrence of which was also suggested by Abel (1). It is formed by the reaction

$$OH + C_2O_4^{-2} \rightarrow C_2O_4^- + OH^-$$

$C_2O_4^-$ is a chain carrier, as it reacts with hydrogen peroxide to yield $2CO_2 + OH^- + OH$. Oxygen inhibits the chain by the reaction:

$$(1) \quad C_2O_4^- + O_2 \rightarrow 2CO_2 + O_2^-$$

$$(2) \quad Fe^{+3} + O_2^- \rightarrow Fe^{+2} + O_2$$

This is the reason why practically no evolution of carbon dioxide is observed in the system ferric ion–hydrogen peroxide–oxalic acid (298). In the presence of mercuric chloride another chain is initiated, according to Weiss:

$$C_2O_4^- + Hg^{+2} \rightarrow \tfrac{1}{2}Hg_2^{+2} + 2CO_2$$

$$\tfrac{1}{2}Hg_2^{+2} + C_2O_4^{-2} \rightarrow Hg + C_2O_4^-$$

$$Hg^{+2} + Hg \rightarrow Hg_2^{+2}$$

This results in the precipitation of calomel from the reaction mixture. Weiss suggests that the $C_2O_4^-$ radical is also the active intermediate species in the reaction of oxalic acid with permanganate ion.

Merz and Waters (245, 246) investigated in detail the mechanism of the oxidation of various substrates by Fenton's reagent. Their main conclusion is that one should distinguish between two types of mechanisms:

(*A*) *Chain oxidation* (OH *and* HR• *radicals are the chain carriers):*

The steps are:

$$(1)\ Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH$$

$$(2)\ Fe^{+2} + OH \xrightarrow{k_0} Fe^{+3} + OH^-$$

$$(3)\ OH + H_2R \xrightarrow{k_i} HR\cdot + HOH$$

(Merz and Waters refer to the substrates as HR)

$$(4)\ HR\cdot + HO\text{—}OH \rightarrow HROH + OH$$

HR• and OH radicals are the chain carriers and HROH is the oxidation product. In the case of ethyl alcohol the radical formed in step 3 is $CH_3\dot{C}HOH$; in step 4 $CH_3CH(OH)_2$ is formed, which by elimination of a water molecule yields acetaldehyde. It is, of course, important to avoid excess hydrogen peroxide; otherwise the reaction $OH + H_2O_2 \rightarrow HOH + HO_2$ cannot be neglected.

Stationary-state kinetics (assuming $d[OH]/dt = 0$ and $d[HR\cdot]/dt = 0$) lead to the equation

$$\frac{-d[H_2O_2]}{-d[H_2R]} = \frac{k_0[Fe^{+2}]}{k_i[H_2R]} + 1$$

For chain oxidations, therefore, a plot of $-d[H_2O_2]/-d[H_2R]$ against $[Fe^{+2}]/[H_2R]$ would have an intercept of 1 on the ordinate axis. In fact, this can be seen from a first glance at the above system of equations 1 to 4. If $[Fe^{+2}]/[H_2R]$ approaches zero, the amount of hydrogen peroxide which disappears in step 1 is negligible when compared with the amount of H_2R which is consumed in step 3. The consumption ratio $\Delta H_2O_2/\Delta H_2R$ will thus approach unity. The substrates in this group include alcohols (but not tertiary ones), aldehydes, ethers, and aliphatic hydroxy acids: e.g., methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, formaldehyde, acetaldehyde, diethyl ether, glycolic acid, lactic acid, and hydroxybutyric acid.

(*B*) *Nonchain oxidation:*

Steps 1 to 3 are the same as for chain oxidations in the previous section.

$$(4)(a)\quad HR\cdot + OH \rightarrow HROH \text{ or}$$

$$(b)\quad HR\cdot + HR\cdot \rightarrow HR\text{—}RH$$

According to Merz and Waters (235, 236) stationary-state kinetics lead to the equation:

$$\frac{-d[H_2O_2]}{-d[H_2R]} = \frac{k_0[Fe^{+2}]}{k_i[H_2R]} + 2$$

Thus when the consumption ratio $\Delta[H_2O_2]/\Delta[H_2R]$ is plotted against $[Fe^{+2}]/[H_2R]$ in the case of nonchain oxidation an intercept of 2 on the ordinate axis is obtained. This nonchain oxidation by Fenton's reagent was shown to apply to tertiary butyl alcohol, methyl acetate, ethyl acetate, chloral hydrate, diethylammonium sulfate, pyridine, pinacol, propionic acid, butyric acid, and such aromatic compounds as benzene, nitrobenzene, benzamide, benzoic acid, and phenylacetic acid.

The method of evaluation of the intercept from a simple plot, which was adopted by Merz and Waters in order to distinguish between chain oxidation and nonchain oxidation, is very impressive. It was, however, omitted from the kinetic analysis and it was not shown experimentally that the intercept of 2 in the nonchain oxidation occurs only when step 4a, i.e., $HR\cdot + OH \rightarrow HROH$, is the terminating step. If step 4b, i.e., $HR\cdot + HR\cdot \rightarrow HR{-}RH$ occurs, such as in the formation of biphenyl by the attack of OH radicals on benzene, the mathematical analysis leads to an intercept of 1. If both step 4a and step 4b take place, then the intercept lies between 1 and 2 according to the relative rates of reactions 4a and 4b. Only in the case where reaction 4b leads by disproportionation to the formation of the original substrate, i.e., $HR\cdot + HR\cdot \rightarrow H_2R + R$, does the intercept remain at 2. This would indicate that there are still a few aspects in the interesting work of Merz and Waters which await clarification. They also include the dependence of the reaction rates on the pH of the reaction mixture and the role of ferric ion. Merz and Waters assume no reaction between ferric ion and such free radicals as $CH_3\dot{C}HOH$ or C_6H_5, a conclusion which is opposed to the experience of other investigators (20, 21, 38, 64). It was, however, ascertained by Merz and Waters that mercuric ion would oxidize many of the intermediate radicals of the type $HR\cdot$. While the evaluation of the intercept of the plot of $\Delta H_2O_2/\Delta H_2R$ allowed Merz and Waters to distinguish between chain and nonchain oxidation, the slope of the same plot was used to evaluate k_i/k_0, i.e., the ratio of the rate constants in reactions 3 and 2. This ratio was found to lie between 10^{-1} and 10, thus indicating that the activation energy of the OH–substrate reaction is small and differs from the reaction of ferrous ion with the OH radical by less than 2 kcal., even allowing for a small difference in the temperature-independent factor. Our theoretical knowledge is not yet sufficient for an accurate comparative study of a slight variation in the k_i/k_0 ratio and structural features of the substrate.

Merz and Waters also observed the retarding action of some compounds, such as acetone and acetic acid, in the OH radical oxidation. This is attributed to radical transfer and the formation of a radical with less oxidizing power; e.g.,

$$RCOOH + OH \rightarrow RCOO\cdot + HOH$$

The same phenomena were studied simultaneously by Kolthoff and Medalia (211, 212).

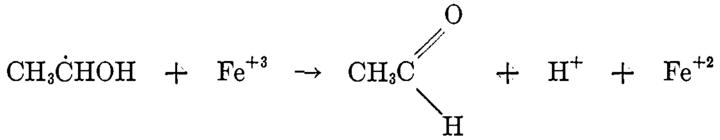
Loebl, Stein, and Weiss (234) investigated the hydroxylation of nitrobenzene. The whole field of hydroxylation of aromatic compounds was recently developed by Stein and Weiss, mainly using ionizing radiations (*cf.* Section XVII);

in this particular study Fenton's reagent was used and evidence was produced for the free-radical mechanism of hydroxylation. Attention was paid to the orientation of the OH radical in the aromatic nucleus. Hey (190) and France, Heilbron, and Hey (139) had previously shown that substitution by free radicals takes place in all three positions (ortho, para, and meta). The differences between heterolytic and homolytic aromatic substitution were critically studied and analyzed recently (13) and a new quantum-mechanical interpretation was put forward (78). Loebl, Stein, and Weiss (234) report substitution with Fenton's reagent by OH radicals in nitrobenzene in the following approximate proportions: *o*-, 0.56; *p*-, 1.0; *m*-, 0.44; the *p*-isomer predominated. The authors consider that this is general agreement with the theoretical considerations of free-radical substitution made by Wheland (339). A small quantity of *m*-dinitrobiphenyl was also formed, a result which indicates that nitrophenyl radicals were present in the reaction mixture. Bates, Evans, and Uri (23), studying the reaction of OH radicals with benzoic acid, found a different substitution ratio: *viz.*, a statistical one. This work was, however, carried out under very different experimental conditions and will be dealt with in the photochemical part of this review. As to the question whether the primary step is an addition of an OH radical to the benzene nucleus or abstraction of a hydrogen atom, the evidence available is not sufficient to make a decision.

Kolthoff and Medalia (211, 212) studied in detail the system ferrous ion–hydrogen peroxide–ethyl alcohol in the presence and in the absence of oxygen. Their investigation led to interesting conclusions which allow a better understanding of the oxidation mechanism with Fenton's reagent. The substrates are classified as (*a*) promoters and (*b*) suppressors. Ethyl alcohol, for example, promotes the decomposition of hydrogen peroxide in the course of the ferrous ion–hydrogen peroxide reaction by the following mechanism:

$$(\alpha)\quad Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH$$

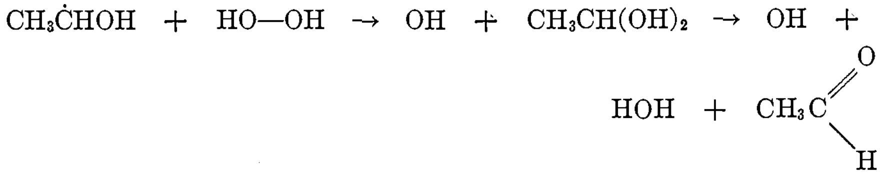
$$(\beta)\quad OH + CH_3CH_2OH \rightarrow CH_3\dot{C}HOH + HOH$$

(γ) 

$$(\gamma)\quad CH_3\dot{C}HOH + Fe^{+3} \rightarrow CH_3C\begin{matrix}\diagup O\\ \diagdown H\end{matrix} + H^+ + Fe^{+2}$$

$$(\delta)\quad Fe^{+2} + OH \rightarrow Fe^{+3} + OH^-$$

An alternative reaction is

(ε) 

$$(\epsilon)\quad CH_3\dot{C}HOH + HO\text{—}OH \rightarrow OH + CH_3CH(OH)_2 \rightarrow OH + HOH + CH_3C\begin{matrix}\diagup O\\ \diagdown H\end{matrix}$$

Reaction ε corresponds to the sum of reactions α and γ. As no experimental data are available on the effect of ferric ion on the relative reaction rates, the work of

Kolthoff and Medalia does not make it possible to distinguish between these two mechanisms. It is noteworthy that there is no effect of the ionic strength on the stoichiometry of the reaction, a result which—as Kolthoff and Medalia point out—indicates an uncharged intermediate species. This is additional evidence that the Haber–Weiss mechanism, involving OH radicals as intermediate species, is to be preferred to the Bray–Gorin mechanism, in which the active intermediate species is the positively charged FeO^{+2} ion. Acetic acid or acetone is not oxidized by Fenton's reagent. This does not, however, mean that they are not attacked by OH radicals; it has been observed that they suppress the oxidation of ethyl alcohol and are therefore termed suppressors. Logically Kolthoff and Medalia conclude that the mechanism of suppression is based on the following steps:

$$CH_3COOH + OH \rightarrow HOH + CH_3COO\cdot$$

$$CH_3COO\cdot + Fe^{+2} \rightarrow CH_3COO^- + Fe^{+3}$$

The $CH_3COO\cdot$ radical would oxidize ferrous ion rather than react with ethyl alcohol. Kolthoff and Medalia have not tried to produce the energetic basis of their classification. This reviewer considers that the major factor is the electron affinity in solution of the free radicals formed by the primary OH radical attack on the substrate. If these readily form ions such as the acetate ion or the ion of acetone, they act as suppressors by reoxidation of ferrous ion by a simple electron-transfer mechanism. So far we have only few quantitative data on the electron affinities of $RCOO\cdot$ radicals in solution. Szwarc (293), however, has recently developed a new method for its evaluation by pyrolysis of the corresponding benzyl ester in the presence of toluene as carrier gas, and estimation of its heat of formation. This method, which fits into the general line of Szwarc's work (292) on bond-dissociation energies, allows one to estimate the $RCOO\cdots H$ bond energy. As there are numerous data in the literature on heats of ionic dissociation of the corresponding acids in aqueous solution, the electron affinity of $RCOO\cdot$ can be evaluated from a thermodynamic cycle. Szwarc obtains for acetic acid a bond energy of 107 kcal. for the $RCOO\cdots H$ bond. This would correspond to a value of $\sim$136 kcal. for the electron affinity of the acetate radical in solution, a value which is practically identical with that of the OH radical. It was pointed out that the OH radical oxidizes either by electron transfer or by abstraction of hydrogen atoms. In principle, the same applies to the acetate radical. While, however, the electron-transfer oxidation would have the same heat change in view of the similar electron affinity, the abstraction of hydrogen would be less exothermic by the acetate radical than by the OH radical by $\sim$13 kcal. (a difference which also expresses itself in the heat of ionic dissociation of water on the one hand and acetic acid on the other). For the very same reason chloride ion acts as a suppressor. The electron affinity of the chlorine atom in solution is larger than that of the OH radical. On the other hand, the $H\cdots Cl$ bond-dissociation energy is smaller than that of $HO\cdots H$ by about 15 kcal. OH could react with chloride ion to give a chlorine atom and hydroxide ion, although this reaction is accompanied by a small positive free-energy change;

hydroxide ion is withdrawn from the equilibrium by neutralization with hydronium ions.

Kolthoff and Medalia have also drawn attention to the effect of inorganic impurities in distilled water. Simultaneously and independently the significance of these impurities was discovered by Barb, Baxendale, George, and Hargrave (20). OH radicals would react with these impurities and the free organic radicals formed could give rise to induced reactions. The effect of these impurities is also marked in photochemical work. Kolthoff and Medalia used water which was distilled from alkaline permanganate solutions. In the experience of this reviewer even this is not sufficient and the organic impurities can be detected by the reduction of $Fe^{+3}OH^-$ when irradiated with ultraviolet light of wave length 365 mμ. In the presence of oxygen Kolthoff and Medalia found that all organic substrates ("promoters" and "suppressors"), present at low concentrations, induce the oxidation of ferrous ion; this implies that more than 2 moles of ferrous ion are consumed per mole of hydrogen peroxide; under optimum conditions the consumption ratio was 6:1. This is attributed to the formation of radicals of organic peroxides which are formed by addition of O_2 to the radical formed in the primary OH radical attack. The mechanism put forward (for the induced oxidation of ferrous ion with hydrogen peroxide and oxygen by acetone) involves the following steps:

$$
\begin{aligned}
&RH + OH \rightarrow R\cdot + HOH \\
&R\cdot + O_2 \rightarrow R{-}O{-}O\cdot \\
&R{-}O{-}O\cdot + Fe^{+2} \rightarrow R{-}O{-}O^- + Fe^{+3} \\
&R{-}O{-}O^- + H^+ \rightarrow ROOH \\
&ROOH + Fe^{+2} \rightarrow R{-}O\cdot + Fe^{+3} + OH^- \\
&RO\cdot + RH \rightarrow ROH + R\cdot \\
&ROO\cdot + RH \rightarrow ROOH + R\cdot \\
&RO\cdot + Fe^{+2} \rightarrow RO^- + Fe^{+3} \\
&RO^- + H^+ \rightarrow ROH
\end{aligned}
$$

All these reactions are likely to occur from an energetic point of view. In addition, a chain autoöxidation of the organic radical is also feasible. It is, of course, impossible to derive the quantitative kinetics of this system. But the principle of the induced oxidation of ferrous ion clearly emerges from this mechanism. Various inorganic compounds, such as salts of alkali metal and heavy metal ions (e.g., cupric ion, manganous ion, stannic ion) were examined, but none showed an inductive effect on the oxidation of ferrous ion. A small effect was observed with phosphoric acid, but, in Kolthoff and Medalia's own view, this could have been due to impurities. On the other hand, chloride ion was found to suppress the induced oxidation of ferrous ion by hydrogen peroxide in the presence of substrates (such as ethyl alcohol). The reviewer considers that this would directly follow from his explanation of the action of chloride ion in the absence of oxygen. Chloride ion would compete with the substrate for OH radicals (particularly if present in large excess). The formation of organic peroxide radicals is thus inhibited. The chlorine atom formed can oxidize by two modes,—electron transfer and abstraction of hydrogen. In view of the energetic preference for the electron-transfer oxidation—when compared with the OH radical—the chlorine atom will oxidize ferrous ion (rather than react with the substrate) and thus tend to preserve the stoichiometric consumption ratio $\Delta Fe^{+2}/\Delta H_2O_2 = 2$. Kolthoff and Medalia have also pointed out the analytical significance of the suppression of the induced oxidation of ferrous ion.

Barb, Baxendale, George, and Hargrave (20) have made further contributions to the mechanism of oxidation by Fenton's reagent. Leuco dyes, such as the leuco form of Acronol Brilliant Blue, were oxidized to dyes, and it was shown that excess hydrogen peroxide acts as suppressor; the same applies to monomers and to the bleaching of methyl orange. This suppression can be readily explained by the competition for OH radicals by the reaction:

$$OH + H_2O_2 \rightarrow HOH + HO_2$$

The observations made by these authors as to the effect of organic impurities in distilled water are of special significance. While Kolthoff and Medalia worked with concentrations of $[H_2O_2]$ and $[Fe^{+2}]$ of the order of $10^{-3}\ M$, this investigation was carried out under conditions in which the concentration of reactants was about a hundred times smaller. Consumption ratios of $\Delta Fe^{+2}/\Delta H_2O_2$ up to 4 were obtained in the presence of oxygen without addition of any substrate. Obviously, this could be attributed to traces of organic impurities and in these experiments the usual laboratory methods to purify the distilled water were of no avail. Reference is made to the work of Fricke and Hart (155, 156), who showed that traces of organic impurities in distilled water could be quantitatively removed only by irradiation with x-rays. It was also observed in these experiments that chloride ions suppress the oxidation of ferrous ion, induced by trace impurities. In view of their observations as to the effect of ferric ion in the reaction kinetics, the authors suggested that the free radical produced in the presence of a substrate by the primary OH radical attack is oxidized by ferric ion rather than by hydrogen peroxide, as Merz and Waters suggested. Baxendale and Magee (38) investigated recently the oxidation of saturated aqueous benzene solutions by Fenton's reagent and it was found that the ratio phenol/biphenyl produced increases on addition of ferric ion. The suggested mechanism is

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH$$

$$C_6H_6 + OH \rightarrow C_6H_5 + HOH$$

Subsequent reactions of the phenyl radical are:

(*a*) Formation of biphenyl:

$$C_6H_5 + C_6H_5 \rightarrow C_6H_5C_6H_5$$

(*b*) Formation of phenol:

$$C_6H_5 + Fe^{+3} \rightarrow C_6H_5^+ + Fe^{+2}$$

$$C_6H_5^+ + OH^- \rightarrow C_6H_5OH$$

However, reaction (*b*) could also occur by the reaction of the phenyl radical with the $Fe^{+3}OH^-$ ion-pair:

$$C_6H_5 + Fe^{+3}OH^- \rightarrow C_6H_5OH + Fe^{+2}$$

XIV. PHOTOCHEMICAL FORMATION OF ATOMS AND FREE RADICALS, AND THEIR SUBSEQUENT REACTIONS

For the purposes of classification three general modes by which atoms and free radicals are formed in solution by the action of light may be considered. The light energy can be used (*a*) to break a chemical bond, (*b*) to effect an electron transfer which may also involve bond breaking, and (*c*) to produce an electronically excited state (possibly accompanied by singlet→triplet transition) of the absorbing molecule and, by subsequent bimolecular reactions, atoms and radicals. There is not as yet any well-established theory as to the physics of the primary photochemical process in solution. However, some fundamental ideas are recognized, such as Einstein's law of photochemical equivalence in its widest sense, the Franck–Condon principle, and the Franck–Rabinowitch (151, 266) primary recombination effect (sometimes referred to as the "cage" effect of the solvent molecules). With these reservations in mind the above classification is very useful from a practical point of view, as it allows immediate insight into the possible subsequent reactions.

A. BOND-BREAKING REACTIONS

The substances which were investigated include hydrogen peroxide, hydrazine, chlorine, and bromine. Urey, Dawsey, and Rice (297) were the first to suggest the photochemical dissociation of hydrogen peroxide into OH radicals.

The work of Kornfeld (218) and of Lea (224) leaves no doubt that the photochemical decomposition of hydrogen peroxide in solution is a chain reaction in accordance with the Haber–Weiss mechanism. The upper wave-length limit for both light absorption and photochemical activity is 370 mμ, corresponding to an energy of 75 kcal. This is ~25 kcal. above the thermal energy required to dissociate hydrogen peroxide into two OH radicals in aqueous solution. This large difference between the thermal energy and the photoenergy can be understood on the basis of the Franck–Condon principle of the constancy of internuclear distances during the photoexcitation process (a similar energetic discrepancy is obtained with photoexcited electron transfer (*vide infra*, 414). The mechanism suggested by Kornfeld consists of the following steps:

$$\begin{array}{lll} (1) & H_2O_2 + h\nu \rightarrow 2OH & \text{initiation} \\ (2) & OH + H_2O_2 \rightarrow HOH + HO_2 & \left.\begin{array}{l} \\ \\ \end{array}\right\} \text{propagation} \\ (3) & O_2^- + H_2O_2 \rightarrow O_2 + OH^- + OH & \\ (4) & OH + HO_2 \rightarrow HOH + O_2 & \text{termination} \end{array}$$

The pH dependence of the quantum yield favors the assumption that O_2^- reacts with hydrogen peroxide rather than with the undissociated radical.

This is also in agreement with other energetic considerations (see page 379). Kornfeld showed that stationary-state kinetics would lead to a quantum yield for the hydrogen peroxide decomposition being inversely proportional to the square root of the absorbed light intensity and varying linearly with the hydrogen peroxide concentration; this was borne out by the experimental results. Quantum yields up to 80 were measured. Lea (224) investigated in greater detail the question of the termination in this photolytic reaction.[5] The conclusion was drawn that there were two ranges of light intensity. Up to intensities of $\sim 10^{17}$ quanta $l.^{-1}$ $sec.^{-1}$ the results were similar to those obtained by Kornfeld. At intensities above 3×10^{17} quanta $l.^{-1}$ $sec.^{-1}$, the photolysis was no longer a chain reaction. The limiting quantum yield (the occurrence of which was first indicated by Heidt (186)) was 1.39 ± 0.11. As this is larger than unity, the reaction

$$OH + H_2O_2 \rightarrow HOH + HO_2$$

obviously occurs. The following termination reactions are considered:

$$(\alpha)\quad 2OH \rightarrow H_2O_2$$
$$(\beta)\quad 2OH \rightarrow H_2O + O$$
$$(\gamma)\quad 2HO_2 \rightarrow H_2O_2 + O_2$$
$$(\delta)\quad OH + HO_2 \rightarrow H_2O + O_2$$

It was suggested by Lea that reactions γ and δ were more likely to occur than reactions α and β. In disagreement with other workers, Lea observed no pH dependence of the quantum yield. For the sake of comparison it is interesting to note that Volman (306) recently observed a quantum yield of 1.7 for the photolysis of hydrogen peroxide in the gas phase. The termination step postulated by Volman is step δ given above. Dainton (84) has shown that OH radicals produced by the photodissociation of hydrogen peroxide initiate the polymerization of vinyl compounds. OH radicals thus produced could of course oxidize many organic substrates, but no extensive investigation of the system hydrogen peroxide–substrate–light has, as yet, been reported. By using H_2O^{18} Collinson and Dainton (74) were able to show that the reaction

$$OH + H_2O_2 \rightarrow HOH + HO_2$$

is much faster than the reaction

$$OH + HOH \rightarrow HOH + OH$$

(OH radicals were produced by photolysis of H_2O_2).

Uri found that hydrazine could, by direct photolysis, be split photochemically into NH_2 radicals, which initiated the polymerization of vinyl compounds (303).[6]

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[5] The results were reported by Dainton after the death of Lea.

[6] In alkaline solution hydrazine acts by itself as initiator of polymerization. This is either an anionic polymerization initiated by the $H_2N—NH^-$ ion present at a small concentration or it might be due to free-radical intermediates formed in the base-catalyzed decomposition of hydrazine in the presence of trace impurities (303).

In the presence of organic substrates one might expect amination reactions to occur when solutions of hydrazine are irradiated with light of wave length <260 mμ, the primary step being

$$H_2N—NH_2 \xrightarrow{h\nu} NH_2 + NH_2$$

The thermal bond-dissociation energy for this reaction was established by Szwarc (291, 292) as 60 ± 4 kcal. Detailed mechanisms of photochemical amination have not yet been put forward. It is, no doubt, an interesting field which is still undeveloped. The same applies to photochemical nitration with nitrogen tetroxide as the light-absorbing species.

Rutenberg and Taube (272) studied the primary quantum efficiency of the photochemical dissociation of chlorine ($Cl_2 \xrightarrow{h\nu} Cl + Cl$) in dilute aqueous solution. This is defined by the number of molecules of chlorine reacting with a substrate per quantum of light absorbed. Manganous and cerous ions were used as substrates, as they are oxidized by chlorine atoms by a simple electron-transfer mechanism and the oxidized states Mn^{+3} and Ce^{+4} are readily converted into complexes by pyrophosphate and sulfate ions, respectively. The maximum primary quantum efficiency was 0.17. This was independent of substrate concentration, chlorine concentration, and light intensity, and was slightly dependent on the ionic strength and temperature. Addition of excess chloride ion has a very marked effect on the quantum efficiency. In the presence of 4 M sodium chloride the primary quantum efficiency rises to 0.58, and it is shown that under these conditions Cl_3^- is the light-absorbing species. A similar but even more striking effect is obtained with analogous systems containing bromine and iodine on addition of bromide or iodide ions. These systems are being further investigated by Rutenberg and Taube. Chlorination studies were also carried out in nonaqueous solvents. Recently the photochlorination of methyl chloroformate in carbon tetrachloride solutions was studied by Batke, Dorfman, and Le Roy (24), the primary step being $Cl_2 + h\nu \rightarrow 2Cl$. Chlorine atoms lead to the chlorination of the substrate by a chain mechanism with overall quantum yields as large as 4×10^3. Numerous studies of chlorine-photosensitized reactions during the 1930's have been extensively reviewed in the monograph on photochemistry by Rollefson and Burton (269) and by Bowen (55). Similarly, the bromine molecule is dissociated photochemically into bromine atoms. Many addition reactions of photochemically produced bromine atoms to double and triple bonds are known to occur. A specific reaction of bromine atoms is the initiation of *cis–trans* isomerization in the system maleic acid–fumaric acid. This change was studied by Eggert (100, 101) and Wacholtz (307), but the theoretical interpretation is not yet completely understood. OH radicals or Cl atoms do not initiate *cis–trans* isomerization. They would appear to be too reactive and lead to the oxidation of the substrate. The effect of NH_2 radicals, which could be produced by irradiation of hydrazine or in the titanous ion–hydroxylamine system studied by Davies, Evans, and Higginson (89), has not yet been investigated, but there is no doubt that, owing to their lesser reactivity, they are more likely to produce *cis–trans* isomerization than the OH radical. A very old observation is the one made by Skraup that the *cis–trans* isomerization of maleic acid was initiated by the reaction $SO_2 + H_2S$ (281). This could be due either to a free-radical character attached to colloidal sulfur or to the SH radical formed as intermediate product.

Griffith, McKeown, and Winn (174) studied the chain reactions of photochemically produced bromine atoms with oxalic acid. The $C_2O_4^-$ radical ion, which Weiss also assumes in the reaction of oxalic acid with Fenton's reagent, was postulated as the active intermediate product. Durrant, Griffith, and McKeown (97) also investigated the photodissociation of I_2 and I_3^- in aqueous solution with nitrite ions as substrate. The maximum quantum efficiency observed for the primary step was 5×10^{-2}, i.e, much below unity, and was interpreted on the basis of the Franck–Rabinowitch hypothesis. Zimmerman and Noyes (347) recently investigated the primary quantum efficiency of the reaction of $I_2 \xrightarrow{h\nu} I + I$ in degassed hexane and reported values of 0.59 for 436 mμ and 0.37 for 578 mμ. The deviation from unity is due (*a*) to primary recombination (in accordance with the proposal of Franck and Rabinowitch) and (*b*) to secondary recombination. The results of Rabinowitch and Wood (266) relating to the stationary iodine-atom concentration are independently confirmed and utilized in this work. The rate constant for the secondary recombination of iodine atoms is evaluated as 1.1×10^{10} (mole/l.)$^{-1}$ sec.$^{-1}$ and corresponds to one-fifth of that observed in the gas phase.

B. PHOTOEXCITED ELECTRON-TRANSFER REACTIONS

1. *The solvent as electron acceptor*

Franck and Scheibe (152) were the first to describe the spectra of halide ions in aqueous solution as "electron affinity" spectra. The spectra of chloride, bromide, and iodide ions show maxima at ~180 mμ, ~200 mμ, and ~230 mμ, respectively, with molar extinction coefficients in the range 5,000–12,000. Franck and Scheibe (152) assumed that in the process of light absorption an electron is ejected from the halide ions and becomes a free solution electron. Franck and Haber (146) revised this scheme and postulated the primary process

$$X^-(H_2O) \xrightarrow{h\nu} H + X + OH^-$$

The mechanism was considered to apply also to the sulfite ion and the first attempt was made to interpret the process of light absorption in terms of bond-dissociation energies and electron affinities. It is to the merit of Farkas and Farkas (122) to have pointed out for the first time that the primary photochemical process consists of a mere electron transfer from the anion to one of the molecules in the hydration layer (hence the term "electron-transfer spectrum"). According to Farkas and Farkas the primary process of light absorption is

$$X^-(H_2O) \xrightarrow{h\nu} X(H_2O^-)$$

The energy change is given by the equation

$$h\nu = E_x^s - E_{H_2O}$$

where E_x^s is the electron affinity of the oriented water molecule, not the free water molecule. Farkas and Farkas have shown that from the light absorption of the halide ion a constant value of ~20 kcal. is obtained for E_{H_2O}. The same authors interpret in a similar way the light absorption of ferrous ion and sulfite ion in aqueous solution. Weiss (325) has extended it to the azide ion and Farkas and Klein (124) to halate ions.

Subsequent reactions following the primary electron transfer to the water molecule lead to the liberation of hydrogen from irradiated ferrous salt solutions, as observed by Potteril, Walker, and Weiss (259). Farkas and Farkas (123) have elegantly applied this photochemical reaction to the separation of hydrogen isotopes. As to the mechanism of hydrogen liberation the following points may be noted: As Farkas and Farkas point out, there seems to be no doubt that in the case of ferric ion, in addition to the primary dark back-reaction

$$Fe^{+3}(H_2O^-) \rightarrow Fe^{+2}(H_2O)$$

the exothermic dissociation reaction

$$Fe^{+3}H_2O^- \rightarrow (Fe^{+3}OH^-) + H$$

takes place. The energy levels of Farkas and Farkas have been rightly corrected by Rabinowitch (262). According to Farkas and Farkas, $Fe^{+3}H_2O^-$ relates to a nonequilibrium state with interatomic distances unchanged when compared with $Fe^{+2}(H_2O)$. The replacement of $XO_3(H_2O)^-$ by $XO_3 + H_2O^-$ (i.e., the use of the + symbol) in some equations by Farkas and Klein might therefore be confusing and it would be better to maintain the original formulation. In the case of $X(H_2O)^-$ Farkas and Farkas postulate a reaction of this excited molecule with hydrogen ion to account for the dependence of the quantum yield of hydrogen liberation. In the photoreduction of water by iodide ions it appears to the reviewer that it would be possible to assume dissociation of $I(H_2O)^-$ into $I + H + OH^-$, the reaction $HI + H \rightarrow I + H_2$ being the main path of hydrogen liberation, whilst competing with the secondary dark back-reaction $H + I \rightarrow H^+ + I^-$; the concentration of undissociated hydrogen iodide is dependent on both the iodide and the hydrogen-ion concentrations. Similar considerations may apply to the sulfite-ion reaction. In the case of ferrous ion too, the hydrogen-producing reaction may be

$$Fe^{+2}(H_2O) + H \rightarrow Fe^{+3}OH^- + H_2$$

If there is any dependence on hydrogen-ion concentration in this case, it could be attributed to the fact that the back-reaction

$$Fe^{+3}OH^- + H \rightarrow Fe^{+2} + HOH$$

is probably more effective than

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

the concentration of the ion-pair $Fe^{+3}OH^-$ being dependent on hydrogen-ion concentration. Warburg and Rump (310) have assumed that the reaction $HI + H \rightarrow H_2 + I$ occurs in hexane solutions.

It should be noted that Franck (141) considers that in the primary electron-transfer process the electron is spread out over the hydration layer as a whole rather than being attached to a specific water molecule.[6a]

An extensive study of the photochemical formation of hydrogen atoms in aqueous solution was recently carried out by Dainton and James (87). It was shown that hydrogen atoms formed by photoreduction of water, i.e.,

$$M^{+n}\cdot H_2O \xrightarrow{h\nu} M^{+(n+1)}\cdot OH^- + H$$

initiated the polymerization of vinyl compounds. It was demonstrated by infrared spectroscopic analysis that the polymer contains hydrogen atoms as end-groups. Termination occurs by combination of two growing polymer chains, and the rate of monomer disappearance is proportional to the monomer concentration and to the square root of the light intensity. At very large stationary concentrations of atoms, termination occurs by combination of atom and growing polymer chain. With chromous salt solutions (irradiated with wave length <380 mμ) the formation of hydrogen atoms is so fast that only water-soluble polymers of low chain length are produced. In very dilute solutions of chromous ion, however, insoluble long-chain polymers are formed and precipitated. Comparison is made by Dainton and James (87) of the light-absorption maxima of the spectra of V^{+2}, Cr^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, and Ni^{+2}, which are interpreted as electron-transfer spectra. It was shown that the shift in the absorption maximum towards shorter wave lengths varies linearly with the increasing ionization potential of M^{+2} in aqueous solution. Moreover, the slope of this plot is such that the difference in the absorption maxima translated into energy terms is almost quantitatively the same as the corresponding difference in the ionization potentials. An interesting aspect of this investigation is the effect of complex formation with monomers on the redox potential. In the case of vanadous ion acrylonitrile would displace the redox potential by 780 mv. and the electron-transfer spectrum shifts by 60 mμ towards shorter wave lengths. The ions which were studied by Dainton and James (87) include also Ti^{+3}, V^{+3}, Mo^{+3}, U^{+3}, U^{+4}, Eu^{+2}, Sn^{+2}, I^-, N_3^-, SH^-, SO_3^{-2}, and $HCOO^-$. Similar systems with chromous ion were studied by Dain and Libezon (81) and with europous ion by Douglas and Yost (94). The latter followed the course of the reaction by measuring the change in the magnetic susceptibility.

2. Photoexcited electron transfer in ion-pairs

Rabinowitch (262) has interpreted the absorption spectra of ion-pair complexes in general and of ferric ion in particular as electron-transfer spectra, the light-absorption process being $Fe^{+3}X^- \xrightarrow{h\nu} Fe^{+2}X$. A comparison of the energies

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[6a] *Note added in proof:* This theory was developed by R. Platzmann and J. Franck as a result of a detailed study of the absorption spectra of the halide ions in aqueous solution and their photochemistry (to be published in the L. Farkas Memorial Volume).

of the light-absorption maxima of ion-pairs of the formula $Fe^{+3}X^-$, where $X^- = F^-, Cl^-, OH^-, O_2H^-, Br^-$ with the electron affinity in solution of X^- shows that the maximum is shifted almost quantitatively to higher wave lengths with decreasing electron affinities. This is expected, as the energy change in the light-absorption process is given by

$$h\nu = -\Delta H_{\text{ass.}} + E^s_{\text{X}} - \text{I}_{\text{Fe}^{+2}} + Q$$

where $\Delta H_{\text{ass.}}$ is the heat-content change in the formation of the ion-pair $Fe^{+3}X^-$ from hydrated Fe^{+3} and X^- ions, E^s_{X} is the electron affinity of X in aqueous solution, $I_{\text{Fe}^{+2}}$ is the ionization potential of ferrous ion in aqueous solution, and Q is the repulsion energy in $Fe^{+2} \cdots X$ with an interatomic distance identical with that in the ion-pair $Fe^{+3}X^-$ and the hydration shell in the corresponding nonequilibrium state (the origin of Q is readily understood on the basis of the Franck–Condon principle). It is interesting that Q does not vary appreciably from anion to anion and is of the order of 45 kcal. The result is that the photo-excited electron transfer in ion-pairs requires an energy which is by 40–50 kcal. larger than the endothermicity of the reaction $Fe^{+3} + X^- \rightarrow Fe^{+2} + X$. Rabinowitch has remarked that chemical changes in these systems have not been studied closely enough. Until recently no experimental evidence has been forthcoming for the occurrence of free radicals. Lately Evans and Uri (113, 114, 116) have obtained such evidence; they have shown that atoms or radicals produced photochemically from ion-pair complexes can lead to (*a*) polymerization of vinyl compounds, (*b*) the oxidation of organic substrates, and (*c*) the photo-oxidation of water.

(a) Polymerization of vinyl compounds

This investigation was carried out by Evans and Uri (113, 114) and by Evans, Santappa, and Uri (111). Conclusive evidence was obtained that the ion-pair complex is the photochemically active species. Uri (299) has pointed out that the ion-pair formation cannot be disregarded in the electron-transfer mechanisms. In this work the following ion-pairs were found to be active photosensitizers: $Fe^{+3}OH^-$, $Fe^{+3}Cl^-$, $Fe^{+3}F^-$, $Fe^{+3}N_3^-$, $Fe^{+3}C_2O_4^{-2}$, $Fe^{+3}HCitr^{-2}$, $Pb^{+2}Cl^-$, $Ce^{+4}OH^-$. In the case of $Fe^{+3}Cl^-$ and $Fe^{+3}F^-$ the polymers were found to contain Cl and F end-groups, respectively. The reaction kinetics were studied by measuring (*1*) the rate of ferrous-ion formation (colorimetrically with *o*-phenanthroline), (*2*) the rate of monomer disappearance (by bromine addition to the excess of unsaturated monomer and by the weight of the dried polymer), and (*3*) the chain length of the polymer (viscometrically). The influence of the following factors was investigated: light intensity, light-absorption fraction due to the ion-pair, concentration of vinyl monomer, and the effect of initially added ferrous ion. On the basis of the experimental results and the kinetic analysis the following mechanism was put forward:

(1) Excitation:

$$Fe^{+3}X^- \xrightarrow[k_eI]{h\nu} Fe^{+2}X$$

(2) Primary dark back-reaction:

$$\mathrm{Fe^{+2}X} \xrightarrow{k_d} \mathrm{Fe^{+3}X^-}$$

(3) Dissociation of excited complex:

$$\mathrm{Fe^{+2}X} \xrightarrow{k_s} \mathrm{Fe^{+2}} + \mathrm{X}$$

(4) Secondary dark back-reaction:

$$\mathrm{Fe^{+2}} + \mathrm{X} \xrightarrow{k_0} \mathrm{Fe^{+3}} + \mathrm{X^-}$$

(5) Initiation of polymerization:

$$\mathrm{X} + \mathrm{CH_2{=}CHR} \xrightarrow{k_i} \mathrm{XCH_2{-}CHR{-}}$$

(6) Propagation of polymerization:

$$\mathrm{X(CH_2CHR)_n{-}} + \mathrm{CH_2{=}CHR} \xrightarrow{k_p} \mathrm{X(CH_2CHR)_{(n+1)}{-}}$$

(7) Termination:

$$\mathrm{X(CH_2CHR)_n{-}} + \mathrm{{-}(CHRCH_2)_mX} \xrightarrow{k_t} \mathrm{X(CH_2CHR)_{n+m}X}$$

Assuming stationary-state conditions for $\mathrm{Fe^{+2}X}$, X, and $\mathrm{X(CH_2CHR)_n{-}}$, the following equations can be derived which are in close agreement with experimental results:

$$[\mathrm{Fe^{+2}X}] = \frac{k_\epsilon I}{k_d + k_s}$$

$$[\mathrm{X}] = \frac{k_s k_\epsilon I}{(k_d + k_s)(k_0[\mathrm{Fe^{+2}}] + k_i[\mathrm{M}])}$$

$$\gamma = \frac{\mathrm{d}[\mathrm{Fe^{+2}}]}{\mathrm{d}t} \Big/ k_\epsilon I = \frac{k_s}{k_d + k_s} \frac{k_i[\mathrm{M}]}{k_0[\mathrm{Fe^{+2}}] + k_i[\mathrm{M}]}$$

A straight line was obtained when $1/\gamma$ was plotted against $[\mathrm{Fe^{+2}}]$. From the slope, (k_0/k_i) was evaluated as being of the order of 10^3–10^4. From the intercept, $k_s/(k_d + k_s)$ was estimated as $\sim 5 \times 10^{-2}$ for $\mathrm{Fe^{+3}OH^-}$, ~ 0.13 for $\mathrm{Fe^{+3}Cl^-}$, and ~ 0.5 for $\mathrm{Fe^{+3}N_3^-}$. On the assumption of initiation of polymerization by the primary product $\mathrm{Fe^{+2}X}$ it would have been impossible to derive quantum yields for $\mathrm{d}[\mathrm{Fe^{+2}}]/\mathrm{d}t$ smaller than unity and yet independent of monomer concentration. Furthermore,

$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = \frac{k_p}{\sqrt{k_t}} \sqrt{\frac{k_s k_\epsilon I}{k_d + k_s}}\,[\mathrm{M}]$$

and the chain length of the polymer is given by the expression:

$$N = \frac{2k_p}{\sqrt{k_t}} \frac{[\mathrm{M}]}{\sqrt{\dfrac{k_s k_\epsilon I}{k_d + k_s}}}$$

It was shown that these equations are obeyed. The quantum yields for monomer disappearance are 50–100 under the experimental conditions of this investigation. Molecular weights up to 300,000 were obtained.

(b) Oxidation of organic substrates

OH radicals produced by photoexcited electron transfer in $Fe^{+3}OH^-$ would be expected to oxidize organic substrates in a similar way as Fenton's reagent. The possibility of an accurate control of the free-radical production by variation of the light intensity eliminates the difficulties experienced with Fenton's reagent due to fast reactions even before mixing is complete. Ferric ion is always present in excess, so that free radicals produced by the primary OH radical attack frequently react with ferric ion rather than with another OH radical. Ferrous ion is accumulated only slowly and back-reactions of ferrous ion and radical produced in the primary step will be less significant. The classification of substrates into "promoters" and "suppressors" put forward by Kolthoff and Medalia (211, 212) does, therefore, not apply and chloride ions have not the "suppression effect" which they have in oxidations by Fenton's reagent. The interest which has been attached recently to the problem of the free-radical attack on the benzene nucleus has led to an investigation of the effect of light on the system $Fe^{+3}OH^-$–benzoic acid–light. In a preliminary note (23) a mechanism was postulated which is in principle similar to that adopted for the initiation of polymerization reactions: *viz.*,

$$(1)\quad Fe^{+3}OH^- \xrightarrow[h\nu]{k_\epsilon I} Fe^{+2}OH$$

$$(2)\quad Fe^{+2}OH \xrightarrow{k_d} Fe^{+3}OH^-$$

$$(3)\quad Fe^{+2}OH \xrightarrow{k_s} Fe^{+2} + OH$$

$$(4)\quad OH + C_6H_5COOH \xrightarrow{k_i} \cdot C_6H_4COOH + HOH$$

$$(5)\quad OH + \cdot C_6H_4COOH \xrightarrow{k_t} HOC_6H_4COOH$$

$$(6)\quad Fe^{+2} + OH \xrightarrow{k_0} Fe^{+3} + OH^-$$

$k_s/(k_d + k_s)$ was evaluated as $\sim 5 \times 10^{-2}$ and k_0/k_i was found to be of the order of unity. From evidence obtained by Bates and Uri (23a) recently it appears that reaction 5 of this scheme has to be replaced by the equation:

$$\cdot C_6H_4COOH + Fe^{+3}OH^- \rightarrow HOC_6H_4COOH + Fe^{+2}$$

This indicates that the termination step is certainly different from that in the work by Stein and Weiss (referred to in Section XVII) on ionizing radiations. This is the most likely reason that in the work of Bates, Evans, and Uri (23) the statistical ratio (2:2:1) of *o*-, *m*-, and *p*-hydroxybenzoic acids was obtained, while in the experiments with ionizing radiations the *p*-isomer predominates. In addition, it was shown that chlorine and fluorine atoms attack the benzene nucleus. As these experiments were carried out in acid solutions, the concentration of hydroxide ion is too small to compete with the substrate for chlorine and fluorine atoms to cause radical–ion transfer and ultimately an OH radical attack on the benzene nucleus. On the other hand, the reaction

$$Cl + H_2O \rightarrow Cl^- + OH + H^+$$

is considerably endothermic, while it appears that the reaction

$$F + H_2O \rightarrow F^- + OH + H^+$$

requires an activation energy of the order of 5–10 kcal. The attack of OH radicals on a disubstituted benzene ring, e.g., toluic acid, was also examined It appears that with *m*-toluic acid as substrate the rate of the OH radical attack on the benzene nucleus is practically unaffected (when compared with benzoic acid). With *p*-toluic acid it drops by 80 per cent, while with *o*-toluic acid no substitution in the nucleus could be measured. In these cases the methyl side chain is attacked and it would appear that the carboxyl group, particularly in the *o*-position, has a very marked effect on the $C\cdots H$ bond-dissociation energy in the side chain. It is noteworthy that with benzyl alcohol (as substrate), which contains a hydroxyl group in the side chain, it is only the latter which is attacked by OH radicals, leading to $C_6H_5\dot{C}HOH$ radicals which react with $Fe^{+3}OH^-$ ion to give benzaldehyde. It is obvious that this field of research is still largely undeveloped. Further work on these oxidation mechanisms is in progress.

Collinson, Dainton, and Holmes (75) have shown that OH radicals produced from $Fe^{+3}OH^-$ ion-pairs can lead to the destruction of enzymes (inactivation of ribonuclease).

(c) The photoöxidation of water

The importance of this reaction in the process of photosynthesis has been discussed by Rabinowitch (263).

The photoöxidation of water by ceric ions was studied by Weiss and Porret (335), who assumed the formation of an excited Ce^{+4*} ion. The latter would react with water to give $Ce^{+3} + H^+ + OH$; the OH radicals would disproportionate into $HOH + O$. Heidt and Smith (187) carefully reinvestigated this photochemical reaction in great detail and attributed the photochemical activity to ceric dimers. In this reviewer's experience spectrophotometric measurements show no evidence for dimerization, a fact also noted by Heidt and Smith (for 254 mμ). Evans and Uri (115, 116) suggested that their results and also the results obtained by Mr. J. Simons in this laboratory are best interpreted on the basis of the following mechanism:

$$(1)\quad Ce^{+4}OH^- \xrightarrow[h\nu]{k_\varepsilon I} Ce^{+3}OH$$

$$(2)\quad Ce^{+3}OH \xrightarrow{k_d} Ce^{+4}OH^-$$

$$(3)\quad Ce^{+3}OH \xrightarrow{k_s} Ce^{+3} + OH$$

$$(4)\quad Ce^{+3} + OH \xrightarrow{k_0} Ce^{+4} + OH^-$$

$$(5)\quad Ce^{+4}OH + OH \xrightarrow{k} Ce^{+3} + H_2O_2$$

$$(6)\quad 2Ce^{+4}OH^- + H_2O_2 \xrightarrow{\text{not rate-determining}} 2HOH + 2Ce^{+3} + O_2\uparrow$$

This mechanism is similar to that for initiation of polymerization or oxidation, with $Ce^{+4}OH^-$ playing the role of a substrate (in reaction 5). As in the Haber–Weiss back-reaction (page 392) OH radicals act as a reducing species. This reducing effect of OH radicals was first suggested by Haissinsky and Lefort (182) in the radiation chemistry of ceric salt solutions, although these authors do not postulate the formation of the ion-pair complex. Stationary-state kinetics applied to the above scheme lead to the equation:

$$\gamma_{\text{net}} = \frac{\mathrm{d}Ce^{+3}}{\mathrm{d}t} \Big/ k_\epsilon I = \frac{4k_s}{k_d + k_s} \frac{k_1[Ce^{+4}OH]}{k_0[Ce^{3+}] + k_1[Ce^{+4}OH^-]}$$

The similarity of this equation and the one derived with monomers as substrate (page 415) is easily recognized. The results obtained by Heidt and Smith (187) were utilized by Evans and Uri (115) for a plot of $1/\gamma$ against $[Ce^{+3}]/[Ce^{+4}OH^-]$. A straight line was obtained and k_0/k_1 evaluated from the slope as 10 and $k_s/(k_d + k_s) = 5 \times 10^{-2}$ (of the same order as for $Fe^{+3}OH^-$). The maximum quantum yield is $4k_s/(k_d + k_s) = 0.2$. When, however, impurities in the distilled water compete with $Ce^{+4}OH^-$ (at low ceric-ion concentrations) the maximum yield found is, in accordance with expectation, $k_s/(k_d + k_s) = 5 \times 10^{-2}$. The exothermicities of reactions 4 and 5 in the above scheme are ~25 kcal. and ~20 kcal., respectively. The entropies of activation should be similar for both reactions; the value of 10 for the ratio of the rate constants is therefore not unexpected. Reaction 6 of the above scheme would be expected to proceed as follows:

(a) $Ce^{+4}OH^- + HO_2^- \rightarrow Ce^{+3}OH^- + HO_2$

(b) $HO_2 \rightarrow H^+ + O_2^-$

(c) $Ce^{+4}OH^- + O_2^- \rightarrow Ce^{+3}OH^- + O_2 \uparrow$

When we consider the photoöxidation of water by ferric ion, the two competing reactions would be:

$$Fe^{+2} + OH \xrightarrow{k_0} Fe^{+3} + OH^-$$

$$Fe^{+3}OH^- + OH \xrightarrow{k_1} Fe^{+2} + H_2O_2$$

In view of the considerably lower ionization potential of ferrous ion in aqueous solution the ratio k_0/k_1 will be much larger than in the ceric–cerous system. Furthermore, hydrogen peroxide formed will partially reoxidize the ferrous ion. Therefore, extremely high light intensities and also large $Fe^{+3}OH^-$ concentrations would be required to obtain measurable oxygen yields. The hydrated ferric ion $Fe^{+3}(H_2O)_6$ will be inactive with wave lengths > 300 mμ. On the other hand, if sufficient energy is supplied for the primary process

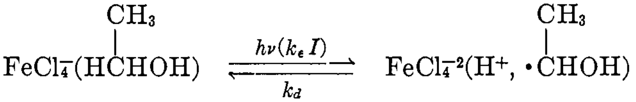
$$Fe^{+3}H_2O \xrightarrow{h\nu} Fe^{+2}H_2O^+$$

the hydrated ferric ion may be active in the photoöxidation of water; this was recently reported by Dain and Kachan (79), who worked with absorbed light intensities of the order of 5 × 10^{-2} $Nh\nu$/hr. liter. These results have not yet been confirmed by other workers in the same field. In view of their importance, repetition of the work under identical conditions would be desirable. The effect of impurities in the distilled water was not considered by Dain and Kachan.

3. Complex ions as electron acceptors

The oxidation–reduction potential can be shifted to a considerable extent by combining the corresponding metal ions in complexes. This has been illustrated in a study of the photochemical activity of $FeCl_4^-$ in alcohol by Brealey and Uri (65) (preliminary results were reported by Brealey, Evans, and Uri (64)). The suggested mechanism for the photoreduction of $FeCl_4^-$ is:

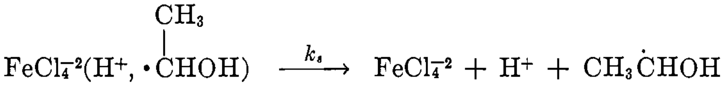
(1) Photoexcitation and primary dark back-reaction:



$$\mathrm{FeCl_4^-(H\overset{CH_3}{\overset{|}{C}}HOH)} \underset{k_d}{\overset{h\nu(k_\epsilon I)}{\rightleftharpoons}} \mathrm{FeCl_4^{-2}(H^+, \cdot\overset{CH_3}{\overset{|}{C}}HOH)}$$

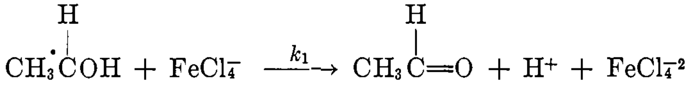
(primary product A)

(2) Dissociation of the primary product:



$$\mathrm{FeCl_4^{-2}(H^+, \cdot\overset{CH_3}{\overset{|}{C}}HOH)} \xrightarrow{k_s} \mathrm{FeCl_4^{-2} + H^+ + CH_3\dot{C}HOH}$$

(3) Reduction of $FeCl_4^-$ by the free radical:



$$\mathrm{CH_3\overset{H}{\overset{|}{\dot{C}}}OH + FeCl_4^-} \xrightarrow{k_1} \mathrm{CH_3\overset{H}{\overset{|}{C}}{=}O + H^+ + FeCl_4^{-2}}$$

(4) Combination of free radicals:

$$\mathrm{2CH_3\dot{C}HOH} \xrightarrow{k_2} \text{products}$$

The experimental results could be interpreted on the basis of the above scheme. At 365 mμ the maximum quantum yield, $2k_s/(k_d + k_s)$, was found to be 0.310 (obtained under those conditions in which reaction 4 is negligible). The full kinetic expression taking into account both reactions 3 and 4 can be written as

$$\gamma - \frac{\gamma_{\text{max.}}}{2} = \frac{k_1 C}{\sqrt{k_2}} \sqrt{\frac{(\gamma_{\text{max.}} - \gamma)V}{k_\epsilon I}}$$

where $C = [FeCl_4^-]$, V = volume of solution, γ = net quantum yield = $\frac{d[FeCl_4^-]}{dt} \cdot \frac{V}{k_\epsilon I}$. From this function $k_1/\sqrt{k_2}$ was evaluated as 2.7 $(\text{mole/l.})^{-1/2}$ $\text{sec.}^{-1/2}$ The undissociated molecule $FeCl_3$ is also photochemically active, but the correct interpretation of the reaction is more difficult to establish in this case. Copestake and Uri (77) have shown that this photochemical activity is not limited to iron complexes. $PbCl_4^{-2}$ shows similar photochemical activity in ethyl alcohol and the same applies to cupric ion complexes such as $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{-2}$.

No photochemical activity of cupric ion complexes in water has yet been reported.

4. Photocatalysis in photoexcited electron-transfer processes

This phenomenon was studied by Brealey and Uri (65) in the system $FeCl_4^-$–thionine–alcohol–light. It was shown that $FeCl_4^{-2}$ is produced in the same reaction in the absence of thionine. In aqueous solution thionine would not react with ferrous ion; in fact, it is oxidized by ferric ion. Complex formation in ethyl alcohol decreases the redox potential of $FeCl_4^{-2}/FeCl_4^-$ to such an extent that $FeCl_4^{-2}$ reduces thionine instantaneously. The shift when compared with the redox potential Fe^{+2}/Fe^{+3} in water corresponds to 0.5 v. As a result the experimental conditions can be so chosen that $FeCl_4^-$ is practically the only light-absorbing species and is maintained at a constant concentration, while the net reaction is the oxidation of alcohol (to acetaldehyde) by the thionine dye. This is a rare case of true photocatalysis as distinct from such photosensitization, in which the sensitizer undergoes a lasting chemical change. Photocatalysis may prove to be of practical importance in various oxidation–reduction processes for which the thermal reaction requires a large activation energy. (The significance of a photocatalytic process of this kind in attempts to produce artificial photosynthesis is discussed on page 426.)

C. PHOTOEXCITED DYES AND THE URANYL ION

It is recognized that the high-intensity absorption bands of dyes correspond to singlet–singlet transitions. Other transitions which lead to long-lived excited states are "forbidden" and therefore weak. The singlet–singlet transitions are accompanied by rapid reversion to the ground state. The absorbed energy can be emitted as heat or fluorescence. On the other hand, it has been assumed that excited dyes can react with other species in solution (such as O_2, O_2^- ions, and OH radicals). These reactions lead by electron transfer to D^+ (with an oxidizing ion or radical) or to D^- (with a reducing ion or radical). These processes are frequently accompanied by the quenching of fluorescence. This case is best illustrated by the system thionine–ferrous ion–light studied by Weiss (319) and Rabinowitch (260). Quenching of the fluorescence of the photoexcited thionine is accompanied by the bleaching of the dye and the oxidation of ferrous ion. In the dark, however, the reaction is reversed. The oxidation–reduction potential of the system is thus different in light and in the dark; the appearance of an electric potential between an electrode in the irradiated part of the solution and the nonirradiated part has been termed the "photogalvanic" effect by Rabinowitch (261).

That a photoexcited dye can be also reduced by a bond-breaking rather than an electron-transfer reaction has been demonstrated conclusively by Bamford and Dewar (16, 17, 18) with tetralin or liquid monomers as substrate, where ionic dissociation is out of the question. While in the early stages of the investigation of the dye-photosensitized oxidation–reduction reactions research was principally concerned with basic fluorescent dyes, Bamford and Dewar have used vat dyes and Blaisdell (44) has studied the photochemistry of azo dyes. Blaisdell considers that in the presence of oxygen the HO_2 radical is formed by hydrogen abstraction from the excited dye. It is noteworthy that Bamford and Dewar (16, 17, 18) assumed in the vat dye–tetralin system quenching of the photoexcited dye by oxygen without electron transfer or hydrogen abstraction. While the theory of the electron-transfer quenching of fluorescence was mainly developed by Weiss (320, 322) on the basis of the fundamental ideas of Franck and his school (145, 148, 158), the importance of the triplet state in dye-photosensitized reactions was recognized by Lewis and his coworkers (*cf.* review by Kasha (202)). It is assumed that a radiationless transition occurs from the excited singlet state to a triplet state (chemically a diradical) and that it is the latter which phosphoresces and has a lifetime sufficiently long to give rise to subsequent reactions. While fluorescence corresponds to a transition singlet excited state → ground state, phosphorescence is postulated to involve the transition triplet excited state → ground state. This view has now become more generally accepted. Franck and Livingston (149) have been the forerunners of this general theory by assuming a long-lived, energy-rich, and thus reactive, tautomer of the excited dye. Bowen (57) has recently summarized the photochemistry of dyes in aqueous solution and suggested the classification of twenty-four reactions in dye-photosensitized systems which is based on the scheme put forward by Franck and Livingston in 1941 but is more complete and comprehensive.

(1)	Excitation by absorption of light	$D + h\nu \rightarrow D^*$
(2)	Deactivation of fluorescence	$D^* \rightarrow D + h\nu_1$
(3)	Deactivation to heat energy	$D^* \rightarrow D$
(4)	Formation of triplet level	$D^* \rightarrow D'$
(5)	Reduction of dye	$D^* + A \rightarrow D^- + A^+$
(6)	Oxidation with molecular oxygen	$D^* + O_2 \rightarrow D^+ + O_2^-$
(7)	Oxidation of dye	$D^* + B \rightarrow D^+ + B^-$
(8)	Triplet–singlet change dependent on small energy difference	$D' \rightarrow D^*$
(9)	Long-duration fluorescence	$D' \rightarrow D + h\nu_2$
(10)	Dismutation reaction	$D' + D \rightarrow D^- + D^+$
(11)	Reduction of dye	$D' + A \rightarrow D^- + A^+$
(12)	Oxidation of dye	$D' + O_2(B) \rightarrow D^+ + O_2^-(B)$
(13)	Semiquinone ionization	$D^- + H^+ \rightleftharpoons DH$
(14)	Re-formation of dye with reduction of B	$D^- + B \rightarrow D + B^-$
(15)	Semiquinone dismutation	$2DH \rightleftharpoons D + DH_2$
(16)	Re-formation of dye	$DH + D^+ \rightarrow 2D + H^+$
(17)	Re-formation of dye plus oxidizing agent	$D^+ + B^-(O_2^-) \rightarrow D + B(O_2)$
(18)	Re-formation of dye plus reducing agent	$DH + A^+ \rightarrow D + H^+ + A$
(19)	Re-formation of dye with oxidation of A	$D^+ + A \rightarrow D + A^+$

(20) Oxidative destruction of dye	$D^+ + O_2 \rightarrow$ oxidation products
(21) Formation of hydrogen peroxide	$DH + O_2 \rightarrow D + HO_2$ $(\rightarrow H_2O_2)$
(22) Removal of hydrogen peroxide	$A + H_2O_2 \rightarrow$ oxidation products
(23) Formation of stable oxidation products	$A^+ + O_2 \rightarrow$ oxidation products
(24) Formation of stable oxidation products	$B^- + O_2 \rightarrow$ oxidation products

It is seen that the understanding of the dye-sensitized photochemical reactions owes a great deal to the Haber–Weiss mechanism, as it involves the same reactive intermediate species, i.e., the OH and HO_2 radicals and the O_2^- radical-ion and also the principle of univalent chemical change. Rowell and La Mer (271) have obtained experimental support for Weiss's theory that the quenching of fluorescence can be interpreted as an electron-transfer process. On the other hand, Kasha (203) developed recently a theory which attributes the process of the quenching of fluorescence to spin orbital perturbation, not excluding, however, subsequent electron-transfer reactions. A highly interesting observation has been made by Livingston, Watson, and McArdle (233) to the effect that chlorophyll does not fluoresce in pure dry hydrocarbons but that normal fluorescence is restored by the addition of traces of water or other polar substances. This is interpreted by the authors as evidence that the fluorescence entity is an addition compound composed of one molecule of chlorophyll and one molecule of the polar substance. As Franck (143, 144) and Livingston (230) point out, fluorescence and photochemical activity are not complementary phenomena. Evidence against the assumption that there is any parallelism between the efficiency of dyes as photosensitizers and their fluorescence yields has also been obtained by Hurd and Livingston (198) in a study of dye-photosensitized oxidation of the iodide ion and even before that by Gaffron (160, 162) in a study of chlorophyll-photosensitized oxidations, such as the oxidation of allylthiourea in acetone. Livingston (229) compared the photochemical activity of uranyl oxalate and samarium oxalate. While both complexes are fluorescent, there was no detectable decomposition of samarium oxalate, while with uranyl oxalate under similar experimental conditions, 60 per cent of the oxalate was decomposed in 20 min. On the other hand, the quenching of fluorescence may, but need not, be accompanied by a chemical change. An example of the former is the system thionine–ferrous ion (260, 319). An example of the latter from the reviewer's own experience is the absence of a polymerization reaction in the system fluorescein (or eosin or quinine bisulfate)–potassium chloride (or bromide)–vinyl monomer in aqueous solution, even under those conditions in which fluorescence is quantitatively quenched. On the assumption that the quenching is an electron-transfer process chlorine (or bromine) atoms would be expected to be formed and to initiate a polymerization reaction. However, lack of polymerization does not conclusively mean that the electron-transfer mechanism is out of the question. It could be interpreted as indicating a very fast back-reaction: $D^- + Cl \rightarrow D + Cl^-$. Possibly a complex of the excited dye and the quenching anion is formed and both the quenching and the reverse electron-transfer process occur within the complex molecule. Similar views were recently expressed by Bowen (58) and by Boaz and Rollefson (46). The latter assume the presence of a quencher molecule in the same solvent cage as the fluorescer molecule.

Rollefson and Stroughton (270) have proposed the classification of fluorescent substances into two classes: Class I: Fluorescence is quenched by reducing agents. This group includes acridone, α- and β-anthracenesulfonic acids, quinine sulfate, fluorescein, eosin, and rhodamine dyes. Class II: Fluorescence is quenched by oxidizing agents. This group includes anthranilic acid, sodium sulfanilate, sodium naphthionate, α-naphthol, and 1-naphthol-4-sulfonic acid. In Class I the quenching efficiency of the reducing ions is roughly of the order $I^- > CNS^- > Br^- > Cl^- > C_2O_4^{-2} > CH_3COO^- > SO_4^{-2} > NO_3^- > F^-$. It is remarkable that this order agrees fairly well with the corresponding electron affinities in solution of the radicals or atoms formed. This is also in good agreement with the recent observations of Rowell and La Mer (271) as to the efficiency of organic bases as quenchers. On the other hand, in Class II there is apparently no such simple correlation in the order of the quenching efficiency, which is $IO_3^- > BrO_3^- > NO_3^- > S_4O_6^{-2}$.

An interesting and important aspect is the formation of hydrogen peroxide as intermediate product. Blum and Spealman (45) observed that hydrogen peroxide was an intermediate product in the aerobic photobleaching of eosin in the absence of an oxidizing substrate. In the absence of air no hydrogen peroxide was formed and no eosin was bleached. It would appear likely that hydrogen peroxide is formed by the interaction of the photoexcited metastable triplet state with oxygen, leading by electron transfer to the O_2^- radical-ion and the sequence:

$$O_2^- \xrightarrow{+H^+} HO_2 \xrightarrow{+e} HO_2^- \xrightarrow{+H^+} H_2O_2$$

It should be pointed out that Egerton (99) considers that the energy of the excited dye can be transferred to oxygen and leads to the formation of an activated oxygen molecule which in turn is responsible for the formation of hydrogen peroxide. On the other hand, Weiss (328) considers such activation of oxygen not accompanied by electron transfer as very unlikely. The idea of the formation of active oxygen molecules was first put forward by Kautsky *et al* (206) but discounted by Franck and Levi (148) in a study of the chlorophyll-photosensitized reactions, and independently by Gaffron (162, 163) in his work on the photoöxidation of rubrene and on bacteriochlorophyll, which acts as photosensitizer even in the near infrared. Another problem is the inhibition of hydrogen peroxide formation at high pressures of oxygen, as observed by Blum and Spealman (45). The effect was marked even when the oxygen pressure was increased from 0.2 atm., as in air, to no more than 1 atm. Possibly this phenomenon, for which the authors suggest no hypothesis, is to be correlated with the recent findings on oxygen quenching made in vat dye systems by Bamford and Dewar (17, 18).

Formation of hydrogen peroxide in irradiated eosin solutions certainly does not occur *via* the process

$$\text{(a)}\quad D^* \text{ (singlet or triplet)} + OH^- \rightarrow D^- + OH$$

$$\text{(b)}\quad OH + OH \rightarrow H_2O_2$$

for the following reason: It has been shown that OH radicals would oxidize benzoic acid to hydroxybenzoic acids (23), a reaction which can be conveniently used to detect the presence of OH radicals as intermediate products. No such effect was, however, observed by Mr. G. J. Brealey in this department. On the other hand, there is experimental evidence for an electron-transfer mechanism which does not involve the prior formation of O_2^- in the system eosin–iodide ion–light, which was investigated by Livingston and Hurd (232). In this case, too, it is likely that the reactive species of the dye is a triplet excited state, formed by a radiationless transition from a singlet excited state. This species was recognized and referred to by Livingston and Hurd (232) as the reactive tautomer of the excited dye (*cf.* Franck and Livingston (149)).

In their work on oxidation photosensitized by vat dyes Bamford and Dewar (17) arrive at the interesting results that the normal frequency factor for free-radical reactions in solution is 10^7. The reviewer considers that this important conclusion holds largely in reactions of large radicals in nonaqueous solvents, but from the considerable experience gathered in the work on the reactions of hydrogen peroxide and its radicals this does not seem to apply to such radicals as OH, HO_2, Cl, NH_2, etc. in aqueous solution, where the normal frequency factor is nearer 10^{12}.

Although it has been shown that the uranyl ion forms ion-pair complexes in solution (43, 171, 289), it appears that the photochemical mechanism of uranyl-sensitized reactions is nearer to that of dye-sensitized reactions than that of photoexcitation in ion-pairs. The latter do not fluoresce, while the uranyl ion and some of its complexes exhibit fluorescence, which is quenched by reducing anions in solution (such as Br^- and I^-) (*cf.* 320). The UO_2^{+2}-photosensitized oxidation of oxalic acid is widely applied in chemical actinometry,—a method which was introduced by Leighton and Forbes (225) and thoroughly developed since then (61, 133, 134, 135). On the other hand, the mechanism of this reaction is not yet fully clarified. Rollefson (268) assumed that both the uranyl hydrogen oxalate complex, present initially, and a uranyl formate complex formed during the reaction were the active species. Carter and Weiss (71) show that from an energetic point of view a direct transfer of the absorbed energy from the uranyl ion to oxalic acid is not feasible if the photochemical activity in the blue region of the visible spectrum is taken into account, and suggest a "true" photocatalytic reaction by an electron-transfer mechanism involving the UO_2^+ ion and COOH radical as intermediates. It appears to the reviewer that the published experimental work is not yet sufficient to allow a full insight into the mechanism. The

UO_2^+ ion has also been postulated as an intermediate product in the polarographic reduction of uranyl ions by Harris and Kolthoff (183) and by Heal (185). Recently Whyte and Melville (340) and independently this reviewer (301) observed that uranyl ions photosensitized the polymerization of vinyl compounds in aqueous solution. Whyte and Melville used methacrylic acid as monomer and showed that hydroquinone and resorcinol inhibit the polymerization; this indicates that the polymerization reactions involve free radicals. Whyte and Melville make no suggestion as to the mechanism of the primary step leading to the formation of free radicals. The reviewer observed that the fluorescence of the uranyl ion in aqueous solution was quenched quantitatively on addition of vinyl monomers such as acrylonitrile or methyl methacrylate. Quenching occurred even in strongly acid solution (e.g., in normal perchloric acid) and in the absence of such anions as could be oxidized by an electron-transfer mechanism. This suggests that it is a reaction of the excited uranyl ion (possibly involving a long-lived metastable state) with the monomer which leads to the initiation of polymerization. A quantitative correlation (if any such exists) of the polymerization kinetics and the quenching of fluorescence has not yet been attempted. Such information would allow a better judgment of the photochemistry of the uranyl ion as a whole.

The general aspects of dye-photosensitized reactions were recently discussed by Bowen (57), Weiss (327), and Livingston (231) at a symposium on photochemistry in relation to textiles. Attention is also drawn to two recent articles by Bowen (56, 59).

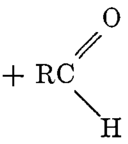
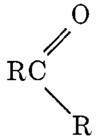
XV. THE SIGNIFICANCE OF FREE-RADICAL REACTIONS IN THE PROCESS OF PHOTOSYNTHESIS

The significance of free-radical reactions in photosynthesis has been admirably treated in Rabinowitch's monograph (263). The chapters of the book dealing with the photoöxidation of water, the primary photochemical processes, the photochemistry of pigments, etc., clearly mark the significance of free-radical intermediates. Rabinowitch's monograph has been complemented by recent reviews (*a*) by Franck (144), surveying the physical background, and (*b*) by Gaffron and Fager (165), dealing with the chemistry of the intermediate products in photosynthesis. The reviewer hopes that the critical compilation in this survey of data relating to inorganic free radicals will be an aid to investigators engaged in work on the process of photosynthesis *in vivo* and *in vitro*. The energetic approach fully brought out in this review could contribute towards a more complete insight into the mechanism of the processes connected with photosynthesis. Particular attention is, therefore, drawn to Sections IV to VII, dealing with the energetics of free-radical reactions; to a new interpretation of the photoöxidation of water (page 417); to the problems of catalysis and promotion (page 394), particularly to photocatalysis (page 420); and to dye-photosensitized reactions (page 420).

It is thought that the process of photosynthesis consists of two steps: (*a*) the photoöxidation of water and (*b*) the reduction of carbon dioxide and carboxylic acids (possibly incorporated in large complex molecules) by a reducing agent formed in step (*a*) (149, 154, 165, 237). Attempts to produce artificial photosynthesis have invariably failed. Linstead, Braude, and Timmons (227) showed that the claims made by Baur and Niggli (26) were unfounded.

A new approach to the problem of artificial photosynthesis is suggested by the reviewer on the basis of his experience in photocatalysis (page 420). By photoexcited electron transfer very unstable valency states can be produced, such as Pb^+: e.g.,

$$Pb^{+2}Cl^- \xrightarrow{h\nu} Pb^+Cl \rightarrow Pb^+ + Cl$$

This was first hinted at by Rabinowitch (262). The reviewer has confirmed this hypothesis by demonstrating that polymerization reactions can be initiated in the system $Pb^{+2}Cl^-$–vinyl monomer–light. To make the reduction of carbon dioxide or carboxylic acids possible, one must obtain by photoexcited electron transfer a reducing agent with an oxidation–reduction potential,[7] $M^{+(n-1)}/M^{+n}$, of the order of magnitude of 0.5 v. (e.g., Cr^{+2}/Cr^{+3}). In order to inhibit the very effective secondary dark back-reaction it is essential to add a *substrate* (e.g., benzene derivatives) which would trap the oxidizing radicals or atoms formed in the primary step by an addition reaction or a bond-breaking mechanism and which are, at the same time, incapable of oxidizing the reducing species by electron transfer. The latter could, under anaerobic conditions, reduce carboxylic acids by electron transfer: *viz.*, $e + RCOOH \rightarrow (RCOOH)^- \rightarrow RCO + OH^-$ (RCO radicals are postulated in the photolysis of ketones). RCO could react with $R' \cdots H$ of weak bond strength to give $R' +$  $RC(=O)H$ or by disproportionation  $RC(=O)R$ + CO. Some preliminary experiments (carried out in collaboration with Mr. B. Copestake in this laboratory) with the system lead chloride–lithium chloride–ethyl alcohol–formic acid–light failed to give yields of formaldehyde clearly distinguishable from blank tests, but as in the case of $FeCl_4^-$ as photocatalyst (page 420 of this review) thionine (in the place of formic acid) was reduced. Janus green, which is more difficult to reduce than thionine (its oxidation–reduction potential in neutral solution is −0.25 v.), was also reduced in this system with $PbCl_4^{-2}$ as photocatalyst; by analogy with the observations on the photocatalytic activity of $FeCl_4^-$ one would conclude that $PbCl_4^{-3}$ is the active reducing species formed by photoexcited electron transfer. It is not unlikely that even more active reducing complex ions (particularly

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[7] Oxidation–reduction potentials are taken as positive if the free-energy change (ΔG^0) in the reaction

$$X^{+(n-1)} + H^+ \rightarrow X^{+n} + \tfrac{1}{2}H_2$$

is positive.

fluoride complexes) could be produced by the same method. Further work along these lines is in progress. While the species acting *in vivo* with chlorophyll as photocatalyst are not the same, a similar photocatalytic system could be imagined in principle. The method described here seems to the reviewer a difficult but not hopeless approach to the problem of artificial photosynthesis.

The important contributions towards a better understanding of the process of photosynthesis *in vivo* are mainly concerned with chlorophyll-sensitized reactions, the activity of chloroplast suspensions (Hill reagents), tracing of intermediates by the use of isotopic carbon, and the energetics of the process: these subjects are dealt with in recent reviews (144, 165). In addition, the reports of the Carnegie Institution contain valuable information on the subject (154).

The most important finding in the chemistry of the intermediate products is the discovery by Calvin and Benson (70) that phosphoglyceric acid is formed as a stable intermediate product. This was confirmed by Fager, Rosenberg, and Gaffron (121). The differences in the interpretation of the results have been summarized by Franck (144).

Data relating to photoöxidation by isolated chloroplasts have been surveyed by Gaffron and Fager (165). Major new findings in this field were made recently with substances of physiological importance. A number of research workers arrived simultaneously and independently at similar conclusions. Arnon (11) has shown that in the presence of certain enzymes (malic enzyme and coenzyme II) not only the photoöxidation of water but also the reductive fixation of carbon dioxide by pyruvic acid can be achieved. The reaction scheme is as follows:

$$(1)\qquad H_2O + \text{coenzyme II} \xrightarrow[\text{chloroplasts}]{\text{light}} \text{coenzyme II}\cdot H_2 + \tfrac{1}{2}O_2$$

$$(2)\qquad \text{pyruvate} + CO_2 + \text{coenzyme II}\cdot H_2 \xrightarrow{\text{malic enzyme}} \text{malate} + \text{coenzyme II}$$

$$\text{Sum:}\qquad \text{pyruvate} + CO_2 + H_2O \xrightarrow[\text{coenzyme II, malic enzyme}]{\text{light, chloroplasts}} \text{malate} + \tfrac{1}{2}O_2$$

Vishniac and Ochoa (305) have observed malate synthesis by the "malic" enzyme system in illuminated spinach chloroplasts in the presence of triphosphopyridine nucleotide (coenzyme II). Tolmach (296), who continued the work with chloroplast suspensions along the lines developed by Franck (140) and Franck and Pringsheim (150), has shown that triphosphopyridine nucleotide can be reduced by isolated chloroplasts as the result of a light reaction and that the reduced coenzyme could be utilized for reductive carbon dioxide fixation. Moreover, this author observed that the fixation of carbon dioxide and the evolution of oxygen from isolated chloroplast suspensions to which the malic enzyme system was added were small compared with the oxygen evolution obtained from crude spinach juice (with the same chlorophyll content) to which only triphosphopyridine nucleotide had been added. Other substrates of physiological importance which were recently found to be oxidizing agents in illuminated chloroplast suspensions are cytochrome-*c* (242) and oxygen (244, 243). A general coherent theory as to the mechanism of the photochemical action of isolated chloroplasts involving such problems as the energetics, quantum yields, and free-radical intermediates is still lacking. Chlorophyll-photosensitized reactions in solution have been investigated with a view to obtaining a better understanding of the process of photosynthesis. Gaffron's (160) pioneering work in this field deals with the oxidation of allylthiourea in acetone in the presence of oxygen. Recently it was shown by Warburg and Schocken (312) that a similar reaction proceeds with a quantum yield which equals practically 1 (thiourea was used as substrate). The only other system which, by irradiation with light in the visible region of the spectrum, would produce in the liquid phase the theoretical Einstein quantum yield is protoporphyrin–oxygen–substrate. Both systems are, therefore, very suitable for being used as chemical actinometers in the visible region of the spectrum. Wassink and coworkers (313) have tried to correlate the fluorescence yield of chlorophyll with its photochemical activity. It has been established by Franck and his school (145, 148, 153, 277) that such correlation is not justified. The fluorescence yield of chlorophyll is negligibly small compared with the photochemical quantum yield, which may rise up to 1. Wassink's view seems, therefore, hardly tenable.

Gaffron was the first to indicate the likelihood of the occurrence of a long-lived state of photoexcited molecules (164). This was clearly recognized by Franck and Livingston (149), who put forward the theory of the energy-rich tautomer of the excited state. This tautomer has been identified with a triplet state. The latter is, according to Kasha (202), responsible for the phenomenon of phosphorescence, which in the case of chlorophyll has not yet been established beyond doubt. Franck (144) and also Weiss (327) tend now to accept the hypothesis that the photochemically active state of chlorophyll is a triplet state. Reinterpreting the early work of Gaffron (161), Weiss put forward the following scheme:

(1) Light absorption followed by	$\mathrm{Chl} + h\nu \rightarrow \mathrm{Chl}^*$ (excited state)
(2) Fluorescence emission or	$\mathrm{Chl}^* \rightarrow \mathrm{Chl} + h\nu'$
(3) Self-quenching of fluorescence or	$\mathrm{Chl}^* + \mathrm{Chl} \rightarrow 2\mathrm{Chl}$
(4) Transition to the triplet state followed by	$\mathrm{Chl}^* \rightarrow \mathrm{Chl}^{(t)}$
(5) Phosphorescence emission or	$\mathrm{Chl}^{(t)} \rightarrow \mathrm{Chl} + h\nu''$
(6) Self-quenching of phosphorescence or	$\mathrm{Chl}^{(t)} + \mathrm{Chl} \rightarrow 2\mathrm{Chl}$
(7) Interaction with the acceptor (which initiates the photosensitized process)	$\mathrm{Chl}^{(t)} + \mathrm{Acc.} \rightarrow$ reaction products

"Reversible bleaching" of chlorophyll was discovered by Rabinowitch and Weiss (265) and studied in greater detail by Livingston (228), Evstingeev, Gavrilova, and Krasnovskii (119). Franck points out that it is not yet possible to judge whether this bleached state corresponds to a metastable triplet state, or to a reduced state as originally suggested by Franck and Livingston (149). The possibilities of migration of absorbed energy from one chlorophyll molecule to another have been recently analyzed by Franck (144) and Bowen (60).

One of the basic problems that has not yet been solved is that of the energetics of photosynthesis. Since the publication of Franck's review, in which this problem is thoroughly discussed, Schenck (273) has put forward a new "four quanta" theory postulating glyoxylic acid hydrate as intermediate product; this is a revision of the latest four-quanta hypothesis of Burk and Warburg (68, 311).[7a] The latter recently suggested a mechanism in which each light quantum reacts with one molecule of carbon dioxide. Only one out of four carbon dioxide molecules which take part in the reaction is consumed in carbohydrate formation; three of them are liberated and returned into the photosynthetic circle. The net reaction is:

$$2H_2O + 4CO_2 + 4 \text{ light quanta} \rightarrow 2H_2C_2O_4 + O_2$$

followed by

$$2H_2C_2O_4 \rightarrow 3CO_2 + (CH_2O) + H_2O$$

Schenck argues that the formation of formaldehyde as a decomposition product of oxalic acid has never been observed; in addition, the energy of the light quantum required would be 54.5 kcal. (thus lying in the green region of the spectrum) and therefore too high. The latter argument does not appear to be valid. The reviewer checked the energy calculations and, basing his scheme on liquid water as Schenck did, arrived at a value of $\sim$36 kcal. for the energy of the light quantum required (the heats of formation used in this calculation are: 195 kcal. for oxalic acid, 99.0 kcal. for carbon dioxide, and 68.5 kcal. for water). The second reaction leading to formaldehyde formation is, accordingly, about thermoneutral. Schenck's scheme is:

$$2H_2O + 2CO_2 + 4 \text{ light quanta} \rightarrow H_2C_2O_3 \cdot H_2O + O_2$$

followed by the slightly exothermic reaction:

$$6(H_2C_2O_3 \cdot H_2O) \rightarrow C_6H_{12}O_6 + 6CO_2 + 6H_2O$$

This implies that two molecules of carbon dioxide per four light quanta take part in the process, of which one molecule of carbon dioxide is returned into the photosynthetic circle. The energy of the light quantum required, according to Schenck, is 34 kcal. (the reviewer arrives at approximately the same result). Schenck claims that both the problems of the energetics and the intermediate products have been solved ("Die Photosynthese der Kohlenhydrate erscheint damit sowohl nach der stofflichen wie der energetischen Seite geklärt."). It would appear, however, that such a claim is premature. The objections raised

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[7a] *Note added in proof:* Since then Warburg has claimed that with intermittent green light even 2.7 quanta are sufficient. A discussion of this work could not be included in this review.

by Franck (142) to a four-quanta process must still be answered. A number of research workers (*cf.* Franck's review (144)) arrived at the conclusion that at least *ten* quanta are required for each carbon dioxide molecule which ultimately takes part in the process of photosynthesis (102). Franck has serious doubts as to whether nature works as economically as possible in the process of photosynthesis. Energy is dissipated by internal conversions (singlet states → triplet states) and in various dark back-reactions. Schenck has not tried to put forward a reaction mechanism based on univalent chemical changes, such as the attempt made by Franck and Herzfeld (147). The energy requirements would then be much higher than those computed from an overall reaction without taking into account the single steps of a feasible mechanism. The understanding of the detailed mechanism is thus intrinsically connected with the energetic problems. Knowledge of the stable and unstable free-radical intermediates actually formed is essential. The discovery of phosphoglyceric acid as a stable intermediate product means, therefore, a major advance in the research work connected with photosynthesis.

The fundamental question whether the oxygen liberated is entirely derived from water has not yet been answered with certainty. The fast isotopic exchange between water and CO_2^{18} makes an accurate quantitative evaluation of experiments with the latter very difficult. If any oxygen at all originates from carbon dioxide, it would not appear thermodynamically impossible that it is obtained from a dimerization of HCO_2 radicals (which could be formed by the reaction of carbon dioxide with the reducing substance formed in the photoöxidation of water), leading to glyoxal and molecular oxygen. Glyoxal would be converted by reductive fixation of carbon dioxide in the presence of enzymes to phosphoglyceric acid, which is at present the one certain intermediate product on which all theories of mechanism must be based.

XVI. MISCELLANEOUS THERMAL REACTIONS

A. THE EQUILIBRIUM $H + H^+(aq) \rightleftharpoons H_2^+(aq)$

The reducing properties of hydrogen atoms are well known. Weiss has claimed recently that there was experimental evidence that hydrogen atoms could react as oxidizing entities in acid solutions, *via* the formation of H_2^+ (329). In the latter we lose the difference in the ionization potentials and solvation energies between H^+ and H_2^+ but gain the bond-dissociation energy. The formation of H_2^+ (in its solvated form, H_4O^+) is therefore feasible. Weiss suggests that the reactions

$$H_2^+ + I^- \rightarrow H_2 + I$$
$$H_2^+ + Fe^{+2} \rightarrow H_2 + Fe^{+3}$$

occur as simple electron-transfer processes. The reviewer suggests (302) that hydrogen atoms could act as oxidizing species in aqueous solutions even without the intermediate formation of H_2^+: e.g.,

$$HI + H \rightarrow H_2 + I$$
$$Fe^{+2}(HOH) + H \rightarrow Fe^{+3}OH^- + H_2$$

or

$$Cu^+(HOH) + H \rightarrow Cu^{+2} + OH^- + H_2$$

These reactions are considerably exothermic. It is noteworthy that Ethier and Haber (103) had considered the possibility of oxidation by the hydrogen atom in 1930, when this mode of thinking was in its very beginning. A termolecular collision, as assumed by these authors, is, however, unlikely.

B. REDUCTION BY THE OH RADICAL

Reducing properties of OH radicals are discussed elsewhere in this review (page 418). A different mechanism has been suggested by Weiss, who atrributes the reducing properties to the anion O^- formed by the ionic dissociation $OH \rightleftharpoons O^- + H^+$ (333).

C. FORMATION OF FREE RADICALS ACCOMPANYING OXIDATION BY COBALTIC OR CERIC ION

An extensive investigation of this subject has been carried out by Bawn and White (27, 28, 29). In the reaction of Co^{+3} ion with water it was observed that the rate of reaction $(-dCo^{+3}/dt)$ is of the second order with regard to cobaltic ion at high cobaltic-ion concentrations, while at low concentrations of the latter the order tends to unity. This is also in agreement with results obtained by Baxendale and Hargrave (36). The overall reaction is assumed to be

$$4Co^{+3} + 2H_2O \rightarrow 4Co^{+2} + 4H^+ + O_2$$

The following mechanism is suggested:

$$(\alpha) \quad Co^{+3} + OH^- \rightarrow Co^{+2} + OH$$

$$(\beta) \quad 2OH \rightarrow H_2O_2$$

$$(\gamma) \quad H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

Bawn and White rightly consider that the reaction is likely to involve the ion-pair, which would be in agreement with the pH dependence of the reaction rate. The above equations account for the first-order reaction, but no plausible explanation is put forward for the second-order reaction (the possibility of cobaltic ion forming polynuclear complexes has been cautiously suggested). The reviewer assumes that the change from the first-order to a second-order reaction can be adequately explained on the basis of a scheme which is similar to the photoöxidation of water by ceric ion: at low cobaltic-ion concentrations the scheme is

$$(\alpha') \ Co^{+3}OH^- \rightarrow Co^{+2} + OH$$

or

$$Co^{+3} + OH^- \rightarrow Co^{+2} + OH$$

$$(\beta') \ OH + \text{impurities} \rightarrow \text{oxidation products}$$

Under these conditions the rate of reaction is proportional to the cobaltic-ion concentration and inversely proportional to the hydrogen-ion activity. No oxygen evolution was measured. The significance of impurities in free-radical reactions has been discussed in other sections of this review (pages 406 and 418). At high cobaltic-ion concentrations the reaction proceeds as follows:

$$(\alpha'')\ \mathrm{Co^{+3} + OH^- \rightarrow Co^{+2} + OH}$$

or

$$\mathrm{Co^{+3}OH^- \rightarrow Co^{+2} + OH}$$

$$(\beta'')\ \mathrm{Co^{+3}OH^- + OH \rightarrow Co^{+2} + H_2O_2}$$

(OH radical being a reducing agent)

$$(\gamma'')\ \mathrm{2Co^{+3}OH^- + H_2O_2 \xrightarrow[\text{}]{\substack{\text{not rate-}\\ \text{determining}}} 2Co^{+2} + 2HOH + O_2}$$

This scheme fits the experimental observations and overcomes the difficulties in explaining the second-order reduction of cobaltic ion,—a problem that has also presented itself in an investigation of the $\mathrm{Co^{+2}/Co^{+3}}$ redox potential (250).

At intermediate concentrations a mixed order

$$\left(\frac{-\mathrm{dCo^{+3}}}{\mathrm{d}t}\right) = k_1[\mathrm{Co^{+3}}] + k_2[\mathrm{Co^{+3}}]^2$$

such as established by Bawn and White, is to be expected. In view of the competing reactions and the high ionization potential of cobaltous ion in aqueous solution, the back-reaction

$$\mathrm{Co^{+2} + OH \rightarrow Co^{+3} + OH^-}$$

could become significant only at high concentrations of the cobaltous ion ($> 0.1\ M$). At comparable cobaltic-ion concentrations the second-order reaction would hold.

Bawn and White estimated the temperature-independent factor of the rate constant of the reaction

$$\mathrm{Co^{+3} + OH^- \rightarrow Co^{+2} + OH}$$

as $\sim 10^{25}$ and the activation energy as $\sim$35 kcal. It is noteworthy that these values are in excellent agreement with the expected entropy of activation, on the one hand, and with the endothermicity of the reaction (if the ionic dissociation of water is taken into account), on the other. The reaction of cobaltic ion with formic acid (as substrate) was also investigated in great detail. The following sequence of reactions is suggested by Bawn and White:

	Heat of reaction *kcal./mole*
$\mathrm{HCOOH + Co^{+3} \rightarrow HCOO\cdot + H^+ + Co^{+2}}$	−21.5
$\mathrm{HCOO^- + Co^{+3} \rightarrow HCOO\cdot + Co^{+2}}$	−21
$\mathrm{HCOO\cdot + H_2O \rightarrow HCOOH + OH}$	−8
$\mathrm{HCOO\cdot + OH \rightarrow CO_2 + H_2O}$	+102
$\mathrm{HCOO\cdot + HCOO\cdot \rightarrow HCOOH + CO_2}$	+110
$\mathrm{HCOO\cdot + Co^{+3} \rightarrow Co^{+2} + H^+ + CO_2}$	+89

The heat values indicated in the scheme were calculated by the reviewer. Bawn and White have shown that carbon dioxide is the only stable oxidation product and that the kinetic results can be accounted for by the above reaction scheme. The possibility of the formation of the ion-pair complex $Co^{+3}HCO_2^-$ should not, however, be excluded, although it might not affect the overall kinetics. Again, the reviewer notes with some interest that the energy of activation of 22 kcal. for the reaction

$$Co^{+3} + HCOO^- \rightarrow Co^{+2} + HCOO\cdot$$

corresponds almost exactly to its endothermicity and that the entropy of activation is of the expected order of magnitude.

With alcohols as substrates the primary step is suggested to lead, by electron transfer, to a free alkoxyl radical:

$$Co^{+3} + C_2H_5OH \rightarrow Co^{+2} + H^+ + C_2H_5O\cdot$$

The authors did not specify the nature of the radical but from a consideration of the bond-dissociation energies it seems that its formula should be given as $CH_3\dot{C}HOH$ rather than $CH_3CH_2O\cdot$. The $CH_3\dot{C}HOH$ radical would be oxidized by cobaltic ion to acetaldehyde. The oxidation of the latter by cobaltous ion in solution, which was studied by Bawn and Williamson (30, 31), is far more complex, as it involves a chain reaction.

One would expect the thermal oxidation by the ceric ion to proceed by means of an electron-transfer mechanism involving free-radical intermediates similar to that for cobaltic ion. Shorter and Hinshelwood (278), who investigated the oxidation of organic substrates by ceric sulfate in aqueous solutions at 70°C., rejected the idea that the primary step could be a reaction leading to the formation of OH radicals, such as

$$Ce^{+4} + OH^- \rightarrow Ce^{+3} + OH$$

Two reasons were quoted: (*a*) no inhibitory effect of cerous ion was observed and (*b*) the pH dependence did not warrant it. It seems that this possibility is worth further examination on the following grounds: The effect of cerous ion should be marked only at considerable concentrations in the presence of a substrate (as in the case of cobaltous ion). Furthermore, the $Ce^{+4}OH^-$ ion-pair complex is far more stable than $M^{+3}OH^-$ complexes; even in normal perchloric acid $Ce^{+4}OH^-$ is practically the only species in solution. If the primary step is

$$Ce^{+4}OH^- \rightarrow Ce^{+3} + OH$$

it should not be affected by the hydrogen-ion activity. The formation of the SO_4^- radical-ion (in the presence of sulfate ions) is also worth consideration.

D. CHAIN REACTIONS OF OZONE IN AQUEOUS SOLUTION

The most important work in this field has been carried out by Taube and Bray (294). The interaction of ozone and hydrogen peroxide in acidic aqueous solutions can be presented by two overall equations:

$$O_3 + H_2O_2 \rightarrow H_2O + 2O_2 \quad \text{(A)}$$

$$2O_3 \rightarrow 3O_2 \quad \text{(B)}$$

The mechanism involves the following steps:

$$H_2O_2 + O_3 \xrightarrow{k_1} OH + HO_2 + O_2 \quad (1)$$

$$HO_2 + O_3 \xrightarrow{k_2} OH + 2O_2 \quad (2)$$

$$OH + O_3 \xrightarrow{k_3} HO_2 + O_2 \quad (3)$$

$$OH + H_2O_2 \xrightarrow{k_4} HO_2 + H_2O \quad (4)$$

The free-energy data given by Taube and Bray were revised by Evans, Hush, and Uri (108). Reaction 1 is the chain-initiating step. Reactions 2 and 4 are the chain-propagation steps for the overall reaction A, and reactions 2 and 3 those for reaction B. Whether the reaction

$$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$$

occurs in this system will not only depend on the ozone/hydrogen peroxide ratio but also on the acidity, as it is likely to proceed *via* the O_2^- ion. In considerably acid solutions (e.g., 0.2 *N*) it cannot occur to a measurable extent in this system, the p*K* of HO_2 being 2 (108). As the reaction

$$O_2^- + H_2O_2 \rightarrow O_2 + OH^- + OH$$

is likely to require an activation energy of ~5 kcal., it could be considerably suppressed in the presence of ozone even at a pH of 2. In alkaline solution the system is far more complex, as the interaction between O_3 and OH^- ions has to be taken into account. Taube and Bray evaluated k_1 as 2×10^{-3} (mole/l.)$^{-1}$ sec.$^{-1}$ and the ratio k_3/k_4 as ~3. The value of k_1 would be surprisingly low if the value for the free-energy change given by Taube and Bray as -0.9 kcal. were maintained.

A most thorough investigation was made by the latter into the effect of inhibitors and catalysts of reactions A and B. The general function of an inhibitor is

$$(\alpha)\ HO + \text{inhibitor} \rightarrow \text{radical} + H_2O$$

or

$$(\beta)\ HO + \text{inhibitor} \rightarrow \text{radical} + OH^-$$

All organic substrates (such as alcohols) act as inhibitors in accordance with reaction α. Carboxylic acids occupy a special position. Chloride and bromide ions act by mechanism β. It is highly interesting to compare the results of Taube and Bray with the recently reported "suppressor effect" (in the system ferrous ion–hydrogen peroxide (211)). The same general features emerge in both cases and can be interpreted on an energetic basis. (The energetics of the radical–ion transfer mechanism are discussed on page 388.) From the thermodynamic data such inhibition is expected to occur with chloride ion and bromide ion but not with fluoride ion, in agreement with the experimental results and the interpretation put forward by Taube and Bray. Evidence is also cited for the reaction

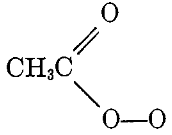
$$Cl + H_2O_2 \rightarrow HO_2 + H^+ + Cl^-$$

which causes a marked effect on the consumption ratio $\Delta O_3/\Delta H_2O_2$. At a concentration of $10^{-3}M$ sodium chloride and, *ceteris paribus*, the latter was decreased from 11.8 (in the absence of chloride ion) to 1.5. The reaction

$$Cl + HO_2 \rightarrow Cl^- + H^+ + O_2$$

is also considered; from an energetic point of view it can hardly be excluded· Experimental evidence is presented for the equilibrium $Cl + Cl^- \rightleftharpoons Cl_2^-$.

A slight effect on the reaction by strong oxy acids (nitric, perchloric, sulfuric) has been found, but in view of the possible effects of trace impurities (recognized by Taube and Bray) it is difficult to base a quantitative interpretation on these observations. The occurrence of NO_3 and ClO_4 radicals in this system must be taken as speculative.

The special position of acetic acid and formic acid (which shows even a "promoter" effect) is interpreted on the assumption that radicals, derived from these acids by hydrogen abstraction, can take the place of OH and HO_2 radicals in the chain mechanism; $CH_3COO\cdot$ corresponding to the former, and the peracetate radical  $CH_3C(=O)O{-}O$ to the latter. In the case of formic acid it is suggested that more OH radicals are formed by the reaction:

$$HCOOH + O_3 \rightarrow OH + HCOO\cdot + O_2$$

The effect of cations was also studied in detail (294). Some of the metal ions were found to be effective catalysts. It was shown that the largest effect is obtained when two conditions are fulfilled: (*a*) the cation is oxidized by ozone by a monovalent valency change and (*b*) the oxidized cation is reduced rapidly by hydrogen peroxide. The net effect is then a larger stationary concentration of free radicals, thus leading to an increased rate of reaction. Cobaltous ion and cerous ion fulfil these conditions, and Taube and Bray have shown that in accordance with expectation these cations induce the decomposition of ozone, even in the absence of hydrogen peroxide. The authors found it difficult to explain the effect of cupric ion, as the existence of an oxidation state Cu^{+3} has not been established beyond doubt.[8] It seems to the reviewer that the basic interpretation of the effect of cupric ion might be similar in principle to its action as promoter in the catalytic decomposition of hydrogen peroxide. Owing to a large $e^{\Delta S/R}$ factor the reaction

$$Cu^{+2} + HO_2 \rightarrow Cu^+ + H^+ + O_2$$

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[8] L. Malatesta (Gazz. chim. ital. **71**, 467 (1941); Chem. Abstracts **36**, 6929 (1942)) claims to have isolated complex compounds of trivalent copper of the formula $M_7^+Cu^{+3}(IO_6)_2 \cdot nH_2O$.

(or the corresponding reaction with the O_2^- ion) is extremely fast and could occur in this system, being followed by the oxidation of cuprous ion by ozone (accompanied in turn by the formation of OH radicals to act as chain carriers), i.e.,

$$Cu^+(HOH) + O_3 \rightarrow O_2 + Cu^{+2} + OH^- + OH$$

The lack of inhibitory effect of chloride ions in the presence of cupric ion is not surprising, as it is in agreement with the considerably increased efficiency of cupric chloro-complexes as catalysts for the decomposition of hydrogen peroxide (300). If the interpretation of the activity of cupric ion which is presented here is correct, one would expect the decomposition of ozone to be induced by cuprous ion even in the absence of hydrogen peroxide. From a quantitative point of view, it is noteworthy that Taube and Bray conclude that the radical-ion transfer reaction $OH + Cl^- \rightarrow OH^- + Cl$ is as much as twenty times faster than the reaction of ozone with OH radicals.

Hush has recently analyzed the energetics of ozone reactions. The data given below are those reported by Evans, Hush, and Uri (108).

REACTION	ΔH^0	ΔS^0	ΔG^0
	kcal./mole	*e.s.u.*	*kcal./mole*
(a) $O_3 + H_2O \rightarrow 2HO_2$	+49	−5	+51
(b) $O_3 + OH^- \rightarrow HO_2^- + O_2$	−17	−2	−16
(c) $O_3 + H_2O_2 \rightarrow OH + HO_2 + O_2$	+19	+5	+18
(d) $O_3 + HO_2^- \rightarrow OH^- + 2O_2$	−54	+6	−56
(e) $O_3 + HO_2 \rightarrow OH + 2O_2$	−42	+9	−45
(f) $O_3 + OH \rightarrow HO_2 + O_2$	−31	−2	−30

The rate constant of reaction (c), 2×10^{-3} (mole/l.)$^{-1}$ sec.$^{-1}$, as measured by Taube and Bray (294), is in excellent agreement with the thermodynamic data on the assumption of a normal temperature-independent factor of 10^{12} (mole/l.)$^{-1}$ sec.$^{-1}$ and an activation energy of $\sim$20 kcal., i.e., roughly equal to the endothermicity of the reaction.

Hill (191) recently studied the decomposition of ozone induced by cobaltous ion and postulated the following mechanism (involving the formation of the $Co^{+3}OH^-$ ion-pair):

$$Co^{+2} + O_3 + H_2O \rightarrow Co^{+3}OH^- + O_2 + OH$$

$$O_3 + OH \rightarrow HO_2 + O_2$$

$$HO_2 + Co^{+3}OH^- \rightarrow Co^{+2} + H_2O + O_2$$

Hill obtained for $\Delta H^\ddagger$, $\Delta F^\ddagger$, and $\Delta S^\ddagger$ values of 9 kcal., 14.7 kcal., and −19 E.S.U., respectively. These values are in good agreement with energy data given in this review, if it is assumed that the formation of the $Co^{+3}OH^-$ ion-pair from cobaltic ion and hydroxide ion is accompanied by a free-energy change similar to that corresponding to the $Fe^{+3}OH^-$ ion-pair.

According to the mechanism suggested by Yeatts and Taube (346), the reaction between chloride ions and ozone in aqueous solution does not proceed through free-radical intermediates, such as OH radicals and Cl atoms, but rather through the hypochlorite ion:

$$\text{(a)}\quad O_3 + Cl^- \rightarrow O_2 + ClO^- \quad \text{and}$$

$$\text{(b)}\quad Cl^- + ClO^- + 2H^+ \xrightarrow[\text{determining}]{\text{not rate-}} Cl_2 + H_2O$$

The reaction

$$O_3 + H_2O \rightarrow HO_3^+ + OH^-$$

and the subsequent equilibrium

$$HO_3^+ + OH^- \rightleftharpoons 2HO_2$$

have been suggested in the OH^--induced decomposition of ozone (6). It is impossible to judge the likelihood of this mechanism from the thermodynamic point of view, as no data on the stability of the HO_3^+ ion are available.

E. HYDROPEROXIDES AND PERSULFATES

In view of the considerable interest which is being attached to redox polymerization, a number of investigations have been carried out with a view to obtaining data relating to the mechanism of the primary reaction. An important hydroperoxide in this connection is cumene hydroperoxide, $C_6H_5C(CH_3)_2OOH$. Kolthoff and Medalia (213) have shown that the system ferrous ion–cumene hydroperoxide is qualitatively similar to the system ferrous ion–hydrogen peroxide–ethyl alcohol. Analogous effects of induced oxidation in the presence and in the absence of oxygen were observed. More detailed work was carried out by Fordham and Williams (137), who determined both the temperature-independent factor of the rate constant and the activation energy relating to the primary step.

$$Fe^{+2} + RO\text{—}OH \rightarrow Fe^{+3}OH^- + RO\cdot$$

Their value for k is $3.9 \times 10^9 \exp.(-11{,}100/RT)$ (mole/l.)$^{-1}$ sec.$^{-1}$, which is very similar to the reaction of ferrous ion with hydrogen peroxide. This similarity would seem to indicate that the bond-dissociation energy of HO···OH is nearly equal to that of HO···OH; therefore, a *homogeneous* decomposition could occur only at very high temperatures. It is likely that the decomposition at temperatures below 100°C. is always catalyzed by the surface of the reaction vessel or impurities in the reaction mixture. Fordham and Williams (138) have also studied the effect of iron(II) complex-forming reagents, such as α,α'-dipyridyl, and their results are in agreement with the corresponding shift of the oxidation–reduction potential. Recently the latter slightly revised their own value for the rate constant; new measurements were carried out in the presence of acrylonitrile and in an atmosphere of nitrogen. The value thus obtained is $1.07 \times 10^{10} \exp.(-12{,}000/RT)$ (mole/l.)$^{-1}$sec.$^{-1}$ This revision does not affect the above comparison of the bond-dissociation energies (in aqueous solutions).

Farkas and Passaglia (125) studied the thermal decomposition of cyclohexyl hydroperoxide. The reaction was used to initiate the polymerization of styrene, which in turn catalyzed the decomposition of the hydroperoxide. While no definite conclusions were drawn, an alternative interpretation by the above authors is based on an electron-transfer mechanism similar to the Haber–Weiss concepts for the catalytic decomposition of hydrogen peroxide.

A careful study of the reaction between ferrous ion and persulfate ion was recently reported by Kolthoff, Medalia, and Raaen (215). Evidence was presented for the occurrence of the primary step

$$Fe^{+2} + S_2O_8^{-2} \rightarrow Fe^{+3} + SO_4^{-2} + SO_4^{-}$$

It has been suggested that the SO_4^- radical-ion then reacts with organic substrates or vinyl monomers (leading to polymerization). In the absence of a substrate and upon rapid mixing of the reactants (which is essential) the SO_4^- radical produced reacts with ferrous ion according to the equation

$$Fe^{+2} + SO_4^{-} \rightarrow Fe^{+3} + SO_4^{-2}$$

Under these conditions the stoichiometric ratio $\Delta Fe^{+2}/\Delta S_2O_8^{-2}$ is 2. Many phenomena observed in this system are similar to those observed with Fenton's reagent; e.g , chloride ion and bromide ion suppress oxidation of the substrate, presumably by the radical–ion transfer of the type $SO_4^- + X^- \rightarrow SO_4^{-2} + X$, and the halogen atom thus formed is more efficient in further oxidation of the ferrous ion present (by electron transfer) than in the hydrogen abstraction of the substrate. According to Kolthoff and Miller (216), one has to distinguish, in the thermal decomposition of persulfates in aqueous solution, between an uncatalyzed and an acid-catalyzed reaction. The mechanisms are:

(a) Uncatalyzed reaction:

$$S_2O_8^{-2} \rightarrow 2SO_4^{-}$$

$$SO_4^{-} + H_2O \rightarrow HSO_4^{-} + OH$$

$$2OH \rightarrow H_2O + \tfrac{1}{2}O_2$$

(b) Acid-catalyzed reaction:

$$S_2O_8^{-2} + H^+ \rightarrow HS_2O_8^{-} \rightarrow SO_4 + HSO_4^{-}$$

$$SO_4 \rightarrow SO_3 + \tfrac{1}{2}O_2$$

(c) In strong acid:

$$SO_4 + H_2O \rightarrow H_2SO_5 \text{ (Caro's acid)}$$

The observed activation energy of 33.5 kcal. for the rupture of the O—O bond is surprisingly low. The question must again be asked whether this value is not affected by impurities in the distilled water, the significance of which has been frequently experienced in recent work; the latter could effect a process of reduction activation which would proceed with a lower activation energy than that corresponding to the bond-dissociation energy. The SO_4^- radical-ion was also postulated by Bartlett and Cotman (22) in a study of the system potassium persulfate–methyl alcohol in aqueous solution.

F. FURTHER EXAMPLES OF REDOX ACTIVATION

The system ferrous ion–bromine–maleic acid was investigated by Derbyshire and Waters (92). It was shown that bromine atoms produced in the primary step, which is

$$Fe^{+2} + Br_2 \rightarrow Fe^{+3} + Br^- + Br$$

lead to the conversion of maleic acid into fumaric acid. The system ferrous ion–chlorine–oxalic acid was investigated by Hochhauser and Taube (194). A chain reaction was postulated, the initiation step being

$$Fe^{+2} + Cl_2 \rightarrow Fe^{+3}Cl^- + Cl$$

Davies, Evans, and Higginson (89) showed that NH_2 radicals produced by the reaction

$$Ti^{+3} + HO—NH_2 \rightarrow Ti^{+4} + OH^- + NH_2$$

can lead to amination reactions. It is likely that the titanic ion pair $Ti^{+4}OH^-$ is formed in the primary step; the latter was recently postulated in the reaction between titanous chloride and iodine (201). The reviewer suggests that the back-reaction

$$Ti^{+4}OH^- + NH_2 \rightarrow Ti^{+3} + HO—NH_2$$

should be considered in the kinetic treatment of the system. In the absence of a substrate the NH_2 radical formed can also oxidize a further titanous ion while being reduced to ammonia. Under these conditions the stoichiometric ratio $\Delta Ti^{+3}/\Delta NH_2OH$ equals 2. Davies, Evans, and Higginson have shown that it can be reduced to 1 in the presence of benzene. The authors suggest that $(C_6H_6NH_2)_2$ is formed, which on steam distillation disproportionates into biphenyl and ammonia.

G. THE PROCESS OF AEROBIC OXIDATION

Franck and Haber (146) were the first to treat this subject on the basis of the modern concepts of free-radical production by electron transfer. The example chosen by them was the autoöxidation of the sulfite ion initiated by traces of cupric ion. In accordance with their mechanism the primary step is

$$Cu^{+2} + SO_3^{-2} \rightarrow Cu^+ + SO_3^-$$

followed by the equilibrium $SO_3^- + H^+ \rightleftharpoons HSO_3$. In the absence of oxygen, dithionic acid is formed by dimerization of the HSO_3 radical. This process is largely suppressed in the presence of oxygen when HSO_3 and HSO_5 radicals act as chain carriers in the autoöxidation of the sulfite ion. Dithionate formation is then a chain-termination reaction. The chain propagation steps are:

$$\rightarrow HSO_3 + O_2 \rightarrow HSO_5$$

$$HSO_5 + SO_3^{-2}\ (HOH) \rightarrow 2HSO_4^- + OH$$

followed by

$$SO_3^{-2} + OH \rightarrow SO_3^- + OH^-$$

and

$$SO_3^- + H^+ \rightleftharpoons HSO_3$$

A slightly modified mechanism involving the HO_2 radical was suggested by Weiss (326) on the basis of the results obtained by Goldfinger and Graf von Schweinitz (172) and by Haber and Wansbrough-Jones (176).

The autoöxidation of leuco-indophenols was studied by Baxendale and Lewin (37). The conclusion was drawn that QH^- was the reducing species. QH^- is formed by the ionic dissociation of the leuco-indophenol: $QH_2 \rightleftharpoons QH^- + H^+$. The rate-determining step is assumed to be

$$QH^- + O_2 \rightarrow Q^- + HO_2$$

or, alternatively,

$$QH^- + O_2 \rightarrow QH + O_2^-$$

The electron affinity (in solution) of the semiquinone QH will affect both the equilibrium constant of the ionic dissociation and the endothermicity of the subsequent reaction of QH^- with oxygen. This is fully borne out by the experimental results obtained by Baxendale and Lewin. On the basis of this work Evans (104) built the hypothesis of the linear relationship of the free energy of reaction and of activation in electron-transfer reactions.

Schwarzenbach and Michaelis (275) demonstrated the stability of the semiquinone radical derived from indophenols. In some cases it has been established that Q^{-2} (rather than QH^-) is the reactive entity, e.g., in the aerobic oxidation of hydroquinone and methylhydroquinones studied by James and Weissberger (200). A complete analysis of the aerobic oxidation on the basis of the semiquinone theory, including the effects of catalysis and inhibition (particularly by metal ions), has been put forward by LuValle and Weissberger (235, 236).

H. MISCELLANEOUS RADICALS

The occurrence of a number of free radicals has been suggested as intermediate products about which quantitative, thermodynamic, and kinetic data are still scarce. The SH radical has been postulated by Fishgold and Weiss (132). Possibly it is the cause of the initiation of *cis–trans* isomerization in the system sulfur dioxide–hydrogen sulfide–maleic acid. It would be very interesting to obtain quantitative information on the dissociation equilibrium $SH \rightleftharpoons S^- + H^+$, in view of a recent suggestion that the OH radical is similarly dissociated (333).

The N_3 radical has been suggested (325) in the reaction

$$Ce^{+4} + N_3^- \rightarrow Ce^{+3} + N_3$$

The N_3 radical breaks up into nitrogen (possibly by bimolecular collisions, $N_3 + N_3$, or the ion-pair complex and the azide radical). On the other hand, the reaction

$$N_3 + H_2O \rightarrow NH + N_2 + OH$$

is thermodynamically feasible and likely to occur. N_3 can also be formed in the reaction of azide ion with bromine or iodine atoms (325) produced by reduction activation of the corresponding halogen molecules. The sum of the electron affinity of the N_3 radical and the solvation energy of the N_3^- ion has been estimated as 125 kcal. (325).

It has been assumed that the NO^- radical-ion is produced by electron transfer from NO in solution according to $e + NO \rightarrow NO^-$ followed by $NO^- + H^+ \rightleftharpoons NOH$ (326).

Abel (3, 4) recently attempted to reinterpret his extensive research work on oxidation by oxy acids (carried out in the 1920's) on the basis of the modern electron-transfer mechanisms. It seems that a great deal of further information is required before definite conclusions on the reduction mechanisms involving permanganates, nitrates, nitrites, periodates, etc. can be drawn. Unfortunately, Abel does not confine himself to species which presumably occur in solution but introduces such ions as O^{-2}. This tends to make the understanding of the kinetics more difficult. In this connection it is noteworthy that the equilibrium

$$MnO_4^- + H_2O \rightleftharpoons MnO_4^{-2} + OH + H^+$$

was postulated by Duke (95).

I. POSITIVE IONS AS UNSTABLE INTERMEDIATE PRODUCTS

The most important findings relating to positive ions as intermediate compounds have been summarized by Weiss (326).

It was conclusively established by the thorough researches of Ingold and his school (196, 197), by Westheimer and Kharasch (337), and also by other investigators (42, 199) that the nitronium ion NO_2^+ (in equilibrium with $H_2NO_3^+$) is the active species in the usual nitration reactions. The corresponding ion derived from nitrous acid is NO^+; recently the ion $N_2O_3^+$ was postulated and given the formula of the mesomeric complex $\overbrace{NO \cdot NO_2}^{+}$ (173). The components of this compound ion are considered to be held together by a reversible one-electron transfer. It would be beyond the scope of the present review to describe the recent work on the mechanism of nitration reactions in detail (attention is drawn to the introduction to a series of twenty-two papers dealing with the subject (197)); the reviewer would, however, like to suggest the possibility of comparing nitration by the nitronium ion, on the one hand, and by uncharged free radicals, on the other. Free radicals that might lead to nitration reactions could be produced by reduction activation of N_2O_4 or by photoexcited electron transfer in such ion-pairs as $Th^{+4}NO_3^-$ or $Ce^{+4}NO_3^-$.

In an interesting analysis of present-day chemical kinetics Hinshelwood (192) put forward the equilibrium $Br_2 \rightleftharpoons Br^- + Br^+$ and applied it to the particular case of the oxidation of oxalic acid. The I^+ ion and the ion-pair I^+OH^- were also suggested (192). Solvated Br^+ ions as intermediate species have been assumed in the reaction between ethyl alcohol and bromine (127).

It has been demonstrated (326) that the reaction between hydrogen peroxide and iodide ions can be accounted for by the following mechanism:

(a) $H_2O_2 + I^- \rightarrow I + OH^- + OH$

(b) $H_3O_2^+ + I^- \rightarrow I + HOH + OH$

(c) $I^- + OH \rightarrow I + OH^-$

(d) $I_2 \rightleftharpoons I^+ + I^-$

(e) $HO_2^- + I^+ \rightarrow HO_2 + I$

(f) $HO_2 + H_2O_2 \rightarrow O_2 + H_2O + OH$

Reaction (b) is understood to proceed only in strongly acid solutions; reaction (f) is understood to proceed through the O_2^- ion. The kinetic analysis on the basis of the above scheme leads to a full confirmation of the experimental results in this complex reaction.

From an energetic point of view the reviewer notes that the reactions involving $H_3O_2^+$ in the place of H_2O_2 as oxidizing agent are less endothermic by the amount of 13.5 kcal. In very endothermic reactions, such as in the case of reduction by the Br^- ion, the relative importance of the acid-catalyzed reaction is expected to increase.

The mechanism of the chromic acid oxidations has been reviewed by Westheimer (336). In a study of the oxidation of isopropyl alcohol by Westheimer and Novick (338) a positively charged protonated ester was assumed as intermediate product. A similar interpretation to the oxidation of isopropyl alcohol by bromate ions in aqueous solution was given by Farkas and Uri (128). The evidence for the formation of the isopropyl chromate ester has been substantiated in more recent work (195).

By analogy with $H_2NO_3^+$ it is not unlikely that other positively charged protonated intermediate compounds derived from strong acids occur in solution. Possibly the frequently observed dependence of the rate of oxidation on the hydrogen-ion concentration is to be accounted for by the formation of protonated acids such as $H_2MnO_4^+$, $H_2IO_4^+$, $H_2BrO_3^+$, etc.

J. WALL EFFECTS

Wall effects are well known in chain reactions involving free radicals in the gas phase (252, 267). A theoretical treatment was recently attempted by

Noyes (251). The number of homogeneous liquid-phase reactions in which a wall effect has been reported are as yet very few. They affect (*a*) the catalytic decomposition of hydrogen peroxide under certain experimental conditions (300), (*b*) the oxygen evolution in the photoöxidation of water by ceric ions (80), (*c*) the oxidation of liquid ethylbenzene, in which peroxides are formed as intermediate products (189), and (*d*) the photoinitiated free-radical polymerization of vinyl compounds in aqueous solution.[9]

Some coördination of these phenomena seems to be required. It is worth noting that in cases (a) to (d) free radicals are formed and the wall appears to catalyze a chain-termination process.

XVII. Inorganic Free Radicals in Radiation Chemistry

A number of review articles have recently been published in the relatively new field of radiation chemistry (69, 85). Summaries of recent achievements are also contained in various articles presented at two symposia (Notre Dame, Indiana, 1947; Paris, 1950). The general aspects of the subject have been discussed by Lind (226). The reviewer will therefore present only a brief outline of this field of research, with particular reference to the significance of inorganic free radicals (a number of papers presented at the two symposia have a strong bearing on the subject of this review (7, 12, 84, 88, 169, 193, 219, 248, 283, 331)).

Recent work with inorganic substances in the liquid phase has been concentrated on aqueous solutions. The main concepts of the Haber–Weiss mechanism were introduced into radiation chemistry by Weiss in 1944 (321). A recent review (69) points out that the same concepts had been applied at that time in the Atomic Energy Project but could not be published. It is now generally assumed that ionizing radiations lead primarily to the H_2O^+ ion and a free solution electron. The former decomposes into H^+ and OH and the latter reacts with water to form H_2O^-, which then decomposes into H atoms and OH^- ions. The ultimate result is thus $H_2O \rightsquigarrow H + OH$. Alternative mechanisms leading to the same overall effect include electron transfer, direct bond dissociation, and production of an excited water molecule (and subsequent dissociation). The following reactions occur in the absence of a substrate (69, 85):

	Heat of reaction in aqueous solution *kcal.*
$H + H \rightarrow H_2$	96
$H + OH \rightarrow H_2O$	116
$H_2 + OH \rightarrow H_2O + H$	20
$H + O_2 \rightarrow HO_2$	37
$OH + OH \rightarrow H_2O_2$	47

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[9] When the conditions chosen were such that practically all the radicals were formed at a distance <2 mm. from the wall, the polymer was produced exclusively on the wall surface.

	Heat of reaction in aqueous solution kcal.
$OH + OH \rightarrow H_2O + O$	15
$H_2O_2 + H \rightarrow H_2O + OH$	69
$OH + HO_2 \rightarrow H_2O + O_2$	77
$2HO_2 \rightarrow H_2O_2 + O_2$	58
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	19
$H + HO_2 \rightarrow H_2O_2$	97
$HO_2 \rightarrow H^+ + O_2^-$	3
$O_2^- + H_2O_2 \rightarrow O_2 + OH^- + OH$	13

The assumptions made as to the heats of hydration of the atoms and free radicals are the same as in table 1. Allen (7) was able to show that steady concentrations of hydrogen peroxide and hydrogen can be obtained by irradiation of water with x-rays, thus providing experimental evidence for the mechanism of the radiolysis of water. The reviewer included in the above list some reactions of the O_2^- ion to which it appears no attention has been paid hitherto in the field of radiation chemistry (of aqueous solutions).

Further evidence relating to the formation of free radicals in solution has been produced largely by three methods.

(a) Polymerization of vinyl compounds

Dainton (83, 84), Chapiro (72, 73), Landler and Magat (222), and Magat and Bonême (50, 238) have applied the method developed in the study of redox polymerization (page 396) to radiation chemistry. It was shown by means of infrared spectroscopy that polymers containing OH end-groups can be obtained (84, 85).

(b) Hydroxylation of benzene derivatives

Extensive studies have been carried out by Stein and Weiss (129, 284, 286, 287, 288). Benzene is oxidized to phenol *via* the reactions:

$$(a)\ C_6H_6 + OH \rightarrow C_6H_5 + HOH$$

and

$$(b)\ C_6H_5 + OH \rightarrow C_6H_5OH$$

The reaction is accompanied by partial dimerization. As Stein and Weiss have shown, this oxidation occurs by irradiation of aqueous solutions of benzene and its derivatives in the absence of oxygen, a result which indicates that OH radicals are produced in the radiolysis of water. With monosubstituted benzene derivatives as substrates the *p*-isomer was always predominant. On the basis of the results obtained by Stein and Weiss, a radiation actinometer was developed by Day and Stein (91).

(c) Oxidation by electron transfer

A classical example is the oxidation of ferrous ion. A recent study of this reaction has been reported by Miller (247). The observation that the yield of ferric ion decreases with increasing pH in the range 1–3 is attributed by Miller to the equilibrium

$$Fe^{+2} + HO_2 \rightleftharpoons Fe^{+3} + HO_2^-$$

as with increasing pH the back-reaction (in the above equilibrium) becomes more important. In the opinion of this reviewer the equilibrium lies well over to the right even at a pH of 3, as the stationary concentration of ferrous ion in the ferric ion–hydrogen peroxide system is very small. A more likely explanation, however, for the pH dependence of the yield of ferric ion is based on the ionic dissociation of the HO_2 radical: $HO_2 \rightleftharpoons H^+ + O_2^-$. With the p$K$ value of 2 as estimated by Evans, Hush, and Uri (108), the pH range 1–3 is indeed critical, as only HO_2 acts as oxidizing agent, whereas O_2^- is an effective reducing agent, e.g.,

$$Fe^{+3} + O_2^- \rightarrow Fe^{+2} + O_2$$

A considerable pH dependence of the yield of ferric ion in this pH range is therefore not surprising. The HO_2 radical will be significant mainly in the presence of oxygen, in view of the reaction $H + O_2 \rightarrow HO_2$. In the absence of oxygen ferrous ion should be oxidized by the OH radical ($Fe^{+2} + OH \rightarrow Fe^{+3} + OH^-$) and the reviewer suggests that ferrous ion might be oxidized even by hydrogen atoms, as the reaction

$$Fe^{+2}(HOH) + H \rightarrow Fe^{+3}OH^- + H_2$$

is exothermic to an extent of ~20 kcal. The reaction

$$Fe^{+2} + OH \rightarrow Fe^{+3} + OH^-$$

could also be affected by the presence of oxygen if traces of organic impurities are present. The important effect of trace impurities on the reaction kinetics, which was recently discovered in the reactions of Fenton's reagent (*cf.* page 406) has not yet been fully applied to radiation chemistry. The yield of ferric ion in air-free solutions is accordingly much smaller than in aerated solutions (220). It appears doubtful whether the reaction

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH$$

is significant, as in view of the very fast reaction

$$Fe^{+2} + OH \rightarrow Fe^{+3} + OH^-$$

hydrogen peroxide cannot be formed in appreciable quantities except in the center of the radiation track. Amphlett (8) has shown that under suitable conditions ferric ion is quantitatively reduced as a result of the radiolysis of water. This applies to systems where the ferrous ion produced forms a very stable complex, e.g., in the presence of *o*-phenanthroline. Various other effects of complex formation in the ferric–ferrous system are described, including the formation of $Fe^{+3}OH^-$, which may account for some observations relating to pH dependence of the final Fe^{+3}/Fe^{+2} ratio. The reviewer considers, however, that the latter cannot be fully understood without taking into account the ionic dissociation of the HO_2 radical.

The radiolysis of aqueous solutions of halide ions has been discussed by Allen (7). Reactions of the type $OH + X^- \rightarrow OH^- + X$ are postulated. Data relating to the energetics of reactions of this kind ("radical–ion transfer") are given in table 2 (page 388).

While OH radicals are the oxidizing species, hydrogen atoms produced by ionizing radiations will frequently be of effective reducing power. This may lead, in some cases, to the establishment of redox equilibria, such as in systems containing nitrate and nitrite ions or arsenate and arsenite ions (Haissinsky and Lefort (180, 181)). The reducing effect of the OH radical was also recognized by the same authors (182). An example given was

$$Ce^{+4} + H_2O + OH \rightarrow Ce^{+3} + H^+ + H_2O_2$$

It is, however, more likely that the reaction proceeds *via* the ion-pair and is bimolecular, i.e.,

$$Ce^{+4}OH^- + OH \rightarrow Ce^{+3} + H_2O_2$$

as postulated by Evans and Uri (115). The energy data given by Haissinsky and Lefort (182) are, to a large extent, based on Pauling's monograph (257) and should be revised in view of recent findings (e.g., the heat of the reaction $H + OH \rightarrow H_2O$ given as 112 kcal. is too low).

In the α-ray-induced oxidation of formic acid to carbon dioxide and water it was shown that both OH radicals and hydrogen atoms were oxidizing entities. The initiation steps (184) are

$$\text{(a)}\ HCOOH + OH \rightarrow HOH + HCOO\cdot$$

and

$$\text{(b)}\ HCOOH + H \rightarrow H_2 + HCOO\cdot$$

The biological importance of the study of radiation chemistry has been recognized, and various investigations of biological interest have been carried out recently. The main aspects of these studies are related to the activity of H atoms and OH radicals, produced by radiolysis of water. These entities can lead to the deactivation of ribonuclease (75), to the hydroxylation of sterols (207, 208, 209), and to the deamination of amino acids (285, 288). The latter was studied by Dale (88). It was shown that ammonia is evolved when solutions of amino acids (e.g., glycine or serine) are irradiated with x-rays. It was also demonstrated that x-ray irradiation splits off hydrogen sulfide from sulfur-containing amino acids such as cysteine or glutathione. There is still some controversy as to whether H atoms or OH radicals are the active entities in deamination reactions (332). In view of the importance of this problem the reviewer suggests that this controversy could best be solved experimentally by comparison with photochemical systems such as

$$H_2O_2 \xrightarrow{h\nu} OH + OH$$

$$Fe^{+3}OH^- \xrightarrow{h\nu} Fe^{+2} + OH$$

$$Ce^{+4}OH^- \xrightarrow{h\nu} Ce^{+3} + OH$$

$$Fe^{+2}(H_2O) \xrightarrow{h\nu} Fe^{+3}OH^- + H$$

$$Ti^{+3}(H_2O) \xrightarrow{h\nu} Ti^{+4}OH^- + H$$

in which either only OH radicals or H atoms are produced but not both entities simultaneously, as they are formed in the radiolysis of water.

An interesting comparison has been made by Miller (248) between the chemical action of ionizing radiations and that of ultrasonic radiations on aqueous solutions.

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