

## Pulse Radiolysis: Fast Reaction Studies in Radiation Chemistry

Direct observation of transient species has provided new insight into mechanisms of radiation chemistry.

Leon M. Dorfman

A complete empirical understanding of the mechanism of any chemical reaction rests on three items of information. These are (i) the identity of the reactive transient species which participate in the overall process, (ii) the definition of the elementary reactions which they undergo, and (iii) the magnitude of the specific rate constants for these elementary reactions. This information is no less a requirement in the case of reactions which are induced by ionizing radiation than for any other type of chemical reaction. Indeed, the very complexity of reactions induced by radiation can make the usual method of speculative inference in the construction of mechanisms a hazardous mental exercise.

Over the past decade or more there have been dramatic advances toward obtaining this information as directly as possible by the development and use of a variety of fast reaction techniques in chemical kinetics (*1*). There have been some notable successes, particularly in the determination of absolute rate constants. The general approach in these methods is to impose upon a system at rest a short-lived perturbation and to observe the subsequent time dependence of the changes which occur in the system as it returns to equilibrium or to a state of quasi equilibrium. The fast de-

tection of these changes is accomplished with electronic aids having a time resolution appropriate to the specific elementary reactions.

Three years ago these techniques were first successfully applied (*2-4*) to the study of radiation chemistry, and they have provided new insight into the reaction mechanisms in the liquid state. Moreover, many of the absolute rate constants which have been determined are of importance in other branches of chemical kinetics. These developments have been made possible by the availability of electron accelerators which can deliver a highly intense electron pulse of microsecond duration. The pulse current is high enough so that, in most systems, the instantaneous concentration of transient species formed is in the range  $10^{-5}$  to  $10^{-4}M$ . At such concentrations the reactive species, such as free radicals or ions, may be observed directly by the recording of their optical absorption spectra, which generally show a frequency shift and sometimes show a higher extinction coefficient compared with the parent compound. The spectra of these short-lived species are observed by synchronized flash absorption spectrophotography. The kinetics are then observed directly by fast spectrophotometric recording.

A detailed description of the experi-

mental technique in use at Argonne National Laboratory was presented in the first of a series of papers (*5-8*) that dealt principally with aquo-organic and organic systems, and I need not repeat all the details here. I do, however, indicate the characteristics of the electron pulse and the physical arrangement for irradiating the sample and detecting transient species.

The accelerator in use at Argonne (*9*) is a linear accelerator built by the Applied Radiation Corporation. A beam energy of 15 Mev has been used, partly because this energy is in the region of optimum performance of the instrument and partly because the higher penetration is advantageous in that the desired large number of species is not contained in an excessively small volume, where the rate of decay through second-order processes would be high. The longest pulse used has a duration of 5 microseconds and a current of 0.12 ampere. The shortest pulse, used primarily in kinetic studies where the effective observation time of a fast process may be less than 2 microseconds, has a duration, or pulse width, of 0.4 microsecond and a maximum current of about 0.2 ampere. It is an important characteristic of the pulse that its time profile is very nearly rectangular, showing a decay time to zero current of less than 0.2 microsecond. This characteristic is extremely helpful in the fast kinetic studies as well as in the determination of molar extinction coefficients from the optical absorption, since it facilitates the definition of a "time concentration" when the rate of formation of transient species may be represented by a step function.

The incident beam has a diameter of about 15 millimeters and is slightly divergent. It may, of course, be focused to a smaller diameter if desired. The physical arrangement is shown in Fig. 1. The electron beam enters the quartz irradiation cell from the left. Since the electron range is approximately 6 centimeters, cell lengths of 4 centimeters or

The author is a senior chemist and group leader at the Argonne National Laboratory, Argonne, Ill.

less are generally used. The beam of analyzing light enters collinearly with the electron beam from the opposite direction. There is a fourfold reflection of the beam of analyzing light, between a plane mirror at the front of the cell and a concave mirror at the rear; thus, the detection sensitivity is increased. The beam of analyzing light is then brought over to a spectrograph for either photographic or fast photometric detection. For photographic detection, a xenon spectroflash lamp is used as the light source. This may be fired at any preselected interval after the pulse of the electron beam. For kinetic studies the flash lamp is replaced by a steady line source, and the time change for the transmitted intensity at a specific wave-

length is displayed on an oscilloscope. More or less similar arrangements are in use in other laboratories where such work is in progress (3, 4, 10). The reader who is familiar with the flash photolysis technique (11) will recognize the method described here as the direct-radiation chemical analog, although there are some important differences.

