# Electron Spin Resonance Studies of Transient Radicals in Aqueous Solutions<sup>1</sup>

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Esr spectroscopy has been used to examine aqueous solutions of various solutes during steady irradiation with a 2.8-MeV electron beam. Radiolysis was carried out directly in the esr cavity; the sample was contained in a silica cell of the usual flat design for aqueous samples. Of the three primary radicals from water (H, OH, and  $e_{aq}^{-}$ ) only H could be detected by its esr spectrum, a 503.2-G doublet (but with the low-field line in emission). Reactions of all three primary radicals have been studied. As is usual, use was made of selective scavengers (e.g., N<sub>2</sub>O for  $e_{aq}^{-}$ , t-butyl alcohol for OH) to help in identifying the source of the various solute radicals. Emphasis has been put upon the ability of esr spectroscopy to provide positive identification of radicals. The technique has been tested upon some well-understood systems and then applied to several more specific problems some of which have been studied by pulse radiolysis. Some of the reactions which were studied are abstraction (by OH) from methyl and isopropyl alcohols and acetate, chloroacetate, malonate, and glycolate ions, addition (of H and OH) to benzene and benzoate ion, attachment of  $e_{aq}^{-}$  to acetone and chloroacetate, and electron transfer from (CH<sub>3</sub>)<sub>2</sub>COH to several nitrobenzene derivatives. It is noteworthy that in only one case (abstraction from CH<sub>2</sub>(COOH)<sub>2</sub> to form CH(COOH)<sub>2</sub>) were qualitatively different results found for OH reactions than observed for the active species in the Ti<sup>3+</sup>-H<sub>2</sub>O<sub>2</sub> system.

### Introduction

Work in these laboratories has shown that esr spectroscopy can be used to detect radicals in liquid hydrocarbons during steady, in situ radiolysis with a highenergy electron beam.<sup>3</sup> This experimental arrangement, however, is limited to relatively nonpolar materials by the requirement of a large sample volume. The desirability of an extension to other systems, including aqueous solutions, is obvious. An early attempt<sup>4</sup> to study radicals in aqueous solutions was successful but was confined by sensitivity considerations to radicals with lifetimes longer than those determined by diffusion-controlled reaction. Publications by Smaller, et al.,<sup>5,6</sup> have shown that lossy samples can be studied with small sample volumes if the absorbed dose rate is increased. One of these papers<sup>6</sup> describes results obtained upon an aqueous solution.

Previously we had determined that the absorbed dose rate could not be greatly increased by using higher electron beam currents because of excessive sample heating and voltage instability problems with the Van de Graaff accelerator. Decreasing the beam diameter and consequently increasing the current density over the beam cross section seemed the only improvement possible. This approach has been implemented by using a hole in the side of the cavity and by moving the beam exit window of the Van de Graaff accelerator closer to the esr cell. A great improvement in signal intensity has resulted, and it is now possible to detect in aqueous solutions radicals with recombination rate constants as large as  $10^9$  to  $10^{10} M^{-1} \sec^{-1}$ .

The results presented here are intended to demonstrate some of the potential applications of esr spectroscopy to the study of the radiolysis of aqueous solutions. We have not attempted to investigate the various points in depth but have chosen applications which illustrate the unique properties of esr spectroscopy. (Two papers based on work subsequent to that reported here and describing in more detail the reactions of two classes of compounds have been published.<sup>7,8</sup>)

One major advantage of esr spectroscopy is that radicals can often be identified with only a minimum of other information and that chemically and structurally similar radicals can be distinguished. Esr spectra are clearly better for this purpose than optical spectra as used in conventional pulse radiolysis. We have in several instances investigated reactions which have already been studied by pulse radiolysis to check that the radicals have been properly identified. The esr

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<sup>(5)</sup> B. Smaller, J. R. Remko, and E. C. Avery, J. Chem. Phys., 48, 5174 (1968).

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method, of course, has limitations (see below), so that it must also draw on the results of other more conventional studies. It is to be hoped that mutual benefit will arise from any comparison of the results of esr and pulse radiolysis studies of similar systems.

All of the experiments to be described were done with a steady electron beam and not a pulsed one. Although the steady-state method does not allow kinetic information to be obtained directly, it has several other advantages. First, the standard 100-kHz field modulation spectrometer can be used, and the resolution provided by that type of spectrometer is available for the study of complex spectra. (We have not yet taken the steps to provide faster response times as have Smaller, et al.<sup>5</sup>) In general before one wishes to study kinetics one must identify the radicals and the reactions they are involved in. The steady-state method allows this. Second, the main difference between pulsed and steady-state experiments is that the latter sees much less of the initial nonequilibrium populations of spin levels with which the radical is formed. This problem, discussed in more detail below, is best avoided for many purposes. Finally, several problems shared by both approaches should be mentioned. If the esr line widths are large, peak heights are reduced and radicals may be undetectable even though present at otherwise adequate concentrations. Also both steady-state and pulsed methods use such high absorbed dose rates that they suffer from the possibility of secondary reactions even with flowing samples. (The pulse repetition period in most pulsed experiments is shorter than the residence time of the sample in the irradiation zone.) In many cases the products of radiolysis can be significantly more reactive toward the primary radicals from the water than the initial solute.

The detailed relationship between the sensitivity of pulsed and steady-state modes has been discussed by Fessenden and Schuler.<sup>9</sup> This treatment shows that for radicals which disappear bimolecularly the pulsed mode can be made nearly as sensitive as the steadystate one if signal enhancement by time sampling is employed and the average beam current is made equal to that in the steady-state experiment. The technique reported by Smaller, et al.,<sup>5</sup> seems to meet these requirements. Although the two methods have comparable sensitivity, the steady-state one has sacrificed the possibility of studying the time dependence of the esr signals. With the present spectrometer system it is possible to study radical disappearance by using a pulsed electron beam with long pulse duration ( $\sim 1$ msec) and a time-average computer but only at considerable loss of signal-to-noise ratio.<sup>4,10</sup> With such an arrangement radical lifetimes are just long enough (>1 msec) to be unaffected by the minimum time constant of the 100-kHz unit.

The phenomenon of nonequilibrium initial population of spin states upon radical formation was first observed

by Fessenden and Schuler<sup>3</sup> for the hydrogen atom produced in liquid methane. They observed that the esr spectra of both H and D atoms exhibited an inverted low-field line, implying an inverted population difference for the appropriate pairs of spin states. Smaller, et al.,<sup>5</sup> have found this phenomenon to be common to other radicals if observations are made before spin relaxation can occur, and they have published a spectrum of cyclopentyl radical with the low-field half-inverted. It is now clear that this effect is not limited to radicals produced by high-energy radiation but may be common to most, if not all, methods of generating radicals.<sup>11</sup> The effect was first observed for radicals other than hydrogen atom by Smaller, et al.,5 because their experiment was the first in which the spectrum could be examined in a time after radical formation which was comparable to the spin relaxation time,  $T_1$ . Usually only small trends in intensity are observed in spectra taken in the steady-state mode as a result of almost complete spin relaxation over the chemical lifetime of the radicals. Only where the chemical lifetime is relatively short or the relaxation time relatively long is the effect very pronounced. We have found the greatest effect (except for the hydrogen atom) for the hydroxycyclohexadienyl radical and suppose that this radical has a long  $T_1$  through the lowering of the hyperfine anisotropy by the reduced spin densities in this conjugated radical. Some effect is seen for the radical  $(CH_3)_2$ -COH from isopropyl alcohol.

It is not clear at this time what factors determine the initial population of spin states. It is likely, however, that many of the considerations are similar to those invoked to explain superficially similar multiplet effect in the nmr spectra of samples undergoing radical reactions. Several discussions of the latter effects have been given,<sup>12-14</sup> and Kaptein and Oosterhoff<sup>15</sup> and also Fischer<sup>16</sup> have specifically considered the esr problem. Their explanation involves the mixing of single and triplet states of a radical pair by the combined action of hyperfine and electron exchange interactions during separation of the radical pair. Although this type of mechanism qualitatively fits many observations (*e.g.*, the effect is larger for larger hyperfine constants), the details are not yet clear enough to be of use in under-

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<sup>(11)</sup> The high-field lines appear stronger in spectra from photolysis, see, e.g., R. Livingston and H. Zeldes, J. Amer. Chem. Soc., 88, 4333 (1966), or P. J. Krusic and J. K. Kochi, *ibid.*, 90, 7155 (1968), and also in those from  $Ti^{3+} + H_2O_2$  reaction, see, e.g., H. Fischer, Z. Naturforsch. A, 19, 866 (1964).



Figure 1. Diagram of irradiation arrangement showing magnet poles and cavity. The extension (A) of the Van de Graaff vacuum system is brought into a chimney (B) on the broad face of the cavity and is terminated by a window (0.025 mm brass) approximately in the plane of the cavity wall. The silica aqueous cell (C, inside cross section  $0.5 \times 10$  mm) is irradiated edgewise as shown. The two broad faces of the cavity are of 0.45-mm Type 304 stainless steel which has been plated with copper and then silver. The modulation coils are external to these faces (D).

standing the radical formation mechanism. For this paper, therefore, the effect will be ignored as much as possible.

