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THE RADIATION CHEMISTRY OF WATER

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As we noted in Chapter Two, few objections can be made to the assumption that the radical OH and its dimer H₂O₂ are the main, and practically the only oxidizing primary products of water radiolysis. It has been shown that the radical HO₂ also appears quite early in the radiolysis of water as a result of the intraspur reaction between OH and H₂O₂. However, its yield is negligibly low for radiations of low LET (such as, for example, ⁶⁰Co γ-radiation), but it may be more appreciable in the case of radiolysis induced by heavy particles [1,2]. Nevertheless, in this chapter we shall consider the hydroperoxyl radical because of the considerable role it often plays as a secondary product of the radiolysis of water and aqueous solutions containing oxygen. In this case, the primary reducing products H and e_{aq}⁻ react very rapidly with oxygen to produce HO₂ and O₂⁻, thereby replacing the reactive reducing species by others with mainly oxidizing character.

There is no doubt that over a wide range of pH the hydroxyl radical is a neutral species properly represented by OH. As we shall see, this conclusion follows from experiments in which its reaction rate constant was measured at different ionic strengths. The question arises as to the extent to which its acid form, H₂O⁺, is formed in acid media; only a few indications exist in its favor, and there is more evidence to the contrary. In alkaline media the reaction of the hydroxyl radical with OH⁻ ions leads to the formation of O⁻ ion radicals. Although this entity is a secondary radical, we shall consider it here at some length; the transformation is very effective in alkaline medium and the behavior of O⁻ does not seem to be identical in every respect with that of OH, although both are oxidizing species.

Considerations of the origin of the primary molecular product (H₂O₂) shed more light upon the water radiolysis model and hence will be discussed in some detail.

We refer the reader who is interested in the subject treated in this chapter to the review articles [3-5]. An account of the thermochemistry of the radicals OH and HO₂ is given in an article by Gray [6].

CHAPTER FOUR

Primary Products of Water Radiolysis: Oxidizing Species— The Hydroxyl Radical and Hydrogen Peroxide

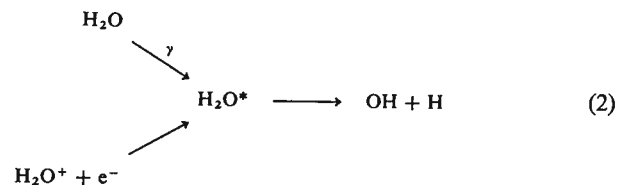
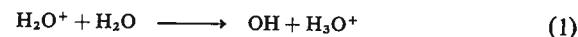
I. PROPERTIES OF THE HYDROXYL RADICAL

A. One of the Most Powerful Oxidizing Short-Lived Species

Baxendale [7] gives the value $E^0 = -2.8$ V for the pair OH-OH⁻ at [H⁺] = 1.0 M. This means, for example, that OH can oxidize all inorganic ions which can exist in higher valence states (such as Co²⁺, Ce³⁺, and Fe²⁺). Of course, whether the net balance of the reaction observed will always be oxidation depends on what other primary and secondary radicals are in the system (namely, H, e_{aq}⁻, and HO₂) and what they will do under given conditions.

The reaction with KMnO₄ is, for the present, the only one in which the OH radical is known to behave as a reducing agent.

We have seen in Chapter Three that elucidation of the origin of the primary reducing species has been the object of numerous studies. The origin of the hydroxyl radical lies, with little doubt, in the following reactions:

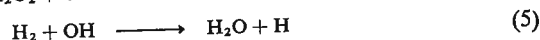
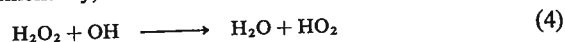


These were considered in Sections III and V of Chapter Two.

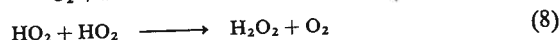
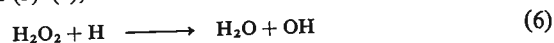
It has long been known that the photolysis of aqueous solutions of H_2O_2 produces hydroxyl radicals. The mechanism of this reaction is not simple [8]:



but under suitably chosen working conditions it can be a very useful source of hydroxyl radicals. Hochanadel [9] reasoned that if the primary oxidizing product of water radiolysis and the OH radical produced in reaction (3) are the same species, then the rate constants of their reactions with different scavengers should be the same within the limits of experimental error. To check this idea experimentally, the author chose the reactions

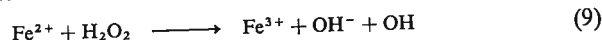


and determined k_5/k_4 . The measurements were carried out in a dilute solution of hydrogen peroxide in which H_2 and O_2 were present at various concentrations. The photolysis was brought about by light of a wavelength of 2537 Å. In addition to reactions (3)–(5), the reaction scheme also includes the reactions

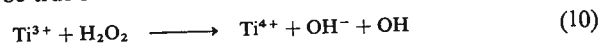


When experimental conditions were adjusted in such a way that $k_7[\text{O}_2] \gg k_6[\text{H}_2\text{O}_2]$, variation of the ratio of H_2 to H_2O_2 made it possible to determine the ratio k_5/k_4 from the competition diagram. The value obtained was almost the same as that previously measured for the radiolytically produced species in water radiolysis, with the presence of oxygen and hydrogen [10]. On this basis he concluded that in both cases the identical entity is involved.

Classical chemical reactions are also used to produce the OH radical for studies concerning its nature and for comparison with the behavior of radiolytically produced species. In Fenton's reagent, the radical is produced by the reaction of ferrous ions with an excess of H_2O_2 :



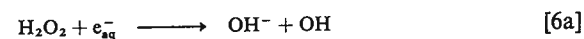
The same should be true for titanous ions:



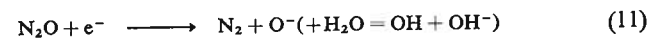
It has been reported [11] that relative rate constants for OH radical reactions with different solutes are in quite good agreement when the radicals are produced by Fenton's reagent or by radiations. However, ESR studies do not confirm clearly that OH is the radical produced in reactions (9) and (10).

Publications [12–14] even point to the opposite: The active species must be a sort of complex between the reactants rather than an OH radical. The agreement between the relative constants does not necessarily indicate that in reactions (9) and (10) free radicals are directly involved. It is sufficient that the form in which the OH is complexed reacts slowly with the scavenger and is in equilibrium with the free OH [4]. In this connection, the following observation is worth attention: The ESR spectra of the hydroxyl radical generated by the titanous ion and hydrogen peroxide in a flow system show two peaks. The minor peak is attributed to the spectrum of the hydroxyl radical associated with the titanous ion. It decays according to a second-order rate equation. The observed rate constant is about four orders of magnitude lower than that for OH radicals [13].

Some other reactions also lead to the production of OH radicals in radiation chemistry. Thus, the primary reducing species reacting with hydrogen peroxide produces OH radicals as given by Eq. (6) or by



Nitrous oxide efficiently converts hydrated electrons into hydroxyl radicals:



This is certainly one of the most frequently used reactions; in the study of aqueous solutions it was introduced by Proskurnin and Kolotyrlin [15].

B. Absorption Spectrum

Some observations in connection with the absorption of light in water vapor [16] indicated that the OH radical might display a weak absorption in the uv region in liquid water. Identification was not easy, since the molar extinction coefficient is small and many other radicals absorb in the same region [17–19]. Figure 4.1 represents the spectrum of the hydroxyl radical. It is worth noticing that the absorption observed in liquid water is less pronounced than that in the gaseous state; it is also shifted toward shorter wavelengths.

The practical importance of this absorption spectrum is far less than that of the hydrated electron (Chapter Three). The molar extinction coefficient is only $4 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ at 2600 Å [19], and the spectral region in which the absorption appears is not very suitable for routine measurements.