In the few years during which this technique has been in use there have been a very considerable number of important and interesting observations. Among these are the primary species in irradiated water, a variety of aromatic and aliphatic free radicals in both water and organic liquids, and one of the primary species formed in the radiolysis of polar organic liquids.

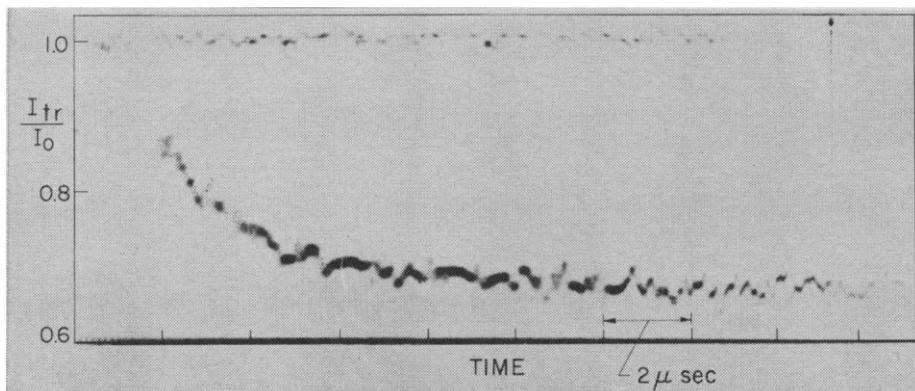
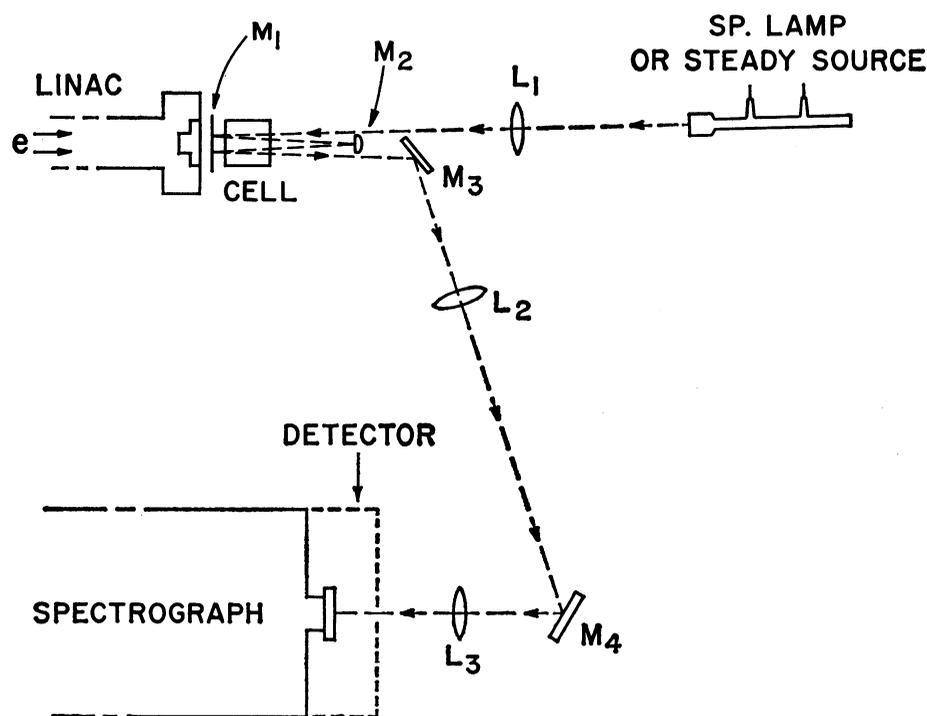
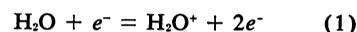


Fig. 1 (top). Experimental arrangement for optical detection of transients in pulse radiolysis. ( $M_1$ – $M_4$ ) Mirrors; ( $L_1$ – $L_3$ ) lenses. Fig. 2 (bottom). Rate curve for the formation of the  $(\text{OH})\text{C}_6\text{H}_6\cdot$  radical in deaerated aqueous solution, observed at 313 millimicrons.