### **Experimental Section**

It was mentioned above that a most important quantity is the production rate of radicals (*i.e.*, current density over the beam cross section) for a given total electron beam current. In the work on nitromethane<sup>4</sup> the window to the vacuum system of the accelerator was inside the pole piece as in Figure 1 of ref 3, and the beam diameter at the cavity wall was  $\sim 10$  mm. To achieve a significant improvement it was necessary to bring this window very close to the cavity and to make a hole in the face of the cavity. These details are shown in Figure 1. At some point in the reduction of the beam diameter any further decrease will be offset by the spreading of the beam in the dense material of the sample and cell. With the present arrangement the approximate average width of the beam in the sample and cell as measured by the coloring produced in a Pyrex cell is 5-6 mm. Calculations of absorbed dose rate based on this beam cross section agree approximately with that determined chemically (see below).

The increased beam currents used in this work produce considerable ionization of the gas within the cavity, and this conductivity affects both cavity Q and resonant frequency. Because the electron beam is not steady dc but has a considerable ac noise component, a considerable increase in noise output of the spectrometer results. Because the main component of this



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Figure 2. Schematic representation of flow system. Esr cavity, cell, and the electron beam have been rotated for clarity. The electron beam is in a horizontal plane. The sample (in a 4-l. bottle) is bubbled with the desired gas (N<sub>2</sub> or N<sub>2</sub>O usually) and forced through the cell by partially evacuating the waste container. A heat exchanger (bath of ethylene glycol-water cooled from an external thermostat bath) is provided to cool the sample. A remote control stopcock is also provided.

HEAT EXCHANGER

SAMPLE

conductivity is a result of free electrons, a shortening of electron lifetime reduces the effect on the spectrometer. We have found that a slow flow of pure  $O_2$ through the cavity is sufficient to reduce the interaction of the electron beam with the spectrometer to an insignificant level.

The system for flowing the sample is shown in Figure 2.The sample is degassed in a 4-l. container and is made to flow through the sample cell by partially evacuating the waste container with an aspirator. The cooling coil is to lower the solution temperature to compensate for the temperature rise produced by the radiolysis. The temperature rise is about 5° for a beam current of  $10 \ \mu A$ . Because of some overcompensation all results pertain to a solution temperature of about 15°. A motor driven stopcock is used to turn the flow on and off remotely. Both the stopcock and a tungsten current collection electrode are downstream from the irradiation zone. We have used a flat silica cell fabricated from Suprasil II<sup>17</sup> with a 0.5-mm internal spacing. Although this material produces a large esr signal, only  $\sim$ 7 G of the spectrum are blanked out when the spectrum is taken as a second derivative with modulation amplitudes appropriate to fairly narrow lines (0.1-0.2-G width).

The esr spectrometer is a Varian V4200 with a 100kHz modulation unit as described previously.<sup>3</sup> A Philco L-4164 detector diode is currently being used (with no amplifier modifications) to give some improvement in signal-to-noise ratio over that for a 1N23G. The field-tracking nmr unit<sup>3</sup> has been modified by the use of a transistorized marginal oscillator. Measurements of the g factors are relative to the main peak in

(17) Amersil, Inc., Hillside, N. J.

the signal from the cell which occurs at g = 2.00044. These measurements are accurate to about  $\pm 0.00003$ .

The electron beam current is collected and monitored at two points: from the cavity itself and from an electrode in the esr cell. The current measured from the cell was  $\sim 15\%$  that from the cavity. The current from the cavity plus cell represents substantially the total beam current entering the magnet gap. Typically the current from the cavity was 8-10  $\mu$ A. Because this represents  $\sim 25$  W of heat for 2.8-MeV energy, it was necessary to water-cool the cavity. The flow of sample solution ( $\sim 1 \text{ cm}^3 \text{ sec}^{-1}$ ) provides cooling for the cell.

The absorbed dose rate was measured by irradiating an oxygen-saturated ferrous solution. For a  $2.5-\mu A$ total beam current and a  $1-cm^3$  sec<sup>-1</sup> flow rate the production rate of Fe<sup>3+</sup> corresponded to an absorbed dose of  $3 \times 10^{18}$  eV g<sup>-1</sup>. A proportional decrease in yield of Fe<sup>3+</sup> was observed when a higher flow rate was used showing that no depletion of  $O_2$  had occurred. This absorbed dose can be compared with that calculated from a beam diameter of 5 mm and a linear energy loss of 1.8 MeV  $g^{-1}$  cm<sup>2</sup>. The value obtained from this calculation is also  $3 \times 10^{18}$ . The close agreement must be regarded as partially fortuitous because the estimate of the beam average diameter is rather approximate. It is clear, however, that the irradiation conditions are known at least semiquantitatively. This knowledge is important in considering possible solute depletion or secondary reaction.

At 1-cm<sup>3</sup> sec<sup>-1</sup> flow rate the sample volume of  $0.8 \times 0.5 \times 0.05 = 0.020$  cm<sup>3</sup> is replenished 50 times per second so that the absorbed dose rate is  $1.5 \times 10^{20}$  eV g<sup>-1</sup> sec<sup>-1</sup>. For a radiation chemical yield of unity this is a radical production rate of  $2.5 \times 10^{-3} M$  sec<sup>-1</sup>. This production rate combined with a radical recombination rate constant of  $10^9 M^{-1}$  sec<sup>-1</sup> leads to a steady-state radical concentration of  $1.6 \times 10^{-6} M$ . Such a radical concentration is readily detectable if the esr spectrum has relatively narrow lines.

The chemicals in this study were used as received, and no special problems were encountered. Reagent grades were used when available. The water was doubly distilled as previously described.<sup>4</sup> In the early work pH was adjusted using only KOH or  $HClO_4$ . Subsequently it became evident that for near-neutral pH values buffering was necessary. This was accomplished with the appropriate sodium phosphate.

#### **Results and Discussion**

As is well known, an important tool in the study of reactions in aqueous solutions during radiolysis is the use of selective scavengers to control the reactions of H, OH, and  $e_{aq}$  with solutes. (The primary yields of these radicals are about 0.6, 2.8, and 2.8, respectively.<sup>18</sup>) Such an approach was important for this esr work because without the use of scavengers it would often have been difficult to determine which of the primary

radicals led to the formation of a particular radical. There are two types of scavengers: those that interconvert the primary radicals (e.g.,  $H^+$  and  $N_2O$ ) and those which yield some other radical. The latter must be chosen so that the spectrum of the radical produced does not interfere with other spectra. The presence of the spectrum derived from the scavenger is useful evidence that the solute is not competing to a great extent with the intended scavenger.

In acid solutions reaction 1 occurs, and a relatively

$$e_{aq}^{-} + H^{+} \longrightarrow H^{-}$$
(1)

large yield of H is produced. Under these conditions it is possible to study the radicals produced from the solute by reaction of  $H \cdot$ . There can also be reactions of OH. Depending on the rate of the OH reaction it may be possible to remove OH by reaction with *t*-butyl alcohol (which is relatively unreactive toward H) and

$$OH + (CH_3)_3COH \longrightarrow HOH + \dot{C}H_2(CH_3)_2COH$$
 (2)

to study only the reactions of H. In basic solution the main solute reactions are with  $e_{aq}^{-}$  and OH because the direct yield of H is only 0.6.<sup>18</sup> Use of the electron scavenger, N<sub>2</sub>O, converts  $e_{aq}^{-}$  into OH so that its reac-

$$H_2O + N_2O + e_{aq} \longrightarrow OH^- + N_2 + OH$$
 (3)

tions can be studied alone. The study of reactions of  $e_{aq}^{-}$  is more difficult because OH reactions are also present. A number of scavengers for OH exist, such as alcohols and formate, but these must be used with caution because the resultant radicals may act as electron transfer or reducing agents and yield<sup>4</sup> the same radical as does  $e_{aq}^{-}$  (cf. reactions 4 and 5). Where a

$$(CH_3)_2COH + CH_3NO_2 \longrightarrow$$

$$CH_3\dot{N}O_2^- + (CH_3)_2CO + H^+ \quad (4)$$

$$e_{aq}^{-} + CH_3 NO_2 \longrightarrow CH_3 NO_2^{-}$$
(5)

reaction analogous to (4) occurs, use of such OH scavengers is advantageous in studies of spectra because a larger yield of the desired radical is obtained. Where no electron transfer reaction (4) occurs, the existence of a reaction analogous to eq 5 can be demonstrated by the addition of N<sub>2</sub>O to the solution. With N<sub>2</sub>O present the radical produced from  $e_{aq}$  - should disappear (provided the rate constants and concentrations are such that N<sub>2</sub>O can compete successfully for  $e_{aq}$ -). If *t*butyl alcohol is used as the OH scavenger (eq 2), no complications are expected because  $CH_2(CH_3)_2COH$ does not seem to be capable of electron transfer.<sup>19</sup>

The discussion immediately above suggests that the radicals observed be discussed as reaction products of

<sup>(18)</sup> See, e.g., the review by M. Anbar in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968, p 651.