The effect of various scavengers on the intensity of absorption provided evidence that the spectrum can be ascribed to the hydroxyl radical. It was shown that only the substance known as scavenger for hydroxyl radicals decreases the optical density. The conversion of hydrated electrons into hydroxyl radicals increased the measured optical densities. From such experiments the rate constants of some reactions could be calculated in good

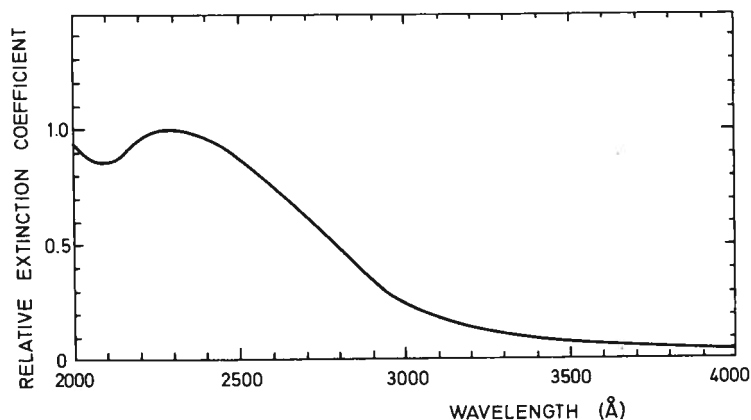


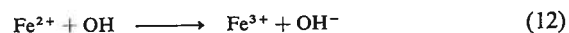
Fig. 4.1. Absorption spectrum of the hydroxyl radical. Normalized to 1.00 at 2300Å. (After Pagsberg *et al.* [19] and Boyle *et al.* [18].)

agreement with those of OH radical reactions obtained by indirect measurements.

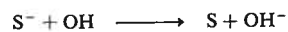
C. Reactivity

The types of reactions of OH with stable species or free radicals are varied. Electron transfer is the most frequent mechanism of OH-induced oxidation of both inorganic anions and cations. Hydrogen atom abstraction and OH addition are the most common types of reaction with organic molecules. Addition reactions also occur with free radicals.

Electron transfer reactions may give rise to a stable product, as is the case in the well-known reaction of oxidation of the ferrous ion to the ferric ion:

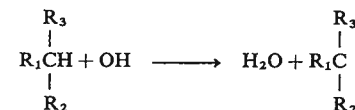


However, radiation-chemical experiments have also revealed the existence of short-lived products with higher degrees of oxidation; for example, Cu^{3+} [20] and Ag^{2+} [21]. In reactions with anions, electron transfer leads to the formation of a free radical. The reaction with halides has been studied in detail:



where S^- is Cl^- , Br^- , or I^- , and S is the corresponding radical Cl, Br, or I. It was found [22–28] that it is more complex than was previously admitted [29–31]. The halogen atoms react with the solute, $\text{S} + \text{S}^- \rightarrow \text{S}_2^-$, producing ion radicals which also take part in the radiation-induced process.

Abstraction of hydrogen in the reaction of OH with an organic molecule can be written in the general case as



where R_1 , R_2 , and R_3 stand for atomic hydrogen or a certain functional group. These reactions are usually slower than electron transfer. Their rate depends on many factors, particularly on the distribution of electrons in the molecule, which is, of course, affected by the type and arrangement of the functional groups. The disappearance of the organic free radical formed may occur through different reactions. If oxygen is present in the aqueous solution, organic free radicals react with it and the rate constants are often close to the diffusion-controlled value [32]. In the absence of oxygen the disproportionation and dimerization often take place.

The case of the recombination of the α -ethanol radical will be treated at some length as a suitable example of a second-order reaction. Let us first consider the general case where free radical R disappears by the recombination process whence product P is formed:



$$-\frac{d[\text{R}]}{dt} = 2k[\text{R}]^2$$

If the radical R has a suitable absorption spectrum in a region where P does not absorb, the reaction may be conveniently followed by observing the variation in [R]. In this case it is easier to deal with optical densities, OD, than with radical concentrations, [R]. According to the Lambert-Beer law,

$$\text{OD} = \epsilon[\text{R}]l$$

or

$$[\text{R}] = \frac{\text{OD}}{\epsilon l}$$

where ϵ is the molar extinction coefficient, [R] is the radical concentration, and l is the path of the light in the sample. Introducing $\text{OD}/\epsilon l$ and integrating the above differential expression in the range $t = 0$ to $t = t$, we have

$$\left(\frac{\epsilon l}{\text{OD}}\right)_t - \left(\frac{\epsilon l}{\text{OD}}\right)_0 = 2kt$$

or,

$$\frac{1}{\text{OD}_t} = \frac{2k}{\epsilon l} t + \frac{1}{\text{OD}_0}$$

We see that in the plot of reciprocal optical densities against time the slope of the straight line ($\tan \alpha = 2k/\epsilon l$) enables one to calculate the rate constant

$$2k = \epsilon l \tan \alpha$$

The value of $2k$ can also be calculated from the initial concentration of the reacting species $[R]_0$ and the experimentally determined initial half-life of the reaction ($t_{1/2}$):

$$2k = \frac{1}{[R]_0 t_{1/2}}$$

The intercept on the y -axis gives $[R]_0 = OD_0/\epsilon l$; hence, the above expression becomes

$$2k = \frac{\epsilon l}{OD_0 t_{1/2}}$$

The α -ethanol radical has a characteristic absorption spectrum with $\epsilon_{2967} = 240 M^{-1} \text{ cm}^{-1}$, and the measurement of OD_{2967} affords a convenient measure of its concentration [33]. A test of the second-order rate law for the disappearance of the α -ethanol radical is shown in Fig. 4.2. We can see that $1/OD_t$ values increase with the time after the pulse. From these data we calculate the slope:

$$\text{ordinate} = 17.1 - 2.9 = 14.2$$

$$\text{abscissa} = 40 \times 10^{-6}$$

$$\tan \alpha = \frac{14.2}{40 \times 10^{-6}} = 0.355 \times 10^6$$

Since $\tan \alpha = 2k/\epsilon l$, $\epsilon = 240 M^{-1} \text{ cm}^{-1}$, and $l = 16 \text{ cm}$, $2k = 0.355 \times 10^6 \times \epsilon \times l = 0.355 \times 240 \times 16 \times 10^6$, that is, $2k = 1.36 \times 10^9 M^{-1} \text{ sec}^{-1}$. Another way of calculating $2k$ is to determine the initial half-life of the reaction ($t_{1/2}$). By taking the double initial concentration on the y -axis, we read the corresponding half-life value on the x -axis: $t_{1/2} = 8.1 \mu\text{sec}$. The intersection of the straight line with the y -axis gives $1/OD_0 = 2.9$. Since $2k = \epsilon l/OD_0 t_{1/2}$, substituting $\epsilon = 240 M^{-1} \text{ cm}^{-1}$ and $l = 16 \text{ cm}$, we obtain

$$2k = \frac{2.9 \times 240 \times 16}{8.1 \times 10^{-6}} = 1.37 \times 10^9 M^{-1} \text{ sec}^{-1}$$

Dorfman *et al.* [34] were the first to show that in aqueous solutions of benzene the addition reaction of the hydroxyl radical occurs. They observed a transient spectrum which was assigned to an OH-benzene adduct (a cyclohexadienyl radical):

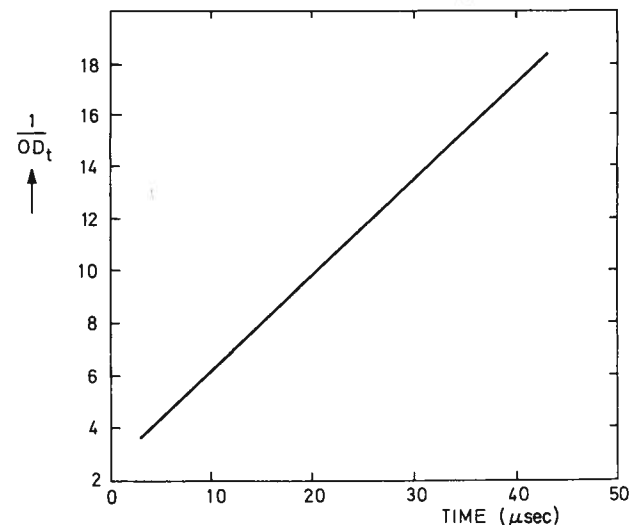


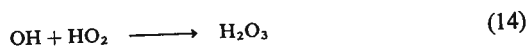
Fig. 4.2. The recombination reaction of the α -ethanol radical in irradiated aqueous solution as an example of a second-order process. (After Dorfman and Taub [33].)