## Primary Species in Irradiated Water

Chemical effects induced by radiation in water and aqueous solutions have for the most part been fairly successfully explained (12) in terms of two types of primary reactive species formed in the water by the ionizing radiation. One of these exhibits oxidizing properties and is considered to be the free hydroxyl radical, OH. This view continues to be supported by a body of indirect but varied experimental evidence. The hydroxyl radical is presumed to be formed in the processes



For  $\gamma$ -rays and electrons of energy greater than 0.3 Mev, in neutral water and aqueous solutions, approximately 2.4 OH radicals are formed for every 100 electron volts of absorbed energy.

The other type (or types) of primary species exhibits reducing properties and was for a number of years thought to be the free hydrogen atom, H. It was thought to be formed in the process



The total yield of reducing species in neutral water and aqueous solutions is approximately 2.9 per 100 electron volts.

As long ago as 1953, however, it was pointed out (13) that the fate of the electron would be greatly influenced by the polar-liquid environment in which it found itself. As the electron reaches thermal energies, its lifetime is longer than the dielectric relaxation time of the liquid ( $\sim 10^{-11}$  sec), and thus it polarizes the surrounding water molecules. The electron, although not completely localized within the surrounding hydration sphere, is bound in stable quantum states.

This hydrated electron,  $e_{aq}^-$ , thus has a considerably longer natural lifetime than a free electron, decaying in pure water according to the process



It was pointed out (13) that this effect upon the reactivity would be of considerable importance in the chemistry of irradiated aqueous solutions.

After 1958, several independent pieces of evidence relating to the reactivity of the reducing species (14) suggested that there were two different forms, one of which was the hydrated electron. In 1962 it was established in an important

quantitative investigation, in which the kinetic salt effect upon a set of reactions of the reducing species was studied (15), that the species did in fact have unit negative charge and was probably the hydrated electron. It appears that there is a small independent yield of hydrogen atoms.

To obtain information about the reactivity of these primary species, and indeed about their very existence, is one of the main objectives of research on the chemistry of irradiated aqueous systems. The pulse radiolysis technique has met with some notable success in this regard.

The first observation of a rate curve for the reaction of one of the primary species in water was reported in an investigation of aqueous benzene solutions (5, 16). The reaction of the hydroxyl radical with benzene,



was recorded with a time resolution of about 0.2 microsecond. The rate curve for this reaction is shown in Fig. 2. This curve was obtained by recording the rate of formation of the adduct, the hydroxycyclohexadienyl radical, which has a peak absorption at 313 millimicrons with a molar extinction coefficient (5) of 3500 molar<sup>-1</sup> per centimeter. The significance of the spectral observations to the interpretation of the chemistry of irradiated aqueous solutions of aromatic molecules is discussed later in this article.

The rate curve with the relative concentrations of the reactants  $[\text{C}_6\text{H}_6]/[\text{OH}] > 30$  was observed. Under this condition the reaction is a pseudo-first-order

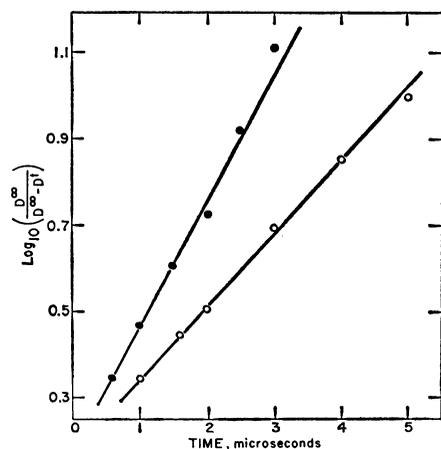


Fig. 3. Test of first-order rate law for the curve for the formation of the  $(\text{OH})\text{C}_6\text{H}_6 \cdot$  radical. Solid circles,  $[\text{C}_6\text{H}_6] = 1.8 \times 10^{-4}$  mole; open circles,  $[\text{C}_6\text{H}_6] = 1.1 \times 10^{-4}$  mole.