<sup>(19)</sup> G. E. Adams, B. D. Michael, and R. L. Willson, Advan. Chem. Ser., 81, 289 (1968).

the three primary radicals or of electron transfer from reducing agents such as alcohol radicals or  $\dot{C}O_2^{-}$ . This approach will be followed as much as is practical.

Such a classification of the reactions is also convenient for a comparison of radiolytic generation of radicals with other production methods which have been used in esr experiments. In this sense only the H-atom and  $e_{aq}$  reactions are unique to radiation chemistry. Reactions of an agent which is most likely OH radical have been studied by esr spectroscopy in flow systems of  $Ti^{3+}$  and  $H_2O_2^{20-22}$  and in photolytic systems containing H<sub>2</sub>O<sub>2</sub>.<sup>23</sup> The Ti<sup>3+</sup>-H<sub>2</sub>O<sub>2</sub> system is mechanistically rather complex,  $^{\rm 22}$  but at the level of the work here only a few detail differences in reaction paths have been seen for radiolytically produced OH radical as compared with these other sources. Because of the greater radical concentrations available using these other methods of generation, the spectroscopic study of radicals produced from OH is best done by these other techniques in the pH regions available to them. Production of OH by radiolytic means does have the advantage that the strongly alkaline region pH > 10 can be investigated and that no changes in the nature of the chemical agents occur as pH is varied (cf. Ti<sup>3+</sup> in acid and as complexed for pH 2-10<sup>24-26</sup>). Electron transfer reactions have been studied by esr spectroscopy in work with  $Ti^{3+}-H_2O_2^{27,28}$  so that again the radiolytic work is not unique. However, the full pH range is available in the radiolytic work. The major advantages of the use of radiolytic generation (in aqueous systems) of radicals, then, are a mechanistically well-understood initial generation of radicals, the possibility of studying the reactions of  $e_{aq}^{-}$  and H atoms, and the availability of the full pH range with no other changes in conditions.

OH Reactions. Reactions of OH radical will be discussed first because they are the easiest to study without interference from those of the other primary radicals. Both reaction by hydrogen atom abstraction and by addition have been studied. The radicals resulting from abstraction have been observed in the cases of methyl and isopropyl alcohols and several organic acids. A number of these substances and the resultant radicals have been studied by esr spectroscopy using other techniques for OH production. However, it is important to establish that the reactions are the same in all cases. Furthermore, because these radicals are to be expected in studies of other reactions (e.g.,  $CH_2CO_2^-$  from  $e_{ag}^-$ +  $H_2NCH_2CO_2^{-7}$ , it is important to have accurate spectral parameters. In fact, much of the data from these other studies pertains to other conditions such as nonaqueous solution or strong acid where a different degree of dissociation is expected.<sup>29</sup>

The reactions with methyl and isopropyl alcohols can be used as an initial illustration of the practicality of studying radiolytically generated radicals in aqueous solutions. In neutral and acid solutions these reactions are expected to be

$$OH + CH_3OH \longrightarrow \dot{C}H_2OH + H_2O$$
 (6)

$$OH + (CH_3)_2 CHOH \longrightarrow (CH_3)_2 \dot{C}OH + H_2 O$$
 (7)

while in strong base (pH  $\sim$ 12) the resulting radicals can dissociate

$$OH^- + \dot{C}H_*OH \longrightarrow \dot{C}H_*O^- + H_*O$$
 (8)

$$OH^- + (CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2\dot{C}O^- + H_2O$$
 (9)

The pK values reported by Asmus, et al.,<sup>30</sup> are respectively, 10.7 and 11.6. The results of experiments with N<sub>2</sub>O-saturated neutral and basic solutions of the alcohols are shown in Figures 3 and 4. A significant decrease in hyperfine constant and increase of g factor upon dissociation are evident from the figures in both cases. Hyperfine constants for these spectra are given in Table I. The spectra in neutral solution are like those found by Zeldes and Livingston<sup>31</sup> for aqueous solution and exhibit a splitting by the hydroxyl proton. As the pH is raised, exchange of the OH proton occurs causing first broadening of the doublets corresponding to this splitting and then narrowing to a single line. At still higher pH values where appreciable concentrations of both undissociated and dissociated forms are present the spectrum represents a weighted average over these forms because of the rapid dynamics of the equilibrium. The dynamics are not quite rapid enough, however, to maintain narrow lines for the outer lines (*i.e.*, those which move the most upon dissociation). The broadening does not prevent determination of the positions of at least some of the lines at all pH values. A detailed study of the variation of hyperfine splitting with pH and of the kinetics of the exchange in basic solu-

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<sup>(20)</sup> W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 3119 (1963).
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<sup>(29)</sup> For example, although the radical CH<sub>2</sub>COOH from acetic acid had been reported several times, it was not until the present work that the spectral parameters for the form CH<sub>2</sub>CO<sub>2</sub><sup>-</sup> were determined (see also ref 7). Also, much of the early work using  $Ti^{s+}-H_2O_2$  did not give hyperfine constants to as great accuracy as is now considered desirable and did not report g factors.



Figure 3. Second-derivative esr spectra of N<sub>2</sub>O saturated 0.1 M methanol solution at two pH values taken during irradiation with 2.8-MeV electrons. Magnetic field increases to the right. A portion of the spectrum to the right of the center is recorded at  $\sim 100 \times$  less gain and shows the signal from the silica cell. A stick spectrum of the basic form,  $\dot{C}H_2O^-$ , is shown for reference.



Figure 4. Esr spectrum of an N<sub>2</sub>O-saturated 0.1 M solution of isopropyl alcohol at two pH values.

tions of the OH proton is under way.<sup>32</sup> In the most basic solutions the lines for each radical all become of the same width. For the radical  $(CH_3)_2\dot{C}O^-$  this width is small (~0.1 G) and second-order splittings can readily be resolved (Figure 3). For  $\dot{C}H_2O^-$  the line width is greater (~0.4 G) for some reason not yet understood.<sup>33</sup> The signal-to-noise ratio of these spectra is adequate and demonstrates the practicality of studying radicals with recombination rate constants of ~10<sup>9</sup>  $M^{-1} \sec^{-1}$ .

The absence of lines from the radical  $\dot{C}H_2(CH_3)$ -CHOH in the experiments with isopropyl alcohol deserves some comment because this radical is relatively prominent in flow experiments with Fe<sup>2+34</sup> or Ti<sup>3+20</sup> and H<sub>2</sub>O<sub>2</sub>. Several discussions of the variable ratio of

Table I: Radicals Produced by OH<sup>a</sup> (H-Atom Abstraction)

Radical <sup>b</sup>	$a_{\alpha}^{\mathrm{H}}$	$a_{eta}^{ ext{H}}$	aoh <sup>H</sup>	$a^{C1}$	g
ĊH₂OH⁰	17.56		1.01		2.00329
ĊH₂O⁻	14.34				2.00367
(CH <sub>3</sub> )2ĊOH°		19.90	0.48		2.00315
(CH <sub>3</sub> ) <sub>2</sub> ĊO <sup>-</sup>		17.31			2.00335
ĊH₂COO−	21.20				2.00323
ĊH(COO~)2	$19.95^{d}$				2.00341
-OCHCOO-	14.17				2.00435
ĊHClCOO-	20.48			3.36°	2.00640

<sup>a</sup> Hyperfine constants in gauss, accurate to about  $\pm 0.03$  G. Values of g factor accurate to about  $\pm 0.00003$ . <sup>b</sup> Radical formed at pH ~11-12. <sup>c</sup> Parameters reported previously by Zeldes and Livingston<sup>31</sup> for aqueous solution are: CH<sub>2</sub>OH,  $a_{\alpha} =$ 17.52, g = 2.00335; (CH<sub>3</sub>)<sub>2</sub>COH,  $a_{\beta} = 19.96$ , g = 2.00313. <sup>d</sup> Splitting for CH(COOH)<sub>2</sub> at pH 0.9 is 20.44 G. <sup>e</sup> Value for <sup>35</sup>Cl; for <sup>37</sup>Cl it is 2.79. The ratio is 0.830 and can be compared with the expected ratio of 0.832.