Direct measurements showed that k_{13} is almost diffusion-controlled. This was most surprising, since OH addition must result in the loss of some of the resonance energy of the aromatic nucleus. Nevertheless, subsequent work has confirmed the very large rate constants for reactions of this type [35].

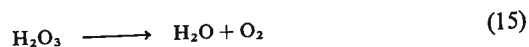
Many absolute rate-constants of OH radical reactions were measured by exploiting the convenient absorption spectrum of the OH adduct of the studied compound. In these experiments it is important to take into account the possibility of simultaneous formation of an H atom adduct; this may have very similar properties and can influence the conclusions regarding the hydroxyl adduct. It has been taken into consideration in the pulse radiolysis of nitrobenzene solutions [36], as well as in pulse studies of aqueous benzoic acid solutions [37].

The fate of an OH adduct has been considered in detail in the case of the cyclohexadienyl radical; Čerček [38] has shown how the substituent X in $\text{HOC}_6\text{H}_5\text{X}$ influences recombination reactions and the reactions with oxygen. Chambers *et al.* [39-41] have reported data concerning adducts of vinyl compounds.

It is interesting that not only addition reactions to stable molecules but also to free radicals have been observed. It has been shown [42] that the following reaction occurs in aqueous solutions at high electron dose rates obtained with an accelerator:



In acid medium ($0.02 M \text{H}_3\text{O}^+$) the product obtained has a half-life of 2 sec, which decreases with the change of pH. The disappearance of H_2O_3 can be represented as

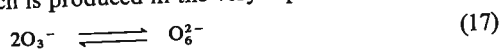


Polarographic measurements made during irradiation under the same conditions [43], allowing H_2O_2 and O_2 to be followed simultaneously, called in question the importance of reaction (14). Bielski [44] subsequently ascribed to the H_2O_3 species a characteristic absorption spectrum with a peak below 2000 \AA . For the molar extinction coefficient he gave values of 100 and $200 M^{-1} \text{cm}^{-1}$ at 2400 and 2000 \AA , respectively. The presence of oxygen is necessary for the generation of this product in irradiated water, and scavengers for hydroxyl radicals decrease or completely inhibit its formation.

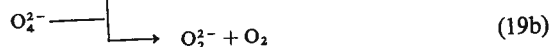
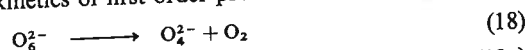
There is no evidence that the OH radical reacts with oxygen. However, the addition of the O^- ion radical to O_2 ,



is not only known to occur, but has also been studied in some detail [45-50]. The product of this reaction—the ozonide ion—has a characteristic absorption maximum at 4300 \AA , where the molar extinction coefficient is about $2000 M^{-1} \text{cm}^{-1}$. The rate constant of reaction (16) is very high, $2.5 \times 10^9 M^{-1} \text{sec}^{-1}$ [45,47]. The half-life of the O_3^- ion radical amounts to several milliseconds and is longer with higher pH [46] and concentration of oxygen in solution [48]. It has been observed to disappear in a first-order process, and also in a second-order process at higher concentrations. The pseudo-first-order process was accounted for as follows [48]: The species which we directly observe by measuring the absorption spectrum of the irradiated solution is not O_3^- but its dimer, which is produced in the very rapid reaction



and which has the same absorption spectrum and molar extinction coefficient as the ozonide ion. Possible reactions proposed for the disappearance of the dimer which satisfy the kinetics of first-order processes were the following:



In a recent work [50], however, it is assumed that the decay of the ozonide ion in aqueous solution occurs through the thermal dissociation reaction, $\text{O}_3^- = \text{O}_2 + \text{O}^-$, for which the rate constant is $3.3 \times 10^3 \text{ sec}^{-1}$ and the activation energy is $11 \text{ kcal mole}^{-1}$.

Tables 4.1 and 4.2 summarize the rate constants of OH radical reactions with some free radicals and substances more frequently used in routine experiments.

It should be noted that at the present time our knowledge of OH radical rate constants is much less complete than for the hydrated electron. The lack

TABLE 4.1
RATE CONSTANTS FOR OH AND O^- RADICAL REACTIONS
WITH SOME INORGANIC SOLUTES AND FREE RADICALS

Reactant	Rate constant, $M^{-1} \text{sec}^{-1}$	pH	Reference
Br^-	5×10^9	2	[25]
	1.2×10^9	5-9	[26]
CNS^-	2.8×10^{10}	2; Neutral	[28]
	6.6×10^9	Neutral	[51]
(+ O^-)	1×10^9	13	[52a]
CO_3^{2-}	4.2×10^8	10.76	[53]
(+ O^-)	$<3 \times 10^6$	13.5	[53]
Cu^{2+}	3.5×10^8	Neutral	[20]
e_{aq}^-	3×10^{10}	11	[54,55]
(+ O^-)	2.2×10^{10}	13	[54]
$\text{Fe}(\text{CN})_6^{4-}$	1.1×10^{10}	3-10	[56]
	1.07×10^{10}	—	[57]
(+ O^-)	$<7 \times 10^7$	13.5	[57]
H	3.2×10^{10}	—	[58]
	7×10^9	—	[17]
H_2	6×10^7	7	[17]
	4.5×10^7	7	[59]
(+ O^-)	8×10^7	13	[54]
HCO_3^-	1.5×10^7	8.4	[53]
H_2O_2	4.5×10^7	7	[59]
	1.2×10^7	0.4-3	[58]
	2.25×10^7	—	[60]
	1.7×10^7	Neutral	[61]
HO_2^- (+ O^-)	7×10^8	13	[49]
	2.74×10^8	13	[62]
I^-	3.4×10^{10}	2; 7	[28]
	1.02×10^{10}	Neutral	[60]
O_2 (+ O^-)	2.5×10^9	13	[45,47]
O^- (+ O^-)	1×10^9	13	[56,57]
	8×10^8	13	[5]
OH	6×10^9	0.4-3	[56-58]
	5.0×10^9	—	[17,19]
	4×10^9	—	[59]
(+ O^-)	$\sim 1 \times 10^{10}$	~ 12	[5,57]
OH^-	3.6×10^8	—	[9,63]

TABLE 4.2
RATE CONSTANTS FOR OH AND O⁻ RADICAL REACTIONS
WITH SOME ORGANIC SOLUTES

Reactant	Rate constant, $M^{-1} \text{ sec}^{-1}$	pH	Reference
Benzene	4.3×10^9	—	[34]
	7.8×10^9	7	[35]
Benzoate ion (+O ⁻)	6×10^9	6-9.4	[35]
	$<6 \times 10^6$	13	[50]
Benzoic acid	4.3×10^9	≤ 3	[37]
Benzonitrile	4.9×10^9	7	[35]
Ethanol	1.6×10^9	Neutral	[61]
	1.83×10^9	—	[35]
	1.0×10^9	10.7	[51]
	7.2×10^8	7	[60]
(+O ⁻)	8.4×10^8	13	[50]
	2.2×10^9	Neutral	[61]
Formate ion	2.5×10^9	7	[60]
	9.5×10^8	Neutral	[61]
Methanol	8.4×10^8	—	[35]
	4.7×10^8	10.7	[51]
	4.7×10^8	7	[60]
	5.2×10^8	13	[50]
(+O ⁻)	3.2×10^9	7	[35]
	4.7×10^9	7	[36]
PNDA	1.25×10^{10}	Neutral	[61]
2-Propanol	1.5×10^9	Neutral	[61]
	1.74×10^9	Neutral	[60]

of a suitable absorption spectrum of the OH radical is certainly one important reason. Another reason is that most information comes from competition studies, both from classical and pulsed-beam experiments. A serious inconvenience is not only that they are time-consuming, but often the reaction schemes may be more complex and less understood than admitted. The case of the rate constants for hydroxyl radical reactions with ethanol and methanol is quite illustrative of this. Comparison of published values obtained in pulsed-beam competition experiments shows considerable discrepancies. The values obtained with aromatic compounds [35] as competitors are almost twice as large as those measured with carbonate, thiocyanate, and selenite ions [51] or iodides [60]. Some details will be considered in Section III.