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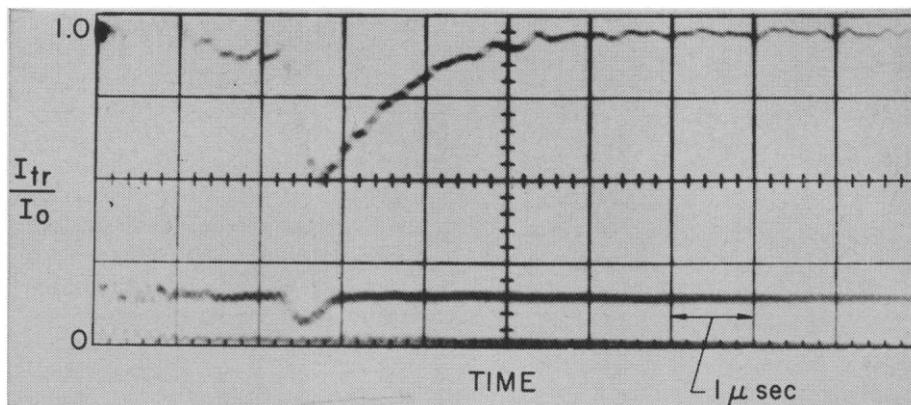


Fig. 4. Rate curve for the reaction of the hydrated electron with the hydrogen ion in deaerated water, observed at 578 millimicrons.  $[\text{H}^+] = 6 \times 10^{-5}$  mole. A simultaneously recorded time profile of the electron pulse is shown just above the 0-percent transmission trace.

reaction, the self-recombination reaction of the hydroxyl radical does not compete, and the differential rate expression

$$\frac{d[(\text{OH})\text{C}_6\text{H}_6 \cdot]}{dt} = k_5 [\text{OH}][\text{C}_6\text{H}_6] \quad (\text{I})$$

becomes

$$\frac{d[(\text{OH})\text{C}_6\text{H}_6 \cdot]}{dt} = k'_5 [\text{OH}] \quad (\text{II})$$

where  $k'_5$  is the pseudo-first-order rate constant. The integrated form of this equation, expressing concentrations in terms of the optical density,  $D$ , of the absorber is

$$\log_{10} \left( \frac{D^\infty}{D^\infty - D^t} \right) = \frac{k'_5}{2.303} t \quad (\text{III})$$

where  $D^t$  and  $D^\infty$  are the optical densities at times  $t$  and  $\infty$ , respectively. A somewhat similar form of Eq. III is obtained if the reactant, rather than a product, is the absorber, or if both the reactant and a product are absorbers. Of course, if the absorption of reactant and product coincides in both wavelength and intensity, the method cannot be used. I have presented this rather elementary analysis here simply because it represents the general method of obtaining, with the pulse technique, absolute rate constants for bimolecular reactions of a transient species with a stable species.

A plot of Eq. III (Fig. 3) shows that the rate curves for reaction 5 do fit closely to a first-order rate law. From the slopes of straight lines such as those of Fig. 3, the absolute rate constant (5, 16) for reaction 5 is found to be

$$k_5 = (4.3 \pm 0.9) \times 10^9 \text{ molar}^{-1} \text{ sec}^{-1}$$

at 23°C. The rate constant for the reaction of a hydroxyl radical with benzene- $d_6$  was found to be  $4.7 \times 10^9$  molar<sup>-1</sup> sec<sup>-1</sup>. The value of  $k_5$  indicates that the reaction is controlled by diffusion.

With respect to the reducing species, an important observation of the hydrated electron (10, 17), which is of far-reaching significance in the chemistry of irradiated aqueous solutions, has recently been made at Mount Vernon Hospital in England. A broad, strong, short-lived absorption extending throughout the visible and the near-infrared regions has been observed in irradiated water. The absorption spectrum, which is relatively structureless but exhibits a strong peak at about 700 millimicrons, has been assigned to the hydrated electron. The molar extinction coefficient at 577 to 579 millimicrons has been determined (7) to be  $9.7 \times 10^3$  molar<sup>-1</sup> cm<sup>-1</sup>.

The important consequence of this work is that knowledge of the absorption spectrum makes it a relatively straightforward matter to study the specific reactivity of many reactions of this species. Thus, for example, the absolute rate constant has been determined for the reaction of the hydrated electron with a hydrogen ion,



A rate curve for this reaction is shown in Fig. 4. A first-order test of a typical curve is shown in Fig. 5. The method is capable of giving results of a high degree of accuracy; the data shown (7) led to the determination of an absolute rate constant of

$$k_6 = (2.26 \pm 0.21) \times 10^{10} \text{ molar}^{-1} \text{ sec}^{-1}$$

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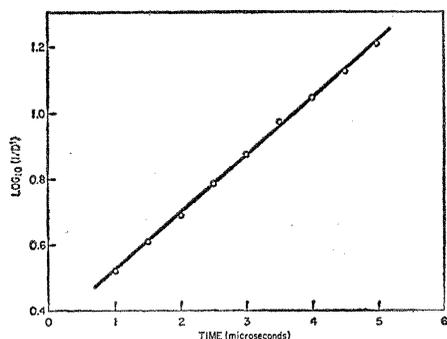