ĊH<sub>2</sub>(CH<sub>3</sub>)CHOH to (CH<sub>3</sub>)<sub>2</sub>ĊOH have been published.<sup>22,35,36</sup> Because the radiolysis of aqueous solutions of low concentrations of solutes (0.1 M) is very well understood, it is clear that the results reported here should be describable by a mechanism involving only the production of the two abstraction product radicals and their bimolecular recombination. The ratio of production of the two radicals has been found<sup>37</sup> to be about 6:1 in favor of  $(CH_3)_2\dot{C}OH$ . If it is assumed that the recombination reactions all have about the same rate constants (a large departure from this condition seems very unlikely), then our experiments should show a 6:1 ratio of radical concentrations. Such a concentration for  $\dot{C}H_2(CH_3)CHOH$  would put its lines at about the noise level in Figure 4 so no inconsistency is present. The spectrum found by Livingston and Zeldes<sup>28b</sup> for  $H_2O_2$  in 75% isopropyl alcohol and 25% water shows about the expected ratio for the two radicals although experiments in the pure alcohol<sup>23a</sup> do not seem to show the weaker set of lines. On the basis of these observations we must conclude that while the photolysis of  $H_2O_2$  produces an active species (OH) which behaves in a fashion similar to or identical with radiolytically produced OH, some complications are present in the metal ion systems. At this time an explanation such as that advanced by Norman and West<sup>22</sup> and involving for the two types of radicals differing reaction rates with metal ions and  $H_2O_2$  seems

- (32) G. P. Laroff and R. W. Fessenden, to be published.
- (33) It should be noted that radicals with a small moment of inertia about at least one axis show anomalously broad lines. Examples in addition to  $\dot{C}H_2O^-$  are  $CH_3$  and perhaps  $CH_3\dot{C}H_2$  (ref 3), and  $\dot{C}H_2CN$  (ref 23d).
- (34) T. Shiga, J. Phys. Chem., 69, 3805 (1965).
- (35) R. E. James and F. Scicilio, ibid., 74, 1166 (1970).
- (36) C. E. Burchill, ibid., 75, 167 (1971).
- (37) C. E. Burchill and I. S. Ginns, Can. J. Chem., 48, 1232 (1970).

more reasonable than an active species which is not free OH.

Other compounds studied which give the expected abstraction product when studied in basic N<sub>2</sub>O-saturated solution are acetate, chloroacetate, malonate, and glycolate (HOCH<sub>2</sub>COO<sup>-</sup>) ions. The radicals found are CH<sub>2</sub>COO<sup>-</sup>, CHClCOO<sup>-</sup>, CH(COO<sup>-</sup>)<sub>2</sub>, and -OCH-COO-, respectively. Spectral parameters for these radicals are given in Table I. Because Fischer. et al.,<sup>38</sup> have found a small change in the  $\alpha$ -proton splitting and a large one in the  $\beta$  splitting of the radical HOOCCH-CH<sub>2</sub>COOH as the carboxyl protons dissociate, it is to be expected that other radicals containing carboxyl groups will also show this trend. Fortunately Fischer, et al.,<sup>38</sup> have also found only a moderate change in the acid pK values in going to the radical so that there is some hope of estimating whether a particular radical from earlier studies is dissociated or not. Our parameters for  $\dot{C}H_2COO^-$  should be compared, therefore, with those of Beckwith and Norman<sup>28</sup> who worked near neutral pH. It is not clear why their values of a= 21.6 G and g = 2.0033 are not closer to those found here. The splitting in acid solutions for (presumably)  $\dot{\mathrm{CH}}_{2}\mathrm{COOH}$  is reported to be 21.8<sup>39</sup> and 21.7 G.<sup>40</sup>

Chloroacetate was studied because of the desire to illustrate by esr the well-known reactions of this compound with the three primary radicals. The spectra found in acid and basic solutions of chloroacetate are shown in Figure 5. The abstraction product CHCl-COO- (or CHClCOOH) is evident in both pH regions. The hyperfine constants for CHClCOO<sup>-</sup> are given in Table I: no values were determined for the acid form because of low signal-to-noise ratio. The parameters reported by Dixon, et al.,<sup>39</sup> for CHClCOOH ( $a^{H}$  = 20.9 G,  $a^{C1} = 3.8$  G) are rather similar to those found here. The high g factor is a result of spin density upon the chlorine. Malonate was studied to establish the spectral parameters of the dissociated form of the radical for comparison with radicals obtained in other reactions. Because Dixon, et al.,<sup>39</sup> found CH<sub>2</sub>COOH to be the reaction product of malonic acid in acid solution, an experiment was done at pH 0.9 in addition to that at pH 12. Interestingly the radical found here at both pH values is that obtained directly by hydrogen abstraction. This is the most striking instance we have found of a difference in reaction product between the two methods of radical generation.

Glycolate was of particular interest because of the dissociation of the alcohol proton as shown by pulse radiolysis<sup>41</sup> and also because the same radical can be

$$OH^- + HO\dot{C}HCOO^- \longrightarrow -O\dot{C}HCOO^- + H_2O \quad (10)$$

formed by electron addition to glyoxylate ion. This

$$e_{aq}^{-} + HCCOO^{-} \longrightarrow HCCOO^{-} \qquad (11)$$

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Figure 5. Esr spectra of  $10^{-2} M$  chloroacetic acid at pH 1.5 and of  $10^{-2} M$  chloroacetate saturated with N<sub>2</sub>O at pH 11.4. The stick spectra represent the analysis of the pH 11.4 spectrum. The pair of lines in the bottom stick spectrum are from an unknown species.

latter compound also is of importance in studying the reactions of oxalate as discussed below. The pK for reaction 10 is ~9<sup>41</sup> and in accord with this value no change in the hyperfine splitting (14.17 G) for  $-O\dot{C}H$ -COO<sup>-</sup> was found over the pH range from 10 to 13. No spectrum was taken in neutral solution, but the  $\alpha$ -proton splitting reported for acid conditions is 17.8 G.<sup>39</sup> The splitting of 14 G must, therefore, represent that of the doubly dissociated form and has no significant contribution from the form HOCHCOO<sup>-</sup>. The change from 17.8 G in HOCHCOOH to the 14.2 G found here parallels the drop of 2.7 G in going from CH<sub>2</sub>OH to CH<sub>2</sub>O<sup>-</sup> and is probably caused mainly by the dissociation of the alcoholic proton.

The lines of  $-O\dot{C}HCOO^-$  are very intense because of the slower recombination for this doubly charged radical. (The pulse radiolysis work by Simic, *et al.*,<sup>41</sup> has shown the recombination rate constant to be 1.5  $\times$  $10^7 M^{-1} \sec^{-1}$ .) As a result sufficient intensity is present to allow a search for lines from <sup>13</sup>C-containing radicals and indeed two sets of lines with proper intensity and described by the same  $a_{\alpha}$  and g factor were found with, respectively,  $a^\circ = 6.90$  and 13.56 G. (See Figure 11 for the same radical from electron addition to glyoxylic acid.) No lines of comparable width and corresponding to values of  $a^\circ$  up to 300 G could be found.

(38) H. Fischer, K.-H. Hellwege, and M. Lehnig, Ber. Bunsenges. Phys. Chem., 72, 1166 (1968).

(39) W. T. Dixon, R. O. C. Norman, and A. L. Buley, J. Chem. Soc., 3625 (1964).

(40) H. Taniguchi, K. Fukui, S. Ohnishi, H. Hatano, H. Hasegawa, and T. Maruyama, J. Phys. Chem., 72, 1926 (1968).

(41) M. Simic, P. Neta, and E. Hayon, ibid., 73, 4214 (1969).



Figure 6. Esr spectra obtained from N<sub>2</sub>O-saturated solutions of benzene (saturated,  $\sim 10^{-2} M$ ) and  $5 \times 10^{-3} M$  benzoate at about pH 12. Stick spectra are shown for the indicated species. (Only the meta radical is shown in the lower although the other two isomers are present.) Note the large intensity differences between high- and low-field lines and the suggestion of emission lines at several points.

Either of the observed values would be reasonable for the carboxylate carbon ( $\beta$  position), but a larger splitting (~35 G) would be expected for the  $\alpha$ - or radical carbon. Because similar values have been found in related radicals,<sup>32</sup> we reject the suggestion that these lines do not come from the <sup>13</sup>C-containing radicals. It must be that the proper electronic description of this radical involves a greater than expected (by us) contribution from all of the structures with the electron located on an oxygen. Structures like II reduce the  $\pi$ -spin density on the  $\alpha$ -carbon, and depending on the sign magnitude

of  $Q_{\rm OC}^{\rm C}$  from the theory of Karplus and Fraenkel<sup>42</sup> structure III could produce a significant negative contribution to the splitting of the  $\alpha$ -carbon and partly cancel the main positive contribution from structure I.

A number of addition reactions of OH radical have been observed by esr spectroscopy in flow systems. Several authors have reported addition to unsaturated compounds<sup>20,43-45</sup> and Dixon and Norman<sup>46</sup> have studied addition to substituted benzenes to form hydroxycyclohexadienyl radicals. Previous radiolytic work<sup>4</sup> demonstrated OH addition to the basic form of

$$OH + CH_2 = NO_2^- \longrightarrow HOCH_2 \dot{N}O_2^- \qquad (12)$$

nitromethane. In the work covered here OH addition to benzene and benzoate ion have been studied as well as the addition reaction to nitrosobenzene and the displacement reaction with p-nitrophenol to form pbenzosemiquinone ion radical.

The spectra of the hydroxycyclohexadienyl radicals from benzene and benzoate ion are shown in Figures 6 and 7. These both show a strong intensity anomaly

$$OH + \bigcap_{R} \rightarrow \bigvee_{R}^{H \to 0H}$$

and the lines at the lowest fields are inverted. The

(42) M. Karplus and G. K. Fraenkel, J. Chem. Phys., 35, 1312 (1961).