A large number of organic substances [64], in particular nucleic acids [65], have been studied in pulsed-beam experiments in the presence of thiocyanate ion. Although the rate constants reported should be taken with some reserve, they afford a valuable general picture of hydroxyl radical reactivities toward

these compounds. In analyzing these and some other data, one finds the following:

- Rate constants for simple aliphatic acids are pH-dependent; the reactivities of the dibasic acids, $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, increase with increasing values of n .
- For simple straight-chain aliphatic alcohols, rate constants increase with chain length.
- Aliphatic esters are, in general, less reactive than the corresponding alcohols.
- Free amino acids are less reactive than the simple peptides.

II. FORMS OF THE HYDROXYL RADICAL IN IRRADIATED WATER AT VARIOUS pH's

A. Kinetic Salt Effect: The Radical Is Uncharged in Neutral Medium

In Section II of Chapter Three we have seen how the primary kinetic salt effect helped to establish that the reducing species is the hydrated electron, that is, a species carrying unit negative charge. Hummel and Allen [66] have proceeded from the assumption that corresponding experiments with variation of ionic strength of solution and measurement of the rate constant of reactions with the species said to be the hydroxyl radical may give answer as to whether a neutral or a charged particle is in question here. The authors followed formation of H_2O_2 for different ratios of Br^- and $\text{C}_2\text{H}_5\text{OH}$ in oxygenated aqueous solutions. The construction of a competition diagram and calculation of the relative rate constant of reaction of the OH radical with Br^- and ethanol show that ionic strength of solution has no effect on the rate constant. The concentration of the electrolytes KClO_4 and LiClO_4 present was amounting to as much as $5 \times 10^{-2} M$; hence, if a charged particle is in question, the rate constant should have changed appreciably. From these experiments, the unambiguous conclusion follows that the oxidizing radical under the conditions studied (neutral pH) is not charged and is most likely to exist in the form of OH.

B. Concerning the Existence of $\text{H}_2\text{O}_{\text{aq}}^+$ in Acid Media

It is certain that the positive water ion, H_2O^+ , produced in the physical stage of radiolysis, is not likely to live sufficiently long to react chemically. We have seen (Chapter Two) that its reaction with another water molecule, to which it is bound by hydrogen bonds ($\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_3\text{O}^+$), takes about 10^{-14} sec. However, some experiments on radiation-induced hydroxylation could be interpreted only by assuming that the hydroxylating

agent is not a neutral but a positively charged particle [67]. Its existence was also assumed in explaining the pH dependence of rate constants of hydroxyl radicals with halide ions [68]. These assumptions are not very plausible. It was shown [69] that the relative rate constant of OH reaction in the system iodide-isopropanol is independent of $[H_3O^+]$ at H_2SO_4 concentrations ranging from 0.05 to 1.00 M. This finding points out that the existence of the equilibrium $H_{aq}^+ + OH \rightleftharpoons H_2O_{aq}^+$ also needs experimental verification.

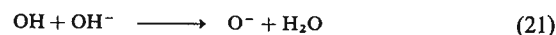
C. Conversion of OH into O^- in Alkaline Media

The dissociation of the hydroxyl radical in alkaline media has been considered frequently. It is represented in terms of formal ionization as

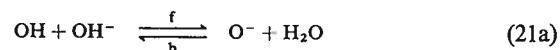


for which $pK_{OH} = 11.9$ is given. This value has been obtained in independent competition experiments with good agreement; Rabani and Matheson [56] were the first to determine it by observing the effect of pH on change in the rate constant of reaction of the hydroxyl radical with ferrocyanide. The oxidation rate decreases with increasing pH and points to alteration of the nature of the OH radical. From the amount of change, the value of pK was derived. Almost the same values were obtained with oxygenated solutions of CNS^- [52a] and deaerated carbonate solutions [53].

As a matter of fact, it seems more convenient to consider the conversion of the hydroxyl radical into O^- simply in terms of the reaction



where the hydroxyl ion is in competition for the OH radical like any other scavenger present; $k_{21} = 3.6 \times 10^8 M^{-1} sec^{-1}$ [9,63]. It is easily seen that reaction (21), the conversion of OH into O^- , becomes important in alkaline solutions where the total reactivity of solute S, defined as $k_{OH+S} \times [S]$, is low as compared to $k_{OH+OH^-} \times [OH^-]$. However, a recent study indicates that k_{21} is much larger than the value quoted above. According to these pulsed-beam experiments [52b], an important feature of the chemistry of OH radical in alkaline solution is the equilibrium



with $k_{21af} = 1.2 \times 10^{10} M^{-1} sec^{-1}$ and $k_{21ab} = 9.2 \times 10^7 sec^{-1}$.

The ion radical O^- absorbs in the uv region, with a peak at 2400 Å and $\epsilon_{2400} = 240 M^{-1} cm^{-1}$ [62]. The mechanism of its decay is not fully understood [5,62]. Like the hydroxyl radical, the O^- ion radical is an oxidizing species, but some differences in their behavior may be quite important:

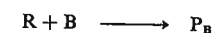
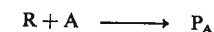
- The radical ion O^- reacts rapidly with oxygen, whereas the hydroxyl radical is inert or reacts very slowly.
- The radical ion O^- reacts more rapidly with H_2 and H_2O_2 than does the OH radical.
- The recombination of O^- is considerably slower than that of OH.
- In electron transfer reactions, the difference in behavior is great; O^- reacts much more slowly than does OH; CNS^- , CO_3^{2-} , and ferrocyanide are less effectively oxidized ($10-10^3$ times) by O^- .
- In hydrogen abstraction reactions, O^- and OH seem to be about equally efficient.

III. RELATIVE RATE CONSTANTS OF HYDROXYL RADICAL REACTIONS; COMPETITION KINETICS

In considering reaction rates we have so far dealt mainly with the direct determination of absolute reaction rate constants. These methods are, although in principle simple since the production or disappearance of one reactant is directly followed, rather limited. The fact that insufficient data are available on the characteristic optical and other physicochemical properties of free radicals often makes interpretation of the results arbitrary and sometimes even impossible. On the other hand, the short duration of the processes considered calls for expensive equipment such as pulsed-radiation sources and detection devices of high sensitivity suitable for these measurements.

Another method is more often used. It consists in adding to the irradiated solution two substances which react in competition with the species studied. Observing a reaction product for different ratios of concentrations of these substances, one determines the ratio of the rate constants of the free radical. The accuracy of these relative rate constants is somewhat lower than that of absolute values. The procedure here is also more time-consuming, but its advantage is that the standard equipment for physicochemical analyses suffices.

