Electron Spin–Lattice Relaxation Times of Transient Free Radicals

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Electron spin-lattice relaxation times of transient free radicals[a]

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The saturation recovery method has been used to measure the electron spin relaxation times of short-lived free radicals in solution. The radicals were produced by continuous *in situ* radiolysis with a 2.8 MeV electron beam (except for two cases where stable radicals were formed by air oxidation). The ESR spectrometer used broad-band amplification of the detected ESR signal (time constant of 100 ns) and signal averaging by means of a transient recorder and minicomputer. The magnetic field was stepped off the ESR line for alternate saturating pulses; the phase of the microwave saturating pulse could be changed by 180° to allow separation of the saturation recovery and free induction decay. The sensitivity was such that T_1 values greater than 1 μs could be determined for samples of 10^{14} spins (i.e., 3×10^{-6} M radical in 50 $\mu\ell$) if the ESR linewidth was 100 mG and transient curves from 40 000 saturating pulses were averaged. Somewhat smaller values of T_1 could be determined with higher radical concentrations. To achieve this sensitivity, it was necessary to use observing microwave powers which significantly perturbed the recovery signal so that an analysis in terms of an exponential decay of the ESR signal to the steady state value was not possible. Curve fitting of solutions to modified Bloch equations was used. Values of T_2 were determined from the damping of Torrey oscillations. Values of T_1 were determined for *p*-benzo-semiquinone anion (2.0), the 2,5-di-*tert*-butyl analog (11.5), ascorbate anion radical (2.3), chelidonic acid trianion radical (5.0), 1,2-dicarboxylvinyl radical (9), and H atoms (13.5), all values in μs and accurate to about $\pm 10\%$. The radicals were produced in aqueous solution except for the semiquinones which were in ethanol. The values of T_2 were similar to the corresponding T_1 except for ascorbate radical and 2,5-di-*tert*-butyl-*p*-benzosemiquinone anion, where unresolved splittings made the apparent values smaller.

I. INTRODUCTION

During recent years, time-domain ESR studies on organic free radicals generated by pulse radiolysis or photolysis have significantly increased our understanding of the phenomenon of chemically induced dynamic magnetic polarization.[1-30] In such studies, the time evolution of the ESR signal intensity is followed within a short time (100 ns) of the generation of the radicals by the pulse of radiation. (The electron spin echo technique has also demonstrated the possibility of following the radical concentration during the radiolysis pulse.)[31,32] The time profile of the ESR signal after the radiation pulse is a function of the chemical kinetic parameters and relaxation times T_1 and T_2 as well as experimental parameters such as microwave field strength at the sample and the offset of the magnetic field from resonance. Verma and Fessenden[1,5,6,8,9] have analyzed the time-dependent signals by means of Bloch equations, modified to take account of changes in radical concentration with time, any initial magnetization upon radical formation, and chemically induced dynamic electron polarization (CIDEP) effects during decay. McLauchlan, Atkins and others,[14,21,33-38] have measured the spin-lattice relaxation times of free radicals produced by pulsed photolysis from the time profile of the ESR signal after the pulsed radiation in cases where the electron spin-lattice relaxation times are an order of magnitude shorter than the chemical reaction times of the radicals. In such cases, the spin states are populated in a very nonequilibrium way so that the return to equilibrium is governed by T_1 and the initial time profile of the ESR signal will depend mainly on T_1. The radicals formed by pulse radiolysis do not experience such large departures from equilibrium and so are appreciably affected by factors other than the relaxation times. In several interesting cases, such as that of hydrogen atoms formed by radiolysis of acid solutions, the chemical lifetimes are similar to the relaxation times and determinations of the latter is difficult. The lack of a good value for T_1 in the important case of the hydrogen atom has prevented determination of the absolute value of the polarization of the ESR signals.

The purpose of the present paper is to describe a method by which it is possible in an independent experiment, to measure the relaxation times T_1 and T_2 of short-lived free radicals and thereby increase the reliability of CIDEP and chemical rate parameters determined by time-resolved ESR experiments. Such studies can also throw light on the inter- and intramolecular interactions of these short lived free radicals as has been done for more stable free radicals.[39] The saturation recovery method, which probes spin relaxation in a rather direct way, was applied to transient radicals maintained at a steady-state concentration by continuous irradiation. By these means, most of the complications involving chemical reaction rates can be avoided.