- (43) H. Fischer, Z. Naturforsch. A, 19, 866 (1964).
- (44) W. E. Griffiths, G. F. Longster, J. Myatt, and P. F. Todd, J. Chem. Soc. B, 530 (1967).

(45) A review of OH addition to vinyl monomers has been published:
K. Takakura and B. Ranby, Advan. Chem. Ser., 91, 125 (1969).

(46) W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 4857 (1968).

Radical (system)					
	>CHX	Ortho	Meta	Para	g
$C_{6}H_{7}$ (aqueous)	48.08	9.06	2.69	13.15	2.00268
$C_6H_7$ (hydrocarbon) <sup>o</sup>	47.71	8.99	2.65	13.04	(2,0025)
$C_6H_6OH$ (basic) <sup>d</sup>	34.34	8.92	2.74	13.05	2.00227
$C_{\theta}H_{\theta}OH$ (acid)	е	8.85	2.76	13.09	e
$OOOCC_{6}H_{5}OH$ (basic)	34.71	8.35	2.59.2.78	12.53	e
MOOCC <sub>6</sub> H <sub>5</sub> OH (basic)	e	8.85, 9.03	2.74	13.08	2.00224
$POOCC_{6}H_{5}OH$ (basic)	e	8.29	2.60		e

#### Table II: Cyclohexadienyl Radicals<sup>a</sup>

<sup>a</sup> Positions labeled with respect to the methylene group >CHX where X is H or OH. <sup>b</sup> In gauss, estimated accuracy  $\pm 0.03$  G. <sup>c</sup> Reference 3. <sup>d</sup> Somewhat different parameters were reported by Dixon and Norman.<sup>46</sup> <sup>e</sup> Because of intensity differences of highand low-field lines only the high-field lines could be measured; consequently no >CHOH splitting could be obtained, and no g factor determined.



Figure 7. High-field side of the spectrum obtained under high resolution with an N<sub>2</sub>O-saturated,  $10^{-2} M$  benzoate solution. Present are lines from the three possible isomers.

spectra were analyzed on the basis of the high-field portions of the spectra, and only those lines on the lowfield side were measured which were necessary to provide the g factor and splitting by the methylene (>CHOH) proton. Figure 7 shows a portion of the high-field half of the spectrum obtained with benzoate ion. The spectra of the three isomers resulting from addition at ortho, meta, and para positions can be seen. The lines from these radicals include essentially all of those visible, and no intense line is unaccounted for. The hyperfine constants are given in Table II. Most striking is the close agreement of the ring proton splittings between the various isomers and with the unsubstituted radical. The meta adduct shows little decrease in spin density over the unsubstituted one because the carboxyl group is at a position of low spin density. In the other two isomers the splittings at para and ortho positions drop by about 4-7% presumably because spin density has been removed to the carboxvlate group. The value of the >CHOH splitting of hydroxycyclohexadienyl radical is smaller by 1.5 G than that reported by Dixon and Norman.<sup>46</sup> This cannot be caused by a dissociation of the OH proton because an identical spectrum was obtained in acid solution. The only other obvious reason for the difference (aside from an error in field scan calibration by them) is that the radical in the  $Ti^{3+}-H_2O_2$  experiment is somehow associated with titanium.

The relative rates of OH addition at the three posi-

tions cannot be accurately determined from the results of Figures 6 and 7 without information on the radical lifetimes. A first approximation is to take the line width to be the same for all radicals because no large differences are evident and to say the disappearance rates are the same. Certainly in the mixed system no great differences can exist. Under these assumptions it is concluded that the meta and para adducts are produced at the same rate and the ortho at about half this rate *per position on the ring*. The lower rate in the ortho position may be related to steric factors. The individual identification of the three adduct radicals illustrates in an excellent fashion the usefulness of esr spectroscopy in systems containing closely related radicals.

Asmus, et al.,<sup>47</sup> have studied the reactions of nitrosobenzene. Their results show that this compound reacts with OH by

$$OH + C_6H_5NO \longrightarrow C_6H_5NO_2H$$
 (13)

$$C_6H_5NO_2H \longrightarrow C_6H_5\dot{N}O_2^- + H^+$$
(14)

The latter reaction occurs in basic solution because the pK of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>H is 4.5.<sup>48</sup> The spectrum observed when an N<sub>2</sub>O-saturated solution of  $5 \times 10^{-4} M$  nitrosobenzene is irradiated is shown in Figure 8. This spectrum can be totally ascribed to the radical anion C<sub>6</sub>H<sub>5</sub>NO<sup>-</sup>. This radical has a pK of 11.7<sup>48</sup> and in the dissociated form is known to display the effects of hindered rotation about the C-N bond.<sup>49,50</sup> The hyperfine splittings determined from the spectrum of Figure 8 are given in Table III and are in accord with those obtained by Russell, *et al.*,<sup>50</sup> in ethanol solution. To explain the formation of C<sub>6</sub>H<sub>5</sub>NO<sup>-</sup> it is necessary to say

(47) K.-D. Asmus, G. Beck, A. Henglein, and A. Wigger, Ber. Bunsenges. Phys. Chem., 70, 869 (1966).

(48) K.-D. Asmus, A. Wigger, and A. Henglein, *ibid.*, **70**, 862 (1966).

(49) E. J. Geels, R. Konaka, and G. A. Russell, Chem. Commun., 13 (1965).

(50) G. A. Russell, E. J. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Kaupp, J. Amer. Chem. Soc., 89, 3821 (1967).

able III: Radicals from CH <sub>3</sub> NO <sub>2</sub> in Acid Solutions						
System	Proposed radical	$a^{\mathbf{N}}$	$a^{\mathrm{H}}$	g		
$CH_3NO_2 + C_2H_5OH$	CH <sub>2</sub> NO <sub>2</sub> CHOHCH <sub>3</sub>	28.09	10.19	2.00507		
$CH_3NO_2 + n - C_3H_7OH$	$CH_3\dot{N}O_2CHOHC_2H_5$	28.22	10.19	2.00506		
$\mathrm{CH}_3\mathrm{NO}_2 + \mathrm{C}_2\mathrm{H}_5\mathrm{OC}_2\mathrm{H}_5$	$\operatorname{CH}_3\dot{\operatorname{NO}}_2\operatorname{CH}(\operatorname{CH}_3)\operatorname{OC}_2\operatorname{H}_5$ $\overset{\dot{\operatorname{O}}}{\mid}$	28.24	9.95	2.00504		
$CH_{\$}NO_{2} + (CH_{3})_{2}CHOH$	$\operatorname{CH}_{3}^{I}\mathrm{NC}(\mathrm{OH})(\mathrm{CH}_{3})_{2}$	16.64	13.82	2.00545		

**Table III:** Radicals from  $CH_3NO_2$  in Acid Solutions<sup>a,b</sup>

<sup>a</sup> Hyperfine constants in gauss, accurate to about  $\pm 0.03$  G. Values of g factor accurate to about  $\pm 0.00003$ . <sup>b</sup> These radicals have also been reported by McMillan and Norman.<sup>26</sup>



Figure 8. Esr spectrum of  $C_6H_5NO^-$  obtained in an N<sub>2</sub>O-saturated,  $10^{-3} M$  solution of  $C_6H_5NO$  at pH 12.4.

that reactions 13 and 14 are followed by the electron transfer

$$C_{6}H_{5}\dot{N}O_{2}^{-} + C_{6}H_{5}NO \longrightarrow$$

$$C_{6}H_{5}NO_{2} + C_{6}H_{5}\dot{N}O^{-} \quad (15)$$

If this reaction has a rate constant of  $>10^7 M^{-1} \sec^{-1}$  (which is very possible), no spectrum of  $C_6H_5NO_2^-$  would be expected. Unfortunately in this case we cannot test the proposed mechanism directly by observing the initial intermediate.

A number of experiments with other aromatics have been tried, but in most cases the spectra are complex, consisting of several overlapping spectra, and no assignments have been made. The case of *p*-nitrophenol is an exception. Over the pH range 7–12 this compound (in the form  $O_2NC_6H_4O^-$ ,  $pK = 7.15^{51}$ ) reacts with OH to form *p*-benzosemiquinone radical ion<sup>52</sup> (a = 2.35 G, g = 2.00453) by the net reaction

$$OH + O_2NC_6H_4O - \rightarrow$$

$$-OC_6H_4O + H^+ + NO_2 - (16)$$

The spectrum obtained at pH 12 is shown in Figure 9 and the great signal intensity, a result of the long radical lifetime, is apparent. A crude estimate of the radical concentration responsible for the signal of Figure 9 gives  $2 \times 10^{-5} M$ . Because the total OH



Figure 9. Esr spectrum of *p*-benzosemiquinone radical ion obtained from an N<sub>2</sub>O-saturated solution of  $10^{-3} M$  *p*-nitrophenol at pH 11.8.

radical production during one pass of the solution through the beam is  $\sim 3 \times 10^{-4} M$ , the production of *p*-benzosemiquinone radical ion must represent at least approximately 10% of the product of reaction. It is not possible to say, of course, whether this radical has some precursor such as a hydroxycyclohexadienyl radical which lives of the order of a few microseconds. At lower pH the same lines are present but at lower intensity. It is likely that under these conditions increased protonation leads to a more rapid decay of the *p*benzosemiquinone ion.<sup>53,54</sup> Suarez, *et al.*,<sup>55</sup> have discussed some chemical results related to this reaction.