If the nature of the competition process is simple, the mathematical expressions used in competition kinetics are also simple. Consider the competition of substances A and B in solution for radical R:



where P_A and P_B are the corresponding products. The probability that radical R will react with substance A is given by the expression

$$\frac{k_A[A]}{k_A[A] + k_B[B]}$$

where k_A and k_B are the corresponding rate constants of reactions of the radical R with the substances A and B. If we express this in terms of the radiation-chemical yields of the product formed, $G(P_A)$, and of the reacting radical, G_R , then we have

$$G(P_A) = G_R \frac{k_A[A]}{k_A[A] + k_B[B]}$$

For convenience, in graphically representing experimental data on the yield $G(P_A)$ for different ratios $[A]/[B]$ of substances used as scavengers for radical R, this expression is reduced by suitable transformations to an equation of the type $y = b + ax$:

$$\frac{1}{G(P_A)} = \frac{1}{G_R} \frac{k_A[A] + k_B[B]}{k_A[A]} = \frac{1}{G_R} + \frac{1}{G_R} \frac{k_B[B]}{k_A[A]} \quad (22)$$

We see that here the yield of product [$y = 1/G(P_A)$] is a variable depending on the ratio of concentrations of scavengers ($x = [B]/[A]$). The segment of the ordinate ($b = 1/G_R$) allows one to calculate the radiation-chemical yield of the free radical whose reaction is being studied. From the slope,

$$\tan \alpha = \frac{1}{G_R} \frac{k_B}{k_A}$$

which is calculated from the diagram, and the segment of the ordinate, one calculates the relative rate constant to be determined for the reaction of the radical (k_B/k_A). Measurement of the yield of product P_B may serve in the same way for the determination, if it is more convenient than that of P_A

$$\frac{1}{G(P_B)} = \frac{1}{G_R} + \frac{1}{G_R} \frac{k_A[A]}{k_B[B]} \quad (22a)$$

Figure 4.3 illustrates the method.

It is worthwhile to point out the importance of some difficulties in determinations of the true initial yield, $G^0(P)$, of the stable product which is followed during a competition study. For a reaction product to be measurable it is necessary that it attains a certain minimum concentration required by the sensitivity of the analytical method. This accumulation, however, may have as a consequence the involvement of the product itself in the reaction mechanism, so that its radiation-chemical yield changes. This is most often noticed as a decrease in the yield with increasing absorbed dose. In such cases, the initial yield $G^0(P)$ should be calculated from a diagram in which the measured $G(P)$ values are presented as a function of the dose absorbed. The ordinate for zero abscissa then gives the initial yield $G^0(P)$ to be determined.

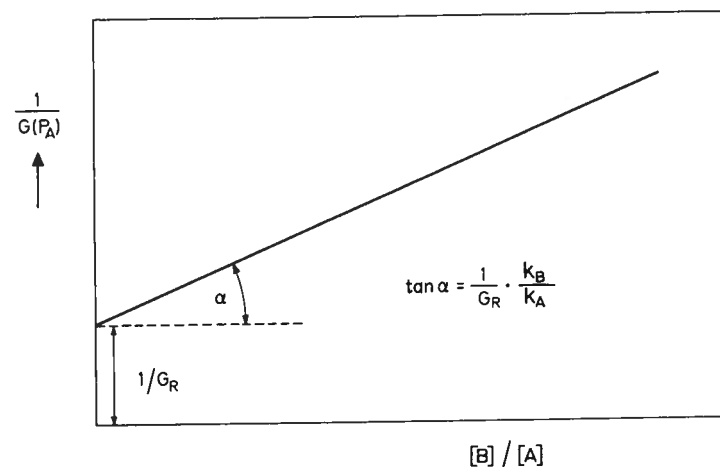


Fig. 4.3. The competition plot used in the relative rate constant determinations.

A cross check is sometimes used for the verification of relative rate constants [70]. For k_A/k_B it consists in the following: The data are also sought for systems B + C and C + D (k_B/k_C and k_C/k_D , respectively). By multiplying $(k_A/k_B)(k_B/k_C)(k_C/k_D)$, the value k_A/k_D is calculated. If the measurements in the system A + D give a value of the relative rate constant in agreement with the one calculated above, then there is the possibility that the verified k_A/k_B ratio is correct. This will not necessarily always be the case; the shortcomings of reaction schemes may influence relative rate constants in such a way that the errors are canceled or diminished and that the agreement is only apparent. It should also be recalled that in the above calculation the errors are accumulated, so that the accuracy of the calculated ratio is quite low.

Most of the published values for $k(\text{OH} + \text{S})$ were obtained by the competition procedure described above. Quite a few of them should be accepted with caution, as the interpretations of reaction mechanisms have turned out to be much more complex than was previously assumed. The number of reported rate constants with OH and O^- radicals is still very limited [71]. The reason lies in the difficulty of choosing a competing solute; the mechanism of its change must be well established and the amount of change must be measurable by a simple and accurate method. As we shall see, both conditions are seldom completely satisfied. In the case where benzoic acid was used as the competitor, Mathews and Sangster [72] used a somewhat complex radioactive tracer method; the radioactivity of $^{14}\text{CO}_2$, formed by acid

decomposition, was measured for various ratios of concentrations of benzoic acid and the solute under study in irradiated solutions. Another procedure was experimentally very simple but, as shown subsequently, the reaction mechanism was more complicated than was initially supposed. This is the case of *p*-nitrosodimethylaniline (PNDA) which has a suitable absorption spectrum and a large molar extinction coefficient ($\epsilon = 34200 M^{-1} \text{ cm}^{-1}$ at 4400 Å). The procedure proposed [73a] was extremely simple: The changes of optical density of PNDA should be measured in irradiated solutions containing different ratios of PNDA and the solute studied. It was assumed that the working conditions could be chosen so that the decrease in optical density is the consequence of only OH radical attack on the chromophoric group of PNDA. However, this assumption was subsequently found to be invalid [61,73b] in most of the experiments, since PNDA reacts efficiently not only with OH but with all primary free radicals (OH, H, and e_{aq}^-), as well as with different organic radicals. The reaction scheme is also complicated by the fact that the recombination of the radical formed in the OH + PNDA reaction is very efficient.

In the case of thymine, the experimental procedure seems very simple: The relative rate constant is determined by measuring the decrease of absorption of the chromotropic group on irradiation of aqueous solutions containing different ratios of studied solute and thymine [65,74]. The light-absorbing substance is thymine; it is assumed that only the OH attack causes the decrease of absorption. It is, nevertheless, worth noticing that many of the rate constants obtained by this procedure are close to the values obtained by PNDA, or by pulse competition with CNS^- , which we saw to be dubious or even incorrect. It is also known that thymine is destroyed by alcohol radicals even in the presence of oxygen; the attack by H atoms can be very important under certain working conditions, as the rate constant for thymine + H was found to be $8 \times 10^8 M^{-1} \text{ sec}^{-1}$ [75]. These findings indicate that a better knowledge of the radiolytic mechanism is still needed if one wishes to avoid surprises similar to those encountered in the PNDA case.

Marketos [76] has shown that the air-saturated aqueous solutions of Safranin T (trade name of 3,6-diamino-2,7-dimethyl-10-phenyl-phenazonium chloride) can be used in competition studies at pH 0.4-5.5. It was assumed that in aerated aqueous solutions this substance is irreversibly oxidized by OH radicals only and that H_2O_2 , HO_2 , and O_2^- do not react with it. Only the rate constants of hydroxyl radical reactions with halide ions were determined, and the system deserves more attention.

In pulsed-beam experiments a simplified competition procedure is quite often used. The measurements consist of optical density determinations of the solution at a fixed time after the electron pulse. In this method, the studied solution contains a substance A which reacts efficiently with the hydroxyl

radical with known $k_{\text{OH}+\text{A}}$ to give a product P_A , having a suitable absorption spectrum. Its concentration is then

$$(\text{OD})_0 = [\text{P}_\text{A}]_0$$

where $(\text{OD})_0$ denotes the absorption measured under strictly defined conditions. If one now adds to the solution a substance B whose rate constant $k_{\text{OH}+\text{B}}$ is to be determined, then it will scavenge a certain fraction of the OH radicals. As a consequence, the light absorption due to P_A will be decreased, and the new value of the optical density (OD) can be expressed by

$$(\text{OD}) = [\text{P}_\text{A}]_0 = \frac{[\text{P}_\text{A}]_0}{1 + \frac{k_{\text{OH}+\text{B}}[\text{B}]}{k_{\text{OH}+\text{A}}[\text{A}]}}$$

From these relations we obtain the following expression, which is convenient for the construction of the competition diagram:

$$\frac{(\text{OD})_0}{(\text{OD})} = 1 + \frac{k_{\text{OH}+\text{B}}[\text{B}]}{k_{\text{OH}+\text{A}}[\text{A}]} \quad (23)$$

On the *x*-axis we plot different ratios of concentrations of scavengers $[\text{B}]/[\text{A}]$, and on the *y*-axis we plot $(\text{OD})_0/(\text{OD})$. In the case of a true competition, we obtain a competition diagram similar to the one in Fig. 4.3. The rate constant to be determined is calculated as $k_{\text{OH}+\text{B}} = \tan \alpha \times k_{\text{OH}+\text{A}}$, where $k_{\text{OH}+\text{A}}$ is known.