Fig. 5. Test of the first-order rate law for the disappearance of the hydrated electron in deaerated acidic aqueous ethanol solution;  $e_{aq}^- + H^+ = H$ ;  $[H^+] = 1.90 \times 10^{-5}$  mole;  $k = 2.14 \times 10^{10}$  molar $^{-1}$  sec $^{-1}$  (23°C).

at 23°C. A large number of such rate constants (7, 18) have been determined at Argonne; some of these are shown in Table 1.

The table, which lists some of the experimentally measured absolute rate constants for the primary species in irradiated water, contains, for the sake of completeness, two absolute rate constants obtained by a repetitive pulsing method (19) analogous to the rotating sector technique of photochemistry (20), which is quite different in principle from the technique described here.

An important specific reactivity of the hydrated electron is its decay in pure water according to reaction 4. The limiting value for the rate constant for this first-order decay process has been determined (7) as

$$k_4 \leq 4.4 \times 10^4 \text{ sec}^{-1}$$

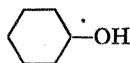
at 23°C. That is, the half-life of the hydrated electron is at least 16 microseconds. This makes it clear that the electrons do escape from the parent spur.

## Organic Free Radicals

Reactions of a number of organic free radicals in water (5-7) and in organic liquids (3, 6, 21-23) have been studied by pulse radiolysis. Spectra of free radicals have been observed in both aromatic and aliphatic systems.

The first transient species to be observed (2, 3) with the pulse radiolysis technique was the benzyl radical; its spectrum had previously been identified in flash photolysis (24). The kinetics of the reactions of the benzyl radical and the  $\alpha$ -ethanol radical have been studied (3), but the absolute rate constants reported appear to be in error because of an oversight on the part of the investigators (3) in neglecting the role of the glyceryl radical in their solutions. The solutions contained 67 percent glycerol to increase the viscosity. These workers estimated the molar extinction coefficient of the benzyl radical in 33 percent ethanol, 67 percent glycerol, at 3175 angstroms, to be 1100 molar $^{-1}$  cm $^{-1}$ .

Pulse irradiation of deaerated cyclohexanol (21) produced a transient absorption in the region 2900 to 3400 angstroms which was assigned to the  $\alpha$ -cyclohexanol radical



The assignment was supported by electron-spin-resonance observations as well as by product analysis. The bimolecular rate constant for the reaction of two  $\alpha$ -cyclohexanol radicals was found to be  $(3.4 \pm 1.5) \times 10^8$  molar $^{-1}$  sec $^{-1}$  at 25°C. This rate constant is, of course, the sum of the rate constants for association and disproportionation of the radical. The  $\alpha$ -cyclohexanolperoxy radical,  $C_6H_{10}(OH)O_2^{\cdot}$ , was also observed in this

system. The bimolecular rate constant for the disappearance of this radical was found to be  $(1.8 \pm 0.8) \times 10^7$  molar $^{-1}$  sec $^{-1}$  at 25°C.

I should point out that the determination of rate constants for radical-radical reactions, which cannot be observed under pseudo-first-order conditions, is subject to a considerable experimental uncertainty, since it is required that one know the concentration of species at any time  $t$ , say at  $t = 0$ . Although this value may be obtained from the appropriate product concentrations or from a knowledge of the concentrations of the precursors at zero time, it is difficult to determine to an accuracy of better than  $\pm 20$  percent.

For radical association in a one-radical system, the differential rate expression is

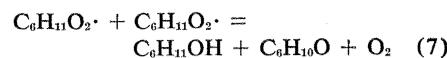
$$\frac{-d[R\cdot]}{dt} = 2k_r [R\cdot]^2 \quad (IV)$$

and the integrated form, expressing concentration in terms of optical density, is

$$1/D_t^k = \frac{2k_r}{\epsilon l} t + \text{constant} \quad (V)$$

where  $D_t^k$  is the optical density at time  $t$ ,  $\epsilon$  is the molar extinction coefficient, and  $l$  is the length of the optical absorption path. For a two-radical system where the three reactions may be concurrent, linear or near-linear plots of  $1/D_t^k$  as a function of time may be obtained. In some cases, as in the example that follows (22), the individual rate constants have been obtained by a graphical approximation in which the initial and final slopes of the curve are utilized.