(51) "Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1966–1967, p D-86.

(54) G. E. Adams and B. D. Michael, Trans. Faraday Soc., 63, 1171 (1967).

<sup>(52)</sup> The parameters found by K. Scheffler and H. B. Stegman [Ber. Bunsenges. Phys. Chem., 67, 864 (1963)] for alkaline alcohol solution are a = 2.35 G and g = 2.00466.

<sup>(53)</sup> I. Yamazaki and L. H. Piette, J. Amer. Chem. Soc., 87, 986 (1965).

*H-Atom Reactions.* The reactions of hydrogen atoms are evident through the observation of product radicals and also through the decrease in intensity of the H-atom esr lines when solute is added to the solution. In several cases this decrease has been used to show that reaction with solute is occurring. In the present work only with oxalic acid and benzene have the product radicals been studied directly. Further work<sup>56</sup> is in progress to put this decrease in intensity on a quantitative basis for measuring H-atom reaction rates.

The distinctive spectrum (a 500-G doublet) of the hydrogen atom is observed during irradiation of perchloric acid solutions (Figure 10). The low-field line is inverted as was found in experiments on liquid methane.<sup>3</sup> In initial experiments two components of the low-field line were present as is shown in Figure 10. After O<sub>2</sub> was bubbled through the solution, one component remained. On the high-field side a remanent line is also present, but here its position is the same as that of the component removed by  $O_2$ . The parameters are for the reactive species a = 503.2 G, g = 2.00210and for the other a = 503.5 G, g = 2.00218. Although the amplitudes of the high- and low-field lines are comparable for both spectra, the low-field lines have somewhat greater peak heights and may in fact have greater area. From the lack of an effect of  $O_2$  on the second pair of lines (the same effect is obtained with isopropyl alcohol) it is evident that the remanent lines are from H atoms in the silica cell. Subsequent experiments with a new cell have shown essentially no signal from the cell. It is interesting that both low-field lines are essentially of the same inverted sense.

A detailed description of the behavior of the hydrogen atom signals is not yet possible. The height of the lines from the solution with no reactive solute is approximately proportional to the electron beam current so that the signal height is not determined only by recombination. Initial signal polarization. polarization upon reaction, and subsequent relaxation may all affect the signal size. Nevertheless, it appears that it is possible to use the decrease in signal height upon addition of solute to measure the rate of reaction with that solute relative to the unknown competing process. Calibration of the competing process can be made with a solute having a known rate constant for reaction with hydrogen atoms. Preliminary experiments showed that  $\sim 5 \times 10^{-4} M$  isopropyl alcohol decreased the signals by about 75%. The rate constant of  $\sim 5 \times 10^7 M^{-1} \sec^{-1.57}$  allows the half-time for decay of the hydrogen atom signals in the absence of solute to be determined. The time so determined is  $\sim$ 85 µsec. Once the decay of the signal has been calibrated in this way other compounds can be studied and their rates of reaction determined. A study of the rates H-atom reactions with a number of compounds is under way.56



Figure 10. Esr lines of H atoms in an experiment with perchloric acid (pH 1.6) solution (a). Note the inverted sense of the low-field lines. At (b) is given further resolution of the low-field line. No resolution of the high-field line was possible. In (c) are shown the lines present when 0.1 M isopropyl alcohol is added. The 506.4-G spacing is not exactly the hyperfine constant because of higher-order effects.

The reaction of H atoms with aromatics is very fast,<sup>57</sup> and the product with benzene is expected to be cyclohexadienyl radical. An experiment at pH 2 with a benzene-saturated solution showed signals from both unsubstituted and hydroxycyclohexadienyl radicals formed, respectively, by addition of H and OH to benzene. These spectra were much like those shown in Figures 6 and 7 for basic solution but were weaker. None of the low-field lines of the hydroxycyclohexadienyl radical spectrum could be seen but the ring proton splittings and the displacement of the center of the high-field group had values identical with those in the spectrum of Figure 6 so there is little doubt that the OH is undisassociated at pH 12. One of the stronger low-field lines of the cyclohexadienyl radical could be seen so that it was possible to determine all of the coupling constants. The values found for aqueous solution are very similar to those for the radical in 1,4-cyclohexadiene.<sup>3</sup> The parameters are given in Table II.

Experiments with nitromethane in acid never gave any significant signal intensity in spite of a demonstrated reaction with hydrogen  $atoms^{66}$  much in excess of that expected for abstraction. It seems likely that as a result of some form of exchange of the acid proton the lines for CH<sub>3</sub>NO<sub>2</sub>H (the expected product) are broadened so much that they cannot be seen.

<sup>(55)</sup> C. Suarez, F. Louys, K. Gunther, and K. Eiben, Tetrahedron Lett., 575 (1970).

<sup>(56)</sup> P. Neta, R. W. Fessenden, and R. H. Schuler, J. Phys. Chem., in press.

<sup>(57)</sup> See the values tabulated by M. Anbar and P. Neta, Int. J. Appl. Radiat. Isotopes, 18, 493 (1967).

The reactions of oxalic acid in irradiated aqueous solution are complex and involve all of the primary radicals but will be discussed here because the net reaction is reduction. Many experiments on oxalic acid were performed. One of the most useful was on an acid solution of  $2 \times 10^{-2} M$  oxalic acid (pH 1.4). Irradiation of the solution with no additive gave a strong single line at g = 2.00397 which was reduced in intensity by 70% when  $2 \times 10^{-2} M$  t-butyl alcohol was added. When  $2.6 \times 10^{-2} M$  isopropyl alcohol was added in addition, the signal intensity recovered to approximately 140% of its initial level. The reaction for the final mixture clearly involves electron transfer

$$(CH_3)_2\dot{C}OH + HOC-COH \longrightarrow$$

$$O O^-$$

$$HOC-COH + (CH_3)_2CO + H^+ (17)$$

(The state of dissociation of the product radical is not necessarily as shown.) This reaction has been observed by Norman and West<sup>22</sup> in Ti<sup>3+</sup>-H<sub>2</sub>O<sub>2</sub> systems and also in photolysis by Zeldes and Livingston<sup>58</sup> and by Arthur and Fessenden.<sup>59</sup> The g factors from these various experiments are in agreement. The  $\sim 50\%$  decrease in the H-atom signals observed when oxalic acid is added at  $2 \times 10^{-2} M$  indicates significant reaction, and the reaction giving the same radical (except for the acid dissociation) as in eq 17 seems obvious. The fact

that the signal level drops upon addition of t-butyl alcohol shows that OH (which the alcohol scavenges) is also producing the same final product. Because OH is an oxidizing species an intermediate step is needed. The reaction

$$O O O \\ \parallel \parallel \\ OH + -OC - COH \longrightarrow O O \\ \parallel \parallel & \parallel \\ \cdot OC - COH \text{ (or } CO_2 + \cdot COH \text{)} (19)$$

followed by electron transfer

$$\begin{array}{cccc}
O & O & O & OO \\
\parallel & \parallel & \parallel & \parallel \parallel \\
\cdot \text{COH (or } \cdot \text{OC-COH)} + \text{HOCCOH} \longrightarrow \\
O & O^{-} \\
\parallel & \parallel \\
\text{HOC-COH} + \text{CO}_2 + \text{H}^{+} (20)
\end{array}$$

seems probable. Norman and West<sup>22</sup> showed that  $\dot{C}O_2^-$  or  $H\dot{C}O_2$  can reduce oxalate. Again the state of



Figure 11. Esr spectra obtained in acid and basic solutions of  $10^{-2} M$  glyoxylic acid (HCOCOOH). The lines from the transients approach the intensity of the line from the cell. Note the several different gain settings. The stick spectra are drawn for the indicated radical and for the two corresponding <sup>18</sup>C-containing radicals. The arrow marks the position of the line ascribed to  $C_2O_4^{3-}$ .

acid dissociation of the various species is not necessarily as specified. The fact that a larger signal is obtained with isopropyl alcohol than with pure oxalate shows that not all of the H and OH radicals are producing the final radical in the absence of the intermediate step forming  $(CH_3)_2\dot{C}OH$ .

In basic solution the situation seems simpler. Only a weak signal at g = 2.00403 is found in  $10^{-2} M$  oxalate solutions. This signal is greatly enhanced by the presence of an OH scavenger such as *t*-butyl alcohol or formate (at  $10^{-2} M$ ); when N<sub>2</sub>O is added to the solution along with the OH scavenger, no signal remains. The radical must be produced by

$$e_{aq}^{-} + C_2 O_4^{2-} \longrightarrow -OC - CO^{-}$$
(21)

(58) H. Zeldes and R. Livingston, J. Phys. Chem., 74, 3336 (1970).
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and not by electron transfer from  $CO_2^-$ . (The photolytic experiments show that  $(CH_3)_2\dot{C}OH$  reacts only with  $HC_2O_4^-$  or  $H_2C_2O_4^{.58,59}$ ) It is not clear why an OH scavenger is necessary for efficient radical production. Possibly a reaction of OH with the radical destroys it as fast as it is formed. From the great signal

$$OH + C_2 O_4^{3-} \longrightarrow OH^- + C_2 O_4^{2-} \qquad (22)$$

intensity possible in either acid or basic solutions it is clear that the radicals do not recombine rapidly and that the rate constant for this reaction is around  $10^6$  to  $10^7 M^{-1} \sec^{-1}$ .