Saturation recovery methods to determine electron spin-lattice relaxation times of free radicals in solution have been described in the literature. The pulse spectrometer utilized by Verma and Fessenden[8] was modified to carry out this function. During this work it was noted that fitting the relaxation-recovery trace to an exponential was inadequate in certain systems and one had to resort to fitting of solutions of the Bloch equations to the experimental data. Such a necessity has also been noticed by McLauchlan[40] in his recent work on measurement of T_1 of free radicals produced by photolysis.

Several other techniques exist for determining relaxation times. The most sensitive (as far as possible radical concentrations is concerned) is conventional progressive saturation. For radicals with values of T_1 and T_2 around 1 μsec or less this technique is quite appropriate (and was applied to $\cdot CH_2CO_2^-$ produced by photolysis[5]). The main problem for radicals formed by radiolysis is that one must compare signal heights taken at different times and it is difficult to exactly match the conditions (production rates). Where the relaxation times are > 2 μsec, the intrinsic linewidths are less than the magnetic field inhomogeneity and only the product $T_1 T_2$ is readily determined. Spin echo methods can be applied along with pulse radiolysis[32] but these also suffer limitations on the minimum radical concentrations. Current applications have been to rather high concentrations where chemical decay and relaxation are not well separated and Heisenberg spin exchange is quite possible.

One of the authors (BV) earlier investigated the electron spin-lattice relaxation times of several semiquinones as a function of temperatures and viscosity in both hydrogen-bonding and nonhydrogen bonding solvents.[39,41,42] These measurements did not separate relaxation and free-induction decay (although contributions from the latter were estimated to be insignificant because T_2 was small compared to T_1). In addition, these studies were limited to free radical concentrations greater than 10^{-3} M, since no form of signal averaging was employed. The dependence of measured T_1 on the observing microwave power level (i.e., the small power utilized to monitor the growth of the signal after the removal of a saturating pulse) was also not thoroughly investigated. It was interesting therefore, to investigate whether the conclusions derived from the earlier measurements on semiquinone radicals would stand the test of more refined experiments: measurements at different observing power levels and extrapolation to zero power conditions; removal of the contribution from free induction decay; and extension to lower concentrations which were accessible in the present investigation because of signal averaging.

II. EXPERIMENTAL

Several pulsed electron spin resonance spectrometers designed primarily for the determination of spin-lattice relaxation times of free radicals in solution have been described.[41,43] Hyde and co-workers[44,45] have paid special attention to techniques for the separation of free induction decay and saturation recovery signals. Among

the methods suggested by them, we have chosed to use the fact that the microwave phase of the free induction decay signal depends on the phase of the pumping (saturating) microwave power, while the saturation recovery signal does not. Since 180° inversion of the phase of the pumping power changes the sign of the free-induction decay signal, addition of two signals taken with phases of the pumping power separated by 180° leads to suppression of the free-induction decay signal. The difference between the two signals gives the free-induction decay. A normal reflection cavity has been used rather than a bimodal cavity[44,45] because of anticipated difficulty in keeping the latter balanced in the remote mode of operation needed for electron irradiation.

The pulsed electron spin resonance spectrometer is essentially similar to that employed by Verma and Fessenden for their time resolved ESR spectroscopy.[8] The same preamplifier and gated signal amplifier were used but with no base line restoration. The response time (time constant) was about 100 ns. The microwave bridge included an additional arm to provide the saturating microwave pulse and microwave switches to gate the saturating power, observing power and the detector. A block diagram of the microwave spectrometer is shown in Fig. 1. We shall describe mainly those modifications which were carried out to convert the spectrometer of Verma and Fessenden[8] for saturation recovery experiments. By setting the microwave switches to the proper states, it is also possible to use the spectrometer for pulse radiolysis experiments with no other conversion necessary.