Oxygenated cyclohexane solutions exhibit (22) a transient absorption in the far ultraviolet. The spectrum has been assigned to the cyclohexylperoxy radical,  $C_6H_{11}O_2^{\cdot}$ . From the observed decay curves, absolute rate constants were determined for the reactions



$$k_7 = (1.6 \pm 0.6) \times 10^6 \text{ molar}^{-1} \text{ sec}^{-1}$$

at 25°C, and



$$k_8 = (3.0 \pm 1.0) \times 10^9 \text{ molar}^{-1} \text{ sec}^{-1}$$

at 25°C. The rate constants  $k_7$  and  $k_8$  are lower than the diffusion-limited value by a factor of approximately  $10^{-4}$ .

Table 1. Absolute rate constants for some reactions of the primary species in irradiated water.

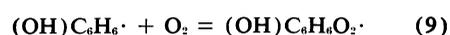
Reaction	Absolute rate constant (molar $^{-1}$ sec $^{-1}$ )	References
$OH + C_6H_6 = (HO)C_6H_6^{\cdot}$	$(4.3 \pm 0.9) \times 10^9$	(5)
$e_{aq}^- + H_{aq}^+ = H$	$(2.3 \pm 0.2) \times 10^{10}$	(7, 18)
$e_{aq}^- + O_2 = O_2^{\cdot -}$	$(1.9 \pm 0.2) \times 10^{10}$	(18, 33)
$e_{aq}^- + H_2O_2 = OH + OH_{aq}^-$	$(1.2 \pm 0.1) \times 10^{10}$	(18)
$e_{aq}^- + Cu_{aq}^{++} = Cu_{aq}^+$	$(3.3 \pm 0.3) \times 10^{10}$	(18)
$e_{aq}^- + H_2O = H + OH_{aq}^-$	$\leq 8.0 \times 10^2$	(7)
$OH + H_2 = H + H_2O$	$(4.5 \pm 0.4) \times 10^7$ *	(19)
$OH + OH = H_2O_2$	$(8.0 \pm 2.0) \times 10^9$ *	(19)

\* The experimental method used in the determination of these hydroxyl rate constants is a repetitive pulsing technique quite different in principle from the pulse radiolysis method. The rate constants for the radical-radical reactions, in this case  $OH + OH$ , are presented as  $2k$ , in terms of the rate of disappearance of the radical.

The investigators (22) determined the temperature coefficient of reaction and reached the interesting conclusion that the low rate constant is primarily the result of a low steric factor, rather than an activation-energy effect, estimated to be  $10^{-4}$  by comparison with the calculated diffusion-limited value.

The observation of the hydroxycyclohexadienyl radical in aqueous benzene solution (5) not only made it possible to determine the rate constant for the hydroxyl radical reaction in this system but answered a basic question concerning the role of this primary transient species. The chemistry of irradiated aqueous benzene solutions had generally been interpreted (25) in terms of the phenyl radical,  $C_6H_5\cdot$ , presumed to be formed in a hydrogen-abstraction reaction by the hydroxyl radical. The observed spectrum was, however, assigned to the  $(OH)C_6H_6\cdot$  radical on the basis of spectral evidence in which a family of spectra consistent with substituted cyclohexadienyl radicals had been observed, and on the basis, also, of kinetic evidence. Thus it was concluded that the hydroxyl radical enters the ring, as had been suggested in recent radiation chemical studies (26). This conclusion also indicated that earlier studies (27) with Fenton's reagent were open to re-interpretation. Recent studies of the electron-spin-resonance spectra (28) in aqueous benzene solution, in which chemically produced hydroxyl radicals were used, confirm the conclusions of the pulse radiolysis studies (5).

The reaction of the hydroxycyclohexadienyl radical with oxygen



was observed. The absolute rate constant (5) was found to be

$$k_9 = (5.0 \pm 0.6) \times 10^8 \text{ molar}^{-1} \text{ sec}^{-1}$$

at 23°C.

The pulse radiolysis of ethanol and of aqueous ethanol solutions has been investigated (6, 7). In both systems a transient ultraviolet absorption was observed which has been assigned to the  $\alpha$ -ethanol radical,  $CH_2\dot{C}HOH$ . The kinetics observed at 297 millimicrons in aqueous solution appear to represent just this one-radical system, since both precursors, the OH radical and the H atom are "instantaneously" scavenged by the ethanol at 0.5M concentration. Thus, the bimolecular disappearance of  $\alpha$ -ethanol radicals alone has been observed. The absolute rate constant was found to be  $(1.4 \pm 0.4) \times 10^9 \text{ molar}^{-1}$

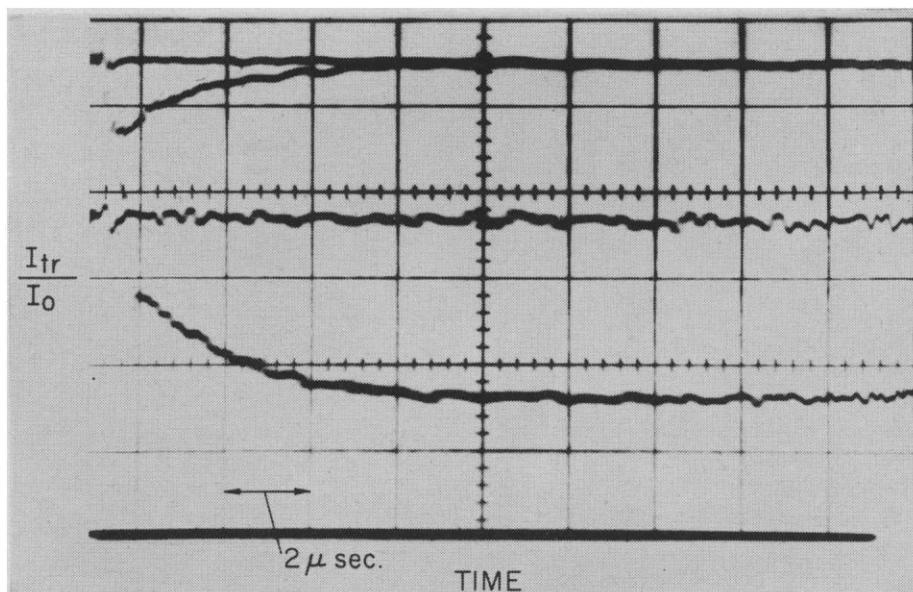


Fig. 6. Simultaneous rate curves for (i) the disappearance of the solvated electron (upper curve, observed at 546  $m\mu$ ) in deaerated ethanol containing diphenyl, and (ii) the formation of a transient species of diphenyl (lower curve, observed at 313  $m\mu$ ).

$\text{sec}^{-1}$  at 23°C. Again, the reaction appears to be diffusion-controlled.

The molar extinction coefficients determined for some of the organic free radicals observed by pulse radiolysis are listed in Table 2. The absolute rate constants for a number of bimolecular reactions of organic free radicals are shown in Table 3.

Solvation of the electron in polar liquids is by no means limited to water. The theoretical considerations (13) apply to polar liquids in general, the occurrence of the phenomenon depending

upon parameters such as the dielectric constant of the liquid.

Some information concerning the role of the electron in organic systems has been obtained in experiments in the solid state (29, 30) at low temperatures. Evidence for electron solvation in organic glasses has been obtained in photochemical experiments in which the electrons were introduced into the matrix from alkali metals in solution or by the photo-oxidation of organic solutes (29). A broad absorption band in the visible region, with a peak at about

Table 2. Molar extinction coefficients of some organic free radicals determined by pulse radiolysis.

Radical	Solvent	Wavelength (Å) of $\epsilon$ -determination	Molar extinction coefficient, $\epsilon$ (molar $^{-1}$ cm $^{-1}$ )	References
$C_6H_5CH_2\cdot$	33% Ethanol, 67% glycerol	3175	1100	(3)
$C_6H_{11}O_2\cdot$	Cyclohexane	2750	2000	(22)
$(HO)C_6H_6\cdot$	Water	3130	$3500 \pm 800$	(5)
$CH_2\dot{C}HOH$	Water	2967	$240 \pm 45$	(7)

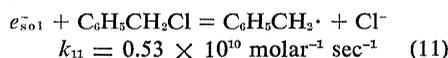
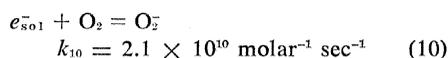
Table 3. Absolute rate constants for some reactions of organic free radicals determined by pulse radiolysis.

Reactant pair	Solvent	Temperature (°C)	Rate constant (molar $^{-1}$ sec $^{-1}$ )	References
$(OH)C_6H_{10}\cdot + (OH)C_6H_{10}\cdot$	Cyclohexanol	25	$(3.4 \pm 1.5) \times 10^8$	(21)
$(OH)C_6H_{10}O_2\cdot + (OH)C_6H_{10}O_2\cdot$	Cyclohexanol	25	$(1.8 \pm 0.8) \times 10^7$	(21)
$C_6H_{11}O_2\cdot + C_6H_{11}O_2\cdot$	Cyclohexane	25	$(1.6 \pm 0.6) \times 10^6$	(22)
$C_6H_{11}O_2\cdot + HO_2\cdot$	Cyclohexane	25	$(3.0 \pm 1.0) \times 10^6$	(22)
$(OH)C_6H_6\cdot + O_2$	Water	23	$(5.0 \pm 0.6) \times 10^8$	(5)
$(OH)C_6H_6O_2\cdot + (OH)C_6H_6O_2\cdot$	Water	23	$< 1.4 \times 10^8$ *	(5)
$CH_2\dot{C}HOH + CH_2\dot{C}HOH$	Water	23	$(1.4 \pm 0.4) \times 10^9$	(7)

\* The near linearity of the second-order test of the rate curve and the near equality of the initial concentration of the  $(OH)C_6H_6O_2\cdot$  radical and the  $HO_2\cdot$  radical in water suggest that the actual rate constant is approximately  $7 \times 10^7 \text{ molar}^{-1} \text{ sec}^{-1}$  at 23°C.

600 millimicrons, was observed in the experiments with alkali metals. It was suggested that this absorption band was attributable to the solvated electron in the matrix, which contained isopentane, ether, and various alkyl amines. In a more recent radiation-chemistry study (30) in hydrocarbon glasses as well as in solid ethanol, evidence of electron attachment has been obtained from observation of the spectra of the mono-negative ions of acceptor molecules such as biphenyl and naphthalene. In pure solid ethanol a visible absorption band was suggested to be that of the solvated electron.

In our studies of irradiated alcohols, made by means of the pulse radiolysis method, we have observed a broad visible absorption band of a transient species in both ethanol and methanol (8). In ethanol there is a peak at about 696 millimicrons and a shoulder at about 520 millimicrons. The nature of the spectrum and the similarity of the reactivities to those of the hydrated electron suggest that this species is in fact the solvated electron. An important confirmatory experiment was carried out in ethanol solutions of biphenyl and naphthalene, in which the rate curves for the disappearance of the electron at 5461 angstroms and the appearance of transient species at 3130 angstroms (where the biphenylide and naphthalenide ions absorb strongly) were measured simultaneously. Such an observation is shown in Fig. 6. Analysis of the curves shows that the disappearance and appearance rates are identical—a finding that supports the view that the absorption band is attributable to the solvated electron. Absolute rate constants for the following reactions of the solvated electron in ethanol have been determined at 23°C:



The role of this species may be of general importance in the chemistry of

irradiated polar organic liquids, depending on the magnitude of the dielectric constants; investigations in this area are continuing.

#### Direction of Future Research

It seems clear from the brief survey I have presented that the pulse radiolysis method has a broad potential, and that many new horizons have yet to be seen.

In water and in aqueous solutions, for example, where the hydrated electron is the only primary species which has been directly observed, it may be possible to observe also the hydroxyl radical. This species absorbs in the region around 300 millimicrons and at longer wavelengths in the gas phase, but the molar extinction coefficient in the liquid may be low. Multiple-reflection techniques, together with use of an appropriate narrow-line source, may make direct observation possible.

Direct observation of reactions in the tracks, which last only about  $10^{-9}$  second, may be possible if much shorter pulses are used, at higher current which is necessary in absorption studies. The experimental restriction is in the pulse itself, for techniques that provide time resolution in the nanosecond range have been used with great success (31) in fast-emission studies where high pulse intensities are not a requirement.

The extension of the pulse technique to systems of biological interest is now a very direct step. This is particularly true with respect to reactions of the hydrated electron.

In organic liquids, free-radical reactions will be a subject of continuing interest. Studies of the solvated electron in polar organic liquids will surely provide information of interest to kineticists and may also add to our understanding of the structure of liquids (32).

#### References and Notes

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