Further confirmation of the identity of the radical giving the line at g = 2.0040 is obtained from the observation that a line at the same position is obtained from glyoxylic acid (HC(=O)COOH) (see Figure 11). The reaction suggested is abstraction from the aldehyde hydrate which is expected to be present in significant concentration. Because this reaction is fast and

$$\begin{array}{c} H & O \\ O & \parallel \\ OH (or H) + HC - COH \longrightarrow \\ O \\ H \\ \end{array}$$

$$\begin{array}{c} H & O \\ O & \parallel \\ \cdot C - COH + H_2O (or H_2) \quad (23) \\ O \\ H \end{array}$$

makes use of both H and OH, somewhat more intense signals of the radical are found than when oxalic acid is used. In this case a search for lines from <sup>13</sup>C-containing radicals is possible, but none were found. This same negative result was obtained by Zeldes and Livingston<sup>58</sup> and must be a consequence of a broadening of the lines of the <sup>13</sup>C-containing radical by end-to-end proton exchange.

Hydrated Electron Reactions. Only in the cases of acetone, glyoxylic acid, oxalate (mentioned above), and chloroacetate were efforts made to demonstrate reactions of specifically the hydrated electron. With acetone the object was to show that the esr method gives the expected result of  $e_{aq}$  attachment. In strongly

$$e_{aq}^{-} + (CH_3)_2 CO \longrightarrow (CH_3)_2 \dot{C}O^{-}$$
(24)

$$(CH_3)_2\dot{C}O^- + H_2O \longrightarrow (CH_3)_2\dot{C}OH + HO^-$$
 (25)

basic solutions of acetone a spectrum identical with that obtained by OH abstraction from isopropyl alcohol was found confirming reaction 24. In neutral solutions the spectrum again agreed with that from isopropyl alcohol demonstrating reaction 25. In both of these cases the OH radical reacted with acetone, but the resultant lines

$$CH_{3}COCH_{3} + OH \longrightarrow CH_{2}COCH_{3}$$
 (26)

are so weak in our experiments that no hyperfine con-

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stants were determined. As well as could be determined, however, these lines are consistent with the known spectrum<sup>31</sup> of this radical. The other ketonic compound studied was  $HC(=0)COO^{-}$ . Reaction with  $e_{aq}^{-}$  in this case gives the same product as obtained from glycolate by abstraction of hydrogen.

$$e_{aq}^{O} + HCCOO^{-} \longrightarrow HC^{-}CO^{-}$$
(27)

The spectrum resulting from such an experiment is shown in Figure 11.

Chloroacetate was chosen because this compound has a special place in radiation chemistry through its role in the discovery of the hydrated electron.<sup>60</sup> When a  $10^{-2} M$  solution of chloroacetate was irradiated at pH 11.4, a spectrum with lines from both  $\dot{C}H_2COO^-$  and  $\dot{C}HClCOO^-$  was found. The parameters for the radi-

$$e_{ag}^{-} + ClCH_2COO^{-} \longrightarrow \dot{C}H_2COO^{-} + Cl^{-}$$
 (28)

$$OH + ClCH_2COO^- \longrightarrow Cl\dot{C}HCOO^- + H_2O \quad (29)$$

cal ClCHCOO<sup>-</sup> have been discussed in an earlier section. Those for  $\cdot$ CH<sub>2</sub>COO<sup>-</sup> are identical with those found for the radical produced from acetate by OH reaction. With no scavenger for  $e_{aq}^{-}$  present the signals from CH<sub>2</sub>COO<sup>-</sup> are very strong. When the solution is saturated with N<sub>2</sub>O, the CH<sub>2</sub>COO<sup>-</sup> signal intensity decreases and a spectrum like that of Figure 5 is found. Some CH<sub>2</sub>COO<sup>-</sup> is still present because of incomplete  $e_{aq}^{-}$  scavenging by N<sub>2</sub>O. Another doublet spectrum which has not yet been identified is also present. This spectrum is not that of  $-OCHCOO^{-}$ , CH-(COO<sup>-</sup>)<sub>2</sub>, or  $-OOCC(O^{-})CHOHCOO^{-}$ . As shown in the figure, lines from both CH<sub>2</sub>COOH and CHClCOOH are present in acid solutions but are rather weak. Here CH<sub>2</sub>COOH is formed by

$$ClCH_2COOH \longrightarrow$$

H +

$$H^+ + Cl^- + \dot{C}H_2COOH \quad (30)$$

Electron Transfer Reactions. Many of the reduction reactions of the hydrated electron can also be accomplished by alcohol radicals such as  $(CH_8)_2\dot{C}OH$  or by  $CO_2^-$ . In this work most of the reduction reactions occur in both ways and emphasis was placed upon the product radical rather than the details of the reaction itself. The first example to be discussed in this section is reaction of alcohol radicals with  $CH_8NO_2$  in acid solution. Nitromethane was studied previously in basic solution where long radical lifetimes are found, and it was of interest to compare the behavior. Nitromethane has been studied in acid by Longster, et al.,<sup>61</sup> and also by McMillan and Norman<sup>26</sup> (who also worked at

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(61) W. E. Griffiths, C. L. Longster, J. Myatt, and P. F. Todd, J. Chem. Soc. B, 533 (1967).



Figure 12. Esr spectra of acid solutions of  $5 \times 10^{-3} M$  CH<sub>3</sub>NO<sub>2</sub> containing 0.1 M ethyl and isopropyl alcohols.

pH 8). Much of our work on this system was performed before we became aware of the latter paper. Our results agree well with those of McMillan and Norman.

In acid solutions of nitromethane itself we have not been able to find any significant signal intensity. This result is surprising in that the studies<sup>56</sup> on the kinetics of H-atom disappearance suggest reaction by other than abstraction. Although other explanations for the lack of signals are possible, it is likely that the lines of  $CH_3NO_2H$  (pK 4.4)<sup>62</sup> are broad and unobservable at our radical concentrations-if the lines were narrow they should have been detected. No signals from other than  $CH_2OH$  were found in solutions containing 0.1 M methanol. In solutions of ethanol a strong spectrum (Figure 12) like what might be expected for  $CH_3\dot{N}O_2H$ was found with the parameters  $a^{\rm N} = 28.09$  G,  $a^{\rm H} =$ 10.19 G, g = 2.00507. McMillan and Norman found that the parameters varied with the reducing radical and therefore concluded that the species is  $CH_3\dot{N}O_2R$ where R is the alcohol radical. Our results with 1propanol and diethyl ether are given in Table III and agree with those of McMillan and Norman.<sup>26</sup> This agreement is significant and shows that the radicals in their system are not perturbed (as by complexing) by the titanium ions.

Our results also agree with theirs when isopropyl alcohol is present. Instead of a radical with  $a^{N} = 28$  G one with  $a^{N} = 16.64$  G is found (Figure 12).

Here the quartet splitting is 13.82 G. This radical is clearly of a different type and is most probably the radical

$$\dot{O}$$
  
 $\downarrow$   
 $CH_3NC(OH)(CH_3)_2$ 

formed by reaction of  $(CH_3)_2$ COH with CH<sub>3</sub>NO produced as a product of radiolysis as suggested by Asmus,

$$2CH_3NO_2H \longrightarrow CH_3N(OH)_2 + CH_3NO_2 \quad (31)$$

$$CH_3N(OH)_2 \longrightarrow CH_3NO + HOH$$
 (32)

et al.<sup>62</sup> In this case McMillan and Norman<sup>26</sup> argue that the tertiary ester  $CH_3NO_2C(OH)(CH_3)_2$  is so labile that electron transfer is preferred to formation of the ester. If so,  $CH_3\dot{N}O_2H$  must also be present (as also required by the proposed formation of  $CH_3NO$ ) and again one is forced to conclude that  $CH_3\dot{N}O_2H$  cannot be seen under these conditions.

A number of aromatic compounds can be reduced by  $(CH_8)_2\dot{C}OH$  (or in base  $(CH_3)_2\dot{C}O^{-}$ ). Those studied include nitrobenzene and the three nitrophenols. The spectrum of  $C_6H_5\dot{N}O_2^{-}$  at pH 11.5 is given in Figure 13. The conditions given in the figure caption are typical. The slow decay of the radical is evident through the high steady-state concentration, and it is clear that this

<sup>(62)</sup> K.-D. Asmus, A. Henglein, and G. Beck, Ber. Bunsenges. Phys. Chem., 70, 459 (1966).

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Radical	pH	$a^{\mathrm{N}}$	$a^{\mathrm{H}}_{\mathrm{ortho}}$	$a^{\mathrm{H}}_{\mathrm{meta}}$	$a^{\rm H}{}_{ m para}$	a <sup>H</sup> OH	g
$C_6H_5\dot{N}O_2 = b$	11.6	14.20	3,38	1.15	3.65		2,00448
$p$ -HOC <sub>6</sub> H <sub>4</sub> $\dot{\mathrm{NO}}_2$ <sup>-</sup>	6.3	15.00	3.41	1.05			2.00448
$p$ OC <sub>6</sub> H <sub>4</sub> $\dot{N}O_2$ -	12.0	15.60	3.26	0.82			2.00449
$m - OC_6 H_4 NO_2 -$	12.6	14.70	3,26	1.04	3.26		2.00443
$o-HOC_6H_4NO_2$	12.0	14.85	3.39°	0.91, 1.04	3.60°	0.38	2.00451
$C_{\theta}H_{5}\dot{N}O^{-d}$	12.4	10.27	7.69	1.31	4.36		2.00544

Table IV: Aromatic Anion Radicals in Aqueous Solution<sup>a</sup>

<sup>a</sup> Hyperfine constants in gauss, accurate to about  $\pm 0.03$  G. Values of g factor accurate to about  $\pm 0.00003$ . <sup>b</sup> Values slightly different than previously reported for aqueous solution, see ref 63 and 64. <sup>c</sup> Assigned on the basis of the values for C<sub>6</sub>H<sub>5</sub> $\dot{N}O_2^{-}$ . <sup>d</sup> Because of hindered rotation only the sum of the two ortho values is available. Values for ethanol solution<sup>50</sup> are slightly different.



Figure 13. Esr spectrum of  $C_6H_6\dot{N}O_2^{-}$  obtained by electron transfer from  $(CH_3)_2\dot{C}O\dot{H}$  to nitrobenzene. The solution was N<sub>2</sub>O saturated and at pH 11.6 and contained 0.1 *M* isopropyl alcohol and  $10^{-3}$  *M* nitrobenzene. Note that the difference between the ortho and para splittings is resolved.

is an excellent means by which to prepare these radicals. Hyperfine constants for this radical and other aromatic nitro anions are given in Table IV. The continuation of the trend of increasing nitrogen hyperfine constant with increased polarity of the solvent<sup>63,64</sup> is evident here in that the nitrogen hyperfine constant in  $C_6H_5NO_2^-$  is larger than for other solvents commonly used in the chemical or electrochemical preparation of such anion radicals. The hyperfine constants for this species are slightly different than previously reported<sup>63,64</sup> for aqueous solutions and may depend weakly on pH or ionic strength.

The three nitrophenols were of interest because of the previous pulse radiolysis experiments of Grünbein and Henglein.<sup>65</sup> However, no attempt was made to check in detail their results regarding the equilibrium constant for the second dissociation of the nitrophenol anion radicals. They reported pK values (for reaction 33) for

$$HOC_6H_4\dot{N}O_2^- \longrightarrow H^+ + -OC_6H_4\dot{N}O_2^- \quad (33)$$

ortho, meta, and para isomers of 9.5, 8.9, and 9.8, respectively. In experiments with the para compound at pH 6.05 and 12.0 we found significantly different hyperfine constants, and if their pK values<sup>65</sup> are approximately correct, then these radicals may be assigned to the singly and doubly dissociated forms, respectively. An experiment with the meta compound at pH 12.6 similarly should yield the doubly dissociated form. These assignments are given in the table. The ortho



Figure 14. Esr spectrum obtained by radiolysis of an  $N_2O$ -saturated solution at pH 12.0 of  $10^{-3}$  *M* o-nitrophenol and 0.1 *M* isopropyl alcohol. Observed spectrum corresponds to the indicated radical anion.

compound presents a problem in that the spectrum observed at pH 12.6 similarly should also yield the doubly dissociated form. In fact the spectrum observed at pH 12 contains an extra hyperfine splitting (Figure 14). This spectrum has previously been assigned to the form HOC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub><sup>-</sup> in work involving chemical generation of the radical.<sup>66</sup> In that work the smallest splitting (0.3 G) was attributed to the phenolic proton. In view of the apparent simplicity of the reaction mechanism we can see no reason to contest this assignment. It must be, therefore, that the pK of the ortho form is greatly shifted from that of the phenol (pK =  $7.17^{62}$ ) and that even at pH 12 most of the compound is in the singly dissociated form (pK > 12). The intramolecular hydrogen bond distinguishes this species from the other isomers and a combination of the strong hydrogen bond to the partially charged oxygen of the anion radical and the close proximity of the negative charges in the form  $-OC_6H_4\dot{N}O_2$  must account for the high pK. A detailed study of spectra at a number of intermediate pH values would be necessary to check the pK values for the meta and para forms, and this has not as yet been attempted.

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(65) W. Grünbein and A. Henglein, Ber. Bunsenges. Phys. Chem., 73, 376 (1969).

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Hyperfine Constants. The main emphasis of this work has been upon the reaction mechanisms, and many of the hyperfine constants (such as those of the cyclohexadienyl radicals) have already been discussed. The radicals formed by abstraction of hydrogen from alcohols and hydroxy acids deserve some comment, however. The radicals CH2OH and (CH3)2COH are well known,<sup>20,23a</sup> but the hyperfine constants for the basic forms  $\dot{C}H_2O^-$  and  $(CH_3)_2\dot{C}O^-$  have not been reported although the spectrum of  $\dot{C}H_2O^-$  has been published.<sup>6</sup> The drop in hyperfine constant upon ionization of the OH group in  $(CH_3)_2\dot{C}OH$ ,  $\dot{C}H_2OH$ , and  $\dot{C}HOHCOO^$ can be related to a drop in spin density on the  $\alpha$ -carbon caused by more conjugation with  $O^-$  than with OH. However, the situation may be more complex in view of the tendency<sup>67</sup> of some of the oxy-substituted radicals to be nonplanar at the radical site. Because of the low <sup>18</sup>C splittings reported for  $-OCHCO_2$ , it is clear that in this case the radical site is planar. The increase in g factor upon ionization of the OH group is consistent with a greater spin density upon the oxygen.

The hyperfine constants for the acid radicals  $\dot{C}H_2$ - $COO^{-}$ ,  $\dot{C}H(COO^{-})_2$ , and  $\dot{C}HClCOO^{-}$  are little changed from the undissociated forms, consistent with the results for  $a_{\alpha}$  in succinic acid.<sup>38</sup> This concern with the form of the radicals with respect to acid dissociations is one which is not particularly familiar to those concerned mainly with other than aqueous solution. It is, of course, clear that the various forms represent different chemical entities. Some examples of the effect of the exact radical form on reaction rates are the effect of a double negative charge on radical recombination<sup>41</sup> and the absence of reaction of  $(CH_3)_2\dot{C}OH$  or  $CO_2$ with  $C_2O_4{}^{2-}$ . Acid dissociation also affects hyperfine constants significantly, and nowhere is this better shown than in the spectra of the radicals  $H_2N\dot{C}HCO_2^{-1}$ and  $H_2N\dot{C}HCO_2H$ . Only the latter of these two forms shows equivalent splittings for the two NH protons.68 It is clear that with radical production techniques now available for studies of aqueous solutions over a wide range of pH more concern with radical pK's will be necessary.

#### Conclusions

The results presented here clearly demonstrate the practicality of studying by esr spectroscopy the radicals produced by the reaction of the primary radicals of water radiolysis with various solutes. The intensity of the esr signals is, of course, dependent on the rate of production of the radicals, their disappearance rate, and the characteristics of the esr spectra (line width and number of hyperfine splittings). With spectra typical of simple organic radicals and reasonably efficient production it is clearly possible to study radicals which disappear bimolecularly with rate constants  $\sim 10^9$  to  $10^{10}$  $M^{-1}$  sec<sup>-1</sup>. The unique advantage of esr spectroscopy in allowing ready identification of radicals has been used to advantage in several cases. Of particular importance is the detection of the three isomeric hydroxycyclohexadienyl radicals formed by OH addition to benzoate. In such cases the esr method can stand alone and does not need information from other techniques such as pulse radiolysis with optical detection methods. In many other cases partnership with the optical studies is necessary, and the two methods greatly strengthen each other. In the case of acid nitromethane solutions, for example, no esr spectrum is observed in spite of a demonstrated reaction to form  $CH_3\dot{N}O_2H$ . Here the formation and decay rates are defined sufficiently that a necessary conclusion is that the esr lines must be relatively broad.

The esr signal intensity obtained with radiolytic generation of radicals is somewhat less than obtained in typical photolytic or mixing experiments with  $Ti^{3+}-H_2O_2$ . Thus for some spectroscopic purposes the latter methods may be preferable. However, radiolytic production has its own advantages. Of the three primary radicals from water only OH (at present) can be generated in these other ways. Furthermore the complexity of these other methods (particularly  $Ti^{3+}-H_2O_2$ ) is such that accurate mechanistic and rate information may not always be obtainable. Also the radiolytic method can be applied over the full 0–14 pH range without the worry of the effects of other added substances (such as metal ions).

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