For such pulse-competition experiments the ions CNS^- [51,52a,64,65,77] and I^- [60] were quite often used as scavenger A. Unfortunately, a large number of rate constants of the OH radical obtained by these experiments seem to be practically of no use. Baxendale *et al.* [28] were the first to show that in the case of CNS^- , contrary to what was assumed, the rate constant measured does not concern



but $(\text{CNS})_2^-$, formed in the reaction

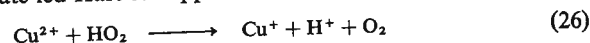


Also, the reaction scheme may become complicated due to the competition of reaction (25) with some other reactions, where the CNS radical disappears attacking the studied solute and/or some secondary radicals. In the same work [28] the conclusion is also drawn that iodide is not suitable as standard in the competition method of determining OH radical rate constants. Here also, the competition kinetics may not apply because of reactions similar to those mentioned for CNS^- as standard competing solute.

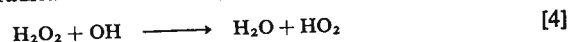
IV. THE HYDROPEROXYL RADICAL

A. More Important as a Secondary Radical Than as a Primary Species in the Radiolysis of Aqueous Solutions

The appearance of oxygen in the radiolysis of degassed solutions of ferrous sulfate-copper sulfate led Hart to suppose the existence of the reaction [1]

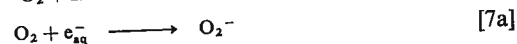


Since the solutions were carefully degassed, the author assumed that the origin of the hydroperoxyl radical is in the intraspur reaction



The concentration of radicals in the spur produced by γ rays is low, and it is obvious that G_{HO_2} cannot be large for radiations with low LET values. However, if the assumption is valid, then an increase in LET also leads to an increase in the concentration of hydroperoxyl radicals existing in the beginning of the chemical stage of water radiolysis. Donaldson and Miller [2] found that G_{HO_2} actually increases from 0.026 for ^{60}Co γ -radiation to 0.25 for 5.4-MeV α -radiation. The value of G_{HO_2} for radiations with low LET is small and comparable to experimental error, so that it need not be taken into account in establishing a quantitative reaction scheme in such cases. This is not the case for high-LET studies, but these are still scarce (Chapter Five, Section VI).

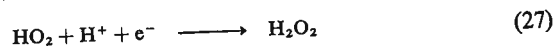
However, the hydroperoxyl radical is very important as a secondary radical in the radiolysis of aqueous solutions in the presence of oxygen. The importance lies in the fact that the very rapid reactions (see Chapter Three)



both of the order of $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, convert reactive species of markedly reducing character into less reactive species of mainly oxidizing character. Since oxygen is usually present in aqueous solutions, the presence of hydroperoxyl radicals is often unavoidable. That is why we shall consider at some length its properties and different reactions, which have been the subject of numerous studies.

B. Properties of the Hydroperoxyl Radical

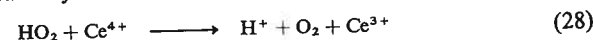
Baxendale's considerations [7] of redox potentials well illustrate the nature of HO_2 . He calculated that in acid solution $E^0 = -1.7 \text{ V}$ for the couple $\text{HO}_2, \text{H}^+/\text{H}_2\text{O}_2$, i.e., for standard change in the free energy of the reaction



IV. THE HYDROPEROXYL RADICAL

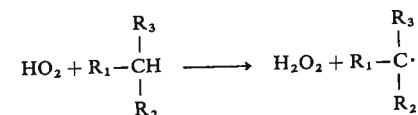
Hence, it follows that under standard conditions the HO_2 radical is as effective an oxidizing agent as, for example, Ce^{4+} ($E^0 = -1.61 \text{ V}$). Evidence was afforded that it takes part in radiation-induced oxidation of a number of inorganic ions (for example, As^{3+} and Fe^{2+}).

The HO_2 radical may also react as a reducing agent:

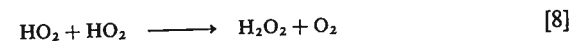


The value of E^0 for the couple $\text{H}^+, \text{O}_2/\text{HO}_2$ was calculated to be 0.3 V. In comparison with $E^0 = 2.1 \text{ V}$ for the couple H^+/H the hydroperoxyl radical turns out to be a considerably weaker reducing agent.

In aqueous solutions, the reaction

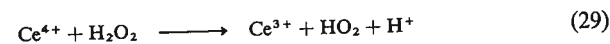


such as that with ascorbic acid [78], or oxidation of cysteine [79], seldom occurs. The hydroperoxyl radical, like hydrogen peroxide, is most often inert toward organic substances. In view of this fact, its fate lies in dismutation, which leads to the formation and accumulation of H_2O_2 in solution:



The hydroperoxyl radical has a characteristic absorption spectrum with a peak in the uv region at about 2300 Å for HO_2 and about 2500 Å for O_2^- . Their molar extinction coefficients also differ.

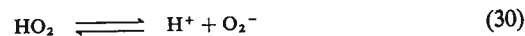
A convenient method for producing the hydroperoxyl radical without radiation is the chemical reaction of the ceric ion with hydrogen peroxide. It may be represented by



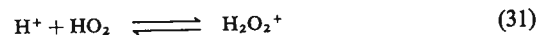
and Eq. (28). Some reported data point out that the radical chemically produced is identical with the hydroperoxyl formed in irradiated solutions. It has been established [80] that the ESR signal measured under suitable conditions in the course of such a reaction in solution is the same as that obtained by Kroch *et al.* [81] in irradiated ice. Also, good agreement was found between the values of the rate constant of the recombination reaction, $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$, by producing HO_2 radicals by chemical means and using the electron beam from an accelerator; the pH of studied solutions varied from 0 to 3 [82]. However, studies show quite clearly that the chemically produced species is not always the free radical (HO_2), but the radical complexed with the ion or molecule which takes part in the chemical process [83-85].

C. The Nature of the Hydroperoxyl Radical in Solutions at Various pH's

The form of the hydroperoxyl radical changes with pH, as shown by kinetic studies of the recombination reaction, $\text{HO}_2 + \text{HO}_2$ [42,46,82], and the reaction $\text{HO}_2 + \text{OH}$ [86,87]. The neutral (HO_2) and basic (O_2^-) forms are generally accepted, and pK values of 4.5 [46,86] and 4.8 [88] have been reported for the equilibrium



It has also been proposed that in acid medium the protonated form of the hydroperoxyl radical exists,



for which pK values are reported to be 1.0 [82] and 1.2 [86]. Taking into account reactions (30) and (31), the formation of hydrogen peroxide by recombination of hydroperoxyl radicals can be represented by the following reactions:

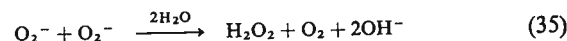
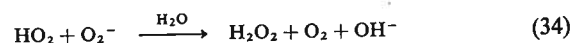
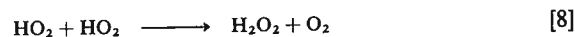
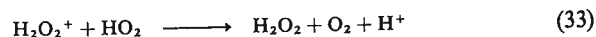
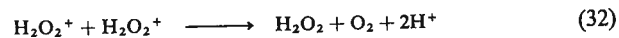


Table 4.3 summarizes the rate constants for the recombination reaction of hydroperoxyl radicals at various pH's. The rate constants obtained at pH values between 0 and 3 are given elsewhere [82]. However, the existence of the H_2O_2^+ form is disputed [87] on kinetic grounds. Also, no specific absorption