The microwave cavity was similar to a Varian V-4531 with one of the ceramic face plates provided with a chimney through which the beam pipe from the Van de Graaff entered the cavity. The loaded Q of this cavity was estimated to be between 1500 and 2000. The klystron is a 1 W Varian klystron (998 275) and the power for the "biasing arm," "observe arm" and "AFC arm" are tapped by suitable directional couplers. Considerable care was taken to minimize loss of pump power and as a result about 500 mW was available at the cavity. Switching of the pump power was achieved by a microwave switch (SW 1) placed in the configuration shown in the block diagram. This configuration is similar to that described by Bowman.[46] The slide screw tuner can be adjusted so that the on/off ratio, is better than 50 dB. The phase of the pump power was controlled by an "electronic" phase shifter (#2 in Fig. 1, Kearfott, V-183-1E-1), the coil of which was driven by a programable DC power supply. The power supply operated between states of zero current and the value for 180° phase shift in a sequence selected by the program in the PDP-8/I minicomputer. The observing and pump powers were coupled to the sample cavity arm without much loss by using a plain "tee" and switch SW2 which reflects power to the cavity when closed during the pump interval. The phase of the "observe" power is adjusted by movable short (1) and the current through the electronic phase shifter (1). The current through this phase shifter (1) is controlled by the automatic phase control (APC) circuit as described by Verma and Fessenden.[8] The APC control ensures the correct relationship between
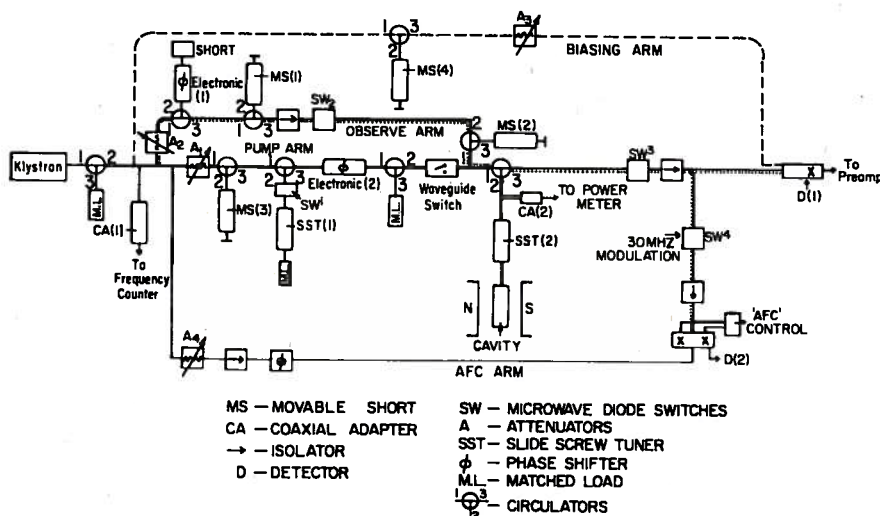
Block Diagram of Pulsed ESR Spectrometer

FIG. 1. Block diagram of pulsed ESR spectrometer used for measurements of saturation recovery times. SW1 is a Philco (L4146) switch in a Philco Mount (P901A). SW2 and SW4 are ARRA X110 switches and SW3 is an ARRA X111 switch. The drivers for SW1 and SW2 are National Semiconductor Corporation DH0035 and for SW3 it is an ARRA DS1,2.

MS — MOVABLE SHORT
CA — COAXIAL ADAPTER
→ — ISOLATOR
D — DETECTOR

SW — MICROWAVE DIODE SWITCHES
A — ATTENUATORS
SST — SLIDE SCREW TUNER
φ — PHASE SHIFTER
M.L. — MATCHED LOAD
⟲ — CIRCULATORS

the biasing power and the power reflected from the sample cavity reaching the detector, even when the phase of the pump power is changed. (There is a small leakage of pump power through the switches.) The maximum observing power available at the sample cavity is about 16 mW. The microwave switch SW3 protects the detector and APC circuit from the pump pulse.

All the other parts of the spectrometer including the detector, preamplifier, signal amplifier circuits, and automatic frequency control (AFC) were as described earlier.[8] The timing sequence of the various pulses is given in Fig. 2. The saturating pulse width can be changed from 1 μsec to 100 mS. In the present experiment the saturating pulse widths were between 10 and 40 μsec. The AFC and signal amplifier were gated to be inoperative during the APC pulse and the pump power pulse. Repetition rates were of the order of 125 sec^{-1} because of the time necessary to read the data from the transient recorder to the computer.

The magnetic field was accurately controlled by the PDP-8/I minicomputer to compensate for changes in the microwave frequency caused by heating of the cavity the electron beam (in spite of water cooling of the cavity).[8]

The frequencies of the microwave signal and that of a field-following proton NMR unit were measured with suitable counters and read by the computer. The computer ensured that the field position (more properly the position in the spectrum) could be maintained within ± 7 mG for long periods of time to enable signal averaging for long periods. The computer also controlled the offset in the field required to record a base line off resonance for subtraction from the accumulation on the center of a line. A digital-to-analog converter from the computer controlled a current driver which fed current to the usual field modulation coils on the cavity to offset the magnetic field to the desired value for off-resonance measurements.

Radiolysis was carried out *in situ* with a beam of 2.8-MeV electrons from a van de Graff accelerator as previously described.[8] For the present experiments, the accelerator was operated in the dc mode; the current incident on the cavity was about 1–10 μA and that collected from an electrode in contact with the aqueous solution was between 0.1–1.0 μA, depending on the system being investigated. The usual flat silica cell of 0.5 mm internal spacing for aqueous samples was irradiated edge on.
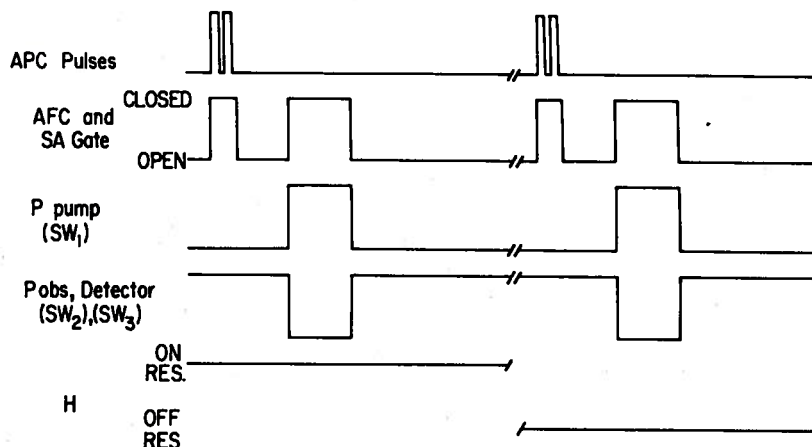

FIG. 2. Pulse sequences.

For recording the time profile, the output of the signal amplifier was fed into a Biomation 8100 transient recorder which was controlled by the PDP-8/I minicomputer. The recording was done in a manner similar to that described earlier.[8] The Biomation was triggered by the trailing edge of the microwave pump pulse so that observation is made after the removal of the pump power. A total of 100 points were transferred from the Biomation to the minicomputer for each microwave pulse. Ten of these are pretrigger points but refer to the signal level during the period when the signal amplifier is gated off. The following 90 points are used for analysis. Because of the large transients associated with the operation of the microwave switches, the data for up to one microsecond following the end of the saturating pulse was not valid. The channel width could be varied between 0.1–100 μsec per point, the choice of the channel width being dependent on the T_1 of the sample. The signals were recorded for R times (R could be varied from 1–2000) with the field at resonance and off resonance on subsequent pulses (step 1). (The field shift off-resonance depended on the particular spectrum under investigation.) The differences between the two signals (S_1) was stored in the computer memory. The phase of the pumping power was then changed by 180° and the averaging done for R times, as before, both on and off resonance and the difference (S_2) was again stored (step 2). The sum $S_1 + S_2$ gives the saturation recovery signal with no contribution from the free induction decay and $S_1 - S_2$ gives the free induction decay. This cycle is repeated as many times (C times) as desired. For example, it is found that with 10^{-5} M radical concentration the product of R and C need not be greater than 4000, e.g., p-benzosemiquinone anion, chelidonic acid trianion radical, etc. However for the hydrogen atom one had to average at least 20 000 times and longer averages were necessary at lower observing power. It took about 30 min for $R \times C = 40\,000$.

The signal channel was AC coupled with the low frequency response extended to very low frequencies so that the square-wave signal (about 60 Hz) produced by moving on and off the ESR line was transmitted with minimum distortion. In this way, the height of the processed ESR signal after recovery from saturation represented the actual height of the ESR line and zero in the processed data represented zero ESR signal. Thus, in fitting calculated curves, there was no question where this level lay.

In some earlier experiments the averaging was carried out in a different way with blocks of R repetitions carried out sequentially for the four combinations of on and off the line with the two phases of the pump power. Data taken in this way were often not reproducible especially for the weaker signals. Slight shifts in conditions such as Van de Graaff beam current made subtraction of signals taken only a few seconds apart unreliable. The technique subsequently adopted of changing the field for alternate pulses (see above) greatly reduced spurious signals. Even severe perturbations such as stopping of the Van de Graaff or solution flow or unlocking of the AFC did not seriously disturb already accumulated data.
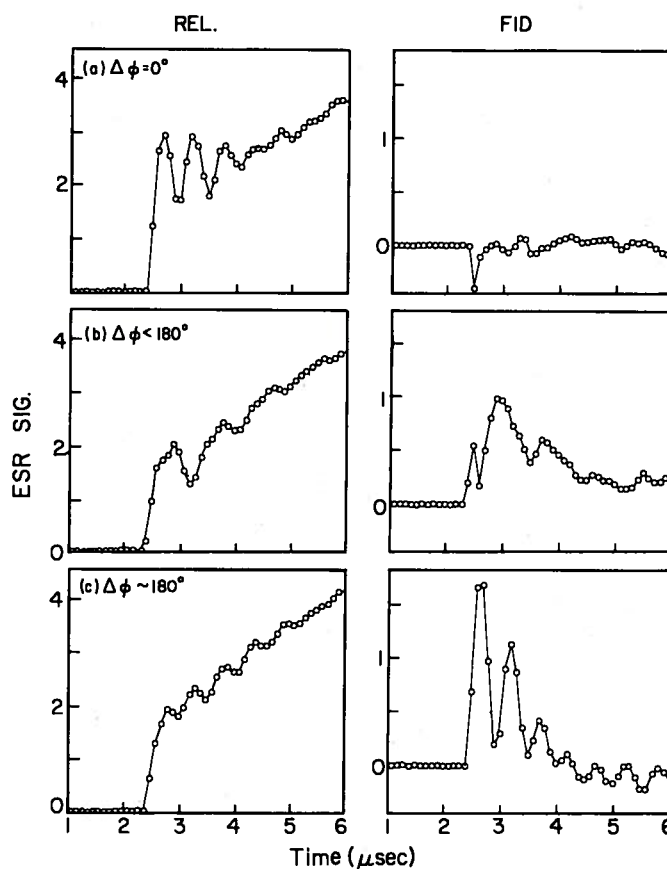

FIG. 3. Saturation recovery and free induction decay of the chelidonic acid trianion radical. Figure 3(a) shows data taken with no change in phase in the pump (saturating) microwave power between step 1 and step 2 of data acquisition. The free-induction decay part has only noise whereas the saturation recovery part exhibits oscillations. Figure 3(b) is for a phase change in pump power between step (1) and step (2) less than 180° (current through the phase shifter, $i_0 = 0.8$ A) and only a partial separation between free-induction decay and saturation recovery is obtained. Figure 3(c) is for a phase change very close to 180° ($i_0 = 1.1$ A) and there nearly complete separation between the two signals is obtained.

The separation of free induction decay from saturation recovery is well demonstrated in Fig. 3. Figure 3(a) was obtained without change of phase of pump power and is a superposition of saturation recovery and free induction decay which are separated in Fig. 3(b) where the phase of pump power is changed between corresponding cycles. The sample chosen in Fig. 3, viz. chelidonic acid trianion radical is a good test sample for adjusting the phase change to 180° since small deviations from the proper adjustment results in the saturation recovery signal exhibiting the presence of an oscillating free induction decay [Fig. 3(c)].

For initial adjustment of the magnetic field to the center of a line, the usual second derivative presentation with modulation of the magnetic field at 200 Hz and 100 kHz was employed. The shift in magnetic field required for obtaining the off-resonance base line was determined from the hyperfine pattern of the spectrum so that the base line was recorded at a spectral position where no absorption was present.

Certain earlier experiments were carried out with CW photolysis using a high pressure mercury–xenon lamp (Hanovia 977 B-1). In both radiolysis and photolysis experiments the usual precautions of deoxygenating the solutions by bubbling with N_2 or N_2O and utilization of flow systems were employed. The temperature of the solution was controlled by precooling the flowing sample with a heat exchange coil just before entering the cell. The temperature of the sample was measured with a thermocouple at the exit of the sample cell.

The concentration of the free radical was estimated by comparing the ESR signal of the free radical with that of a standard viz. 3×10^{-3} M tannol in sec-butyl benzene. From such estimates of concentration we conclude the present system to be capable of measuring T_1 values greater than 1 μsec for a sample of 10^{14} spins where the ESR linewidth is about 100 mg, 40 000 repetitions are averaged, and no electron spin polarization is present. Enhancement of the signals by the presence of CIDEP allows lower concentrations to be studied. The time resolution is adequate for measurement of T_1 values down to 500 ns if the concentration of spins is somewhat higher.

III. ANALYSIS OF THE SATURATION RECOVERY TRACE

An exponential recovery of the sample magnetization after the saturating pulse is expected in a system where the microwave power used to sense the magnetization is sufficiently small. Unfortunately, in some of the systems to be studied, such as hydrogen atoms and 1, 2-dicarboxylvinyl radical, the steady-state concentrations are not large enough to allow observation under such conditions and higher microwave powers which perturb the recovery signal