TABLE 4.3
RATE CONSTANTS FOR HO_2 AND O_2^- RADICALS

Reaction	Rate constant, $M^{-1} \text{sec}^{-1}$	pH	Reference
$\text{HO}_2 + \text{HO}_2$	2.2×10^6	2-3	[42]
	2.7×10^6	1.7-3	[46]
	2.5×10^6	2	[47]
	6.7×10^5		[88]
$\text{HO}_2 + \text{O}_2^-$	5.3×10^7	Neutral	[47]
	7.9×10^7		[88]
	1.5×10^7		[42]
$\text{O}_2^- + \text{O}_2^-$	1.7×10^7	5-8	[46]
	1.7×10^7	5-7	[46]
	$<10^5$		[88]

has been detected in acid solutions which could be attributed to this species. This is surprising, as the effect of ionic strength on the reaction rate constants in acid medium was found to be appreciable and pointed to the existence of a positively charged hydroperoxyl radical form [82]. It is also interesting to note results [88] according to which reaction (35) is practically unimportant because it is very slow; $k_{35} < 10^5 M^{-1} \text{sec}^{-1}$. This work suggests that the fate of the hydroperoxyl radical is in reactions (8) and (34).

V. PRIMARY HYDROGEN PEROXIDE

The amount of hydrogen peroxide present at the beginning of the chemical stage depends, for a given amount of energy absorbed, only slightly on pH. As we shall see in Chapter Five, $G_{\text{H}_2\text{O}_2}$ seems to be beyond controversy; it varies from ~ 0.8 for acid medium to about 0.7 for neutral medium, while it may be slightly lower in alkaline solutions. The origin of $G_{\text{H}_2\text{O}_2}$ also does not seem to present any particular problems. The increase in concentration of any efficient OH radical scavenger leads to a decrease in $G_{\text{H}_2\text{O}_2}$, pointing to recombination reaction of hydroxyl radicals as the most probable source of primary hydrogen peroxide. This reaction seems to be quite well established.

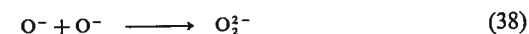
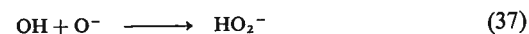
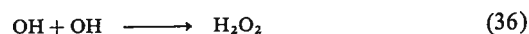
Nevertheless, the above statement on the origin should be considered merely as a reliable qualitative picture which requires rather extensive quantitative verifications. It is true that the increase in the reactivity toward the OH radical decreases the primary H_2O_2 yields, but there are not many results which confirm that the observed decrease is always proportional to the reactivity, as required by the quantitative free-radical spur diffusion model of water radiolysis. One reason lies in the difficulties in choosing a suitable system: The mechanism of radiolysis should be well established, the rate constant for the reaction of the OH radical with the solute S should be accurately known, and it is especially desirable that $G_{\text{H}_2\text{O}_2}$ should be directly measured. The difficulties encountered in measuring true initial hydrogen peroxide yields are not negligible. The amount formed by radiation does not remain unchanged; it decomposes in classical chemical reactions with the substances present in the irradiated solutions, or due to attacks by the e_{aq}^- and H species produced by radiation.

In connection with the origin of molecular products (G_M), some other hypotheses have also been put forward, but they are theoretically and experimentally less treated than the above assumption of recombination of radicals [89-91]. We shall, nevertheless, consider one of them, according to which primary hydrogen peroxide is formed in a pseudo-first-order process in which a primary active species reacts with a water molecule directly producing H_2O_2 . If this hypothesis, as it appears from the present state of

affairs, is far from giving a convincing answer to the question of formation of all $G_{\text{H}_2\text{O}_2}$, it may nevertheless afford an explanation for the origin of a part of it. This might be important for a better formulation of the quantitative model of water radiolysis.

A. Recombination Reaction of Hydroxyl Radicals

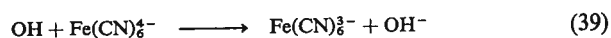
The reactions of recombination of hydroxyl radicals are usually written in such a way as to give hydrogen peroxide as the final product. This also holds for the basic form, the O^- ion radical:



From his experiments, Schwarz [59] calculated $2k_{36} = 8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. The experiments consisted in subjecting water to a pulsed electron beam and studying the steady-state concentration of H_2O_2 as a function of dose rate. A reaction scheme was worked out taking into account the effect of dose rate observed on the measured yield of hydrogen peroxide.

A pulsed electron beam was also used in another work, but molecular hydrogen was measured [58]. The authors varied the pulse length from a time that was short compared to the lifetime of the radical to a time that was relatively long. For this, a special method of treating the data and calculating the results was devised. From the reaction scheme proposed, which involves reaction (36), and experimental data on $G(\text{H}_2)$ at pH 3, a value $2k_{36} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ was derived. Although this measurement was carried out at pH 3 and in the preceding case in neutral medium, the difference between the two values may seem to be large. However, it should be borne in mind that the reaction rate constant in both cases was determined indirectly, from a complex reaction scheme in which reaction (36) was only one of the constituents.

A more direct measurement was carried out [56,57] by studying reaction (36) in competition with the reaction



the rate constant of which is $k_{39} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. Experimental conditions were arranged for following the recombination reaction. The quantity measured was the yield of the ferricyanide produced, which has $\lambda_{\text{max}} = 4200 \text{ \AA}$, with a molar extinction coefficient of $1000 \text{ M}^{-1} \text{ cm}^{-1}$. Since in this spectral region the hydrated electron also absorbs strongly, various scavengers for e_{aq}^- were added to the system. The value obtained for $2k_{36}$ was $(1.26 \pm 0.16) \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. It should be mentioned that this value

could not be obtained directly from competition plots, since the reaction scheme was more complex than the one involving only reactions (36) and (39). Hence, by means of computer, experimental curves were correlated with those calculated for three different mechanisms involving reaction sequences which took into account, in addition to the reactions mentioned above, other reactions ($\text{H} + \text{OH}$ and so on). The value given here was chosen as the most reliable. The authors also carried out measurements in alkaline media at pH 12, 13, and higher than 13. However, the values given for k_{37} and $2k_{38}$ are only approximate ones. Any O_3^- formed may affect the reliability of ferricyanide measurements and hence the information derived from the competition sequences (37) and (39), as well as (38) and (39). Rabani [5] subsequently recalculated these values to be $k_{37} \sim 1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and $2k_{38} < 1.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. It is interesting to note that the recombination of O^- radical ions was found in this work to be considerably slower than that of neutral OH species.

The recombination reaction of OH radicals has been followed directly, and $2k_{36}$ has been calculated from the second-order kinetic plots to be $1.06 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ [17,19].

B. Decrease of $G_{\text{H}_2\text{O}_2}$ with Increasing Reactivity of the OH Scavenger

Sworski [29] was the first to observe that the increase of concentration of bromide ion, a good scavenger for OH radicals, leads to the decrease of primary hydrogen peroxide yields. Other results were subsequently reported, confirming the decrease of measured $G_{\text{H}_2\text{O}_2}$ with increasing [S]. The scavengers used were Br^- [22,31,92], Cl^- [30], I^- [92], Ti^+ [93-95], Ce^{3+} [93,95], NO_2^- [92,96], $\text{Fe}(\text{CN})_6^{3-} + \text{CH}_3\text{OH}$ [97], V^{4+} [95], H_2O_2 [98], and Cr^{3+} [95]. Schwarz [99] was the first to demonstrate that if $G_{\text{H}_2\text{O}_2}/G_{\text{H}_2\text{O}_2}^0$ is plotted against $\log [S]$, the resulting series of curves are all of the same shape and can be brought into coincidence by multiplication of the concentrations by an appropriate factor. If the origin of primary hydrogen peroxide lies in the recombination of hydroxyl radicals, as assumed in the quantitative free-radical model of water radiolysis (see Chapter Six), then this normalization factor is in fact the rate constant for the reaction of the OH radical with the solute. However, the comparison of published data does not clearly confirm the basic quantitative assumption, that is, that the $G_{\text{H}_2\text{O}_2}/G_{\text{H}_2\text{O}_2}^0$ values depend on the reactivity toward the OH radical only. In the carefully studied case of the halide ions, for example, the efficiency in decreasing the hydrogen peroxide yield does not follow the order of their rate constants with the OH radical. It was also reported [97] that methanol, an efficient scavenger for OH radicals, does not contribute, even at 1M concentration, to the $G_{\text{H}_2\text{O}_2}$ decrease in the system $\text{Fe}(\text{CN})_6^{3-} + \text{CH}_3\text{OH}$ at pH 13. All this may raise doubts that reactions (36)-(38) are the source of $G_{\text{H}_2\text{O}_2}$. As we shall see, this does not seem to be the

case, and the reason for the discrepancy between reported experimental results should be sought mainly in the choice of rate constants, experimental conditions, and in the theoretical interpretation of the results obtained. Often, true initial yields were not measured and the reaction schemes were more complex than was assumed; hence, the calculated values for primary hydrogen peroxide yields were often not true $G_{\text{H}_2\text{O}_2}$. In a study of the effect of solute concentration on $G_{\text{H}_2\text{O}_2}$, Draganić and Draganić [100] chose those systems for which the reaction mechanism permits the direct measurement of $G_{\text{H}_2\text{O}_2}$ by measuring the hydrogen peroxide formed. The solutes used were 1-propanol, ethanol, acrylamide, acetone, and potassium nitrate. The pH of solutions varied between 1.3 and 13. Particular care was taken to ensure that the values derived represent the initial yields. The type and concentration of scavenger were such as to protect H_2O_2 from H or e_{aq}^- attack. When the dosage curves were not straight lines, the corrected values were used as the initial yields. These have been obtained as $G_{\text{H}_2\text{O}_2}$ readings at zero dose on diagrams where point-by-point peroxide yields were plotted against dose. Figure 4.4 shows the dependence of $G_{\text{H}_2\text{O}_2}/G_{\text{H}_2\text{O}_2}^0$ on the reactivity of hydroxyl radical scavenger. Regardless of the nature of OH scavenger and the solution pH, the fractional drop of primary peroxide yield decreases with increasing reactivity as is to be expected if the recombination reactions are the source of

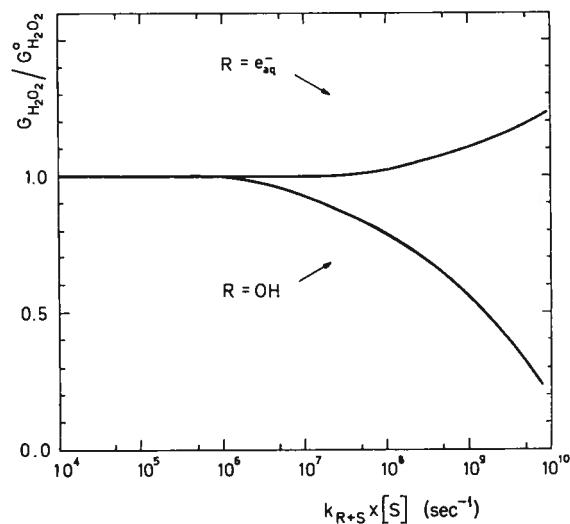
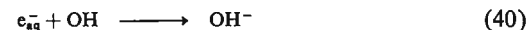


Fig. 4.4. Dependence of the primary hydrogen peroxide yield on reactivity, $k_{R+S} \times [S]$ sec^{-1} . Different scavengers (S) were used at various concentrations (10^{-5} – 1 M) and over a wide range of pH's for the solution (1.3–13). (After Draganić and Draganić [100].)

primary hydrogen peroxide; $G_{\text{H}_2\text{O}_2}$ is the primary yield measured in the presence of a scavenger and $G_{\text{H}_2\text{O}_2}^0$ in the corresponding dilute solution where the solute has no influence on the measured H_2O_2 yield. It has also been shown that the best-fit line through the experimental data agrees well with theoretical [101,102] diffusion kinetic curves.

Another finding from this work may also be of some importance for understanding the origin of primary peroxide. It concerns the measurements of G/G^0 in solutions where the reactivity toward the OH radical is low, but the reactivity toward the hydrated electron increases. As seen in Fig. 4.4, increase in reactivity, contrary to the preceding case, leads here to increase in G/G^0 values. In fact, the quantitative free-radical model predicts such a phenomenon. The increasing reactivity toward e_{aq}^- suppresses the reaction of recombination of primary free radicals:



The remaining hydroxyl radicals disappear partly by reaction (36). Thus, an excess of hydrogen peroxide is produced, larger at higher $k_{e_{\text{aq}}^- + \text{S}} \times [S]$ values. The trend of experimental values was also in agreement, here, with theoretical [101] diffusion kinetic calculations.

C. Pseudo-First-Order Process as a Possible Source of $G_{\text{H}_2\text{O}_2}$ —Homogeneous Kinetics and the Decrease of $G_{\text{H}_2\text{O}_2}$ with Increasing Concentrations of Some Scavengers

The doubt that reactions (36)–(38) are the source of primary H_2O_2 led some authors to the conclusion that nonhomogeneous diffusion kinetics cannot quantitatively express the dependence of primary molecular yields on solute concentration [90,91]. An alternative solution consisted in assuming [100]



to be the cause of the observed dependence of $G_{\text{H}_2\text{O}_2}$ on $[S]$. The nature of the species X is ambiguous; it might be Sworski's "excited water" [90], Voevodski's [89] excited OH radical, or OH^+ according to Anbar [91]. It is essential that use can then be made of the simple competition kinetics expressed by the following equation:

$$\frac{1}{G_{\text{H}_2\text{O}_2}} = \frac{1}{G_{\text{H}_2\text{O}_2}^0} \left\{ 1 + \frac{k_{\text{X+S}}[S]}{k_{\text{X+H}_2\text{O}}[\text{H}_2\text{O}]} \right\} \quad (43)$$

From the intercept on the competition plot, one should calculate $G_{\text{H}_2\text{O}_2}^0$, that is the primary peroxide yield measured in dilute solutions when the solute has no effect.

In some cases, the hydrogen peroxide yields measured at various scavenger concentrations satisfy Eq. (43). What is more interesting is that this can be achieved even with some of the experimental data used in constructing the plot in Fig. 4.4, for solutes known as good OH radical scavengers [100]. It is interesting to note, however, that $G_{\text{H}_2\text{O}_2}^0$ values calculated here from the intercepts are lower than the yields measured in corresponding dilute solutions ($< 2.5 \times 10^{-3} M$). This difference is the same for all solutes and at all pH's: $\Delta G_{\text{H}_2\text{O}_2}^0 = 0.12 \pm 0.02$.

We have seen [90,100] that the same experimental data can be used to express kinetically two different assumptions concerning the origin of G_M . Nevertheless, before considering the assumption on homogeneous kinetics, it should be stressed that more accurate information is needed concerning the chemical nature of the species called X; furthermore, an explanation is needed of the different mechanisms of scavenging the precursor of the primary H_2O_2 , as reflected in the two different $G_{\text{H}_2\text{O}_2}^0$ values (for dilute and concentrated solutions). Finally, the homogeneous kinetic model should give an explanation of why efficient electron scavengers, such as KNO_3 or acetone, lead to an increase in $G_{\text{H}_2\text{O}_2}$ with increasing reactivity. Because of these uncertainties, the conclusion is drawn [100] that at present the recombination of OH radicals, as given by the diffusion radical model, is the more probable explanation of the primary H_2O_2 yield. Qualitatively, this model predicts the experimentally observed decrease as well as the increase in measured $G_{\text{H}_2\text{O}_2}$ values at different scavenger concentrations. Quantitatively, the theoretical curves [101] satisfy fairly well most of the experimental data. It is important to note that the theoretical curves were obtained using the same parameters as those which furnished good agreement with such a different effect as the variation of yields as a function of LET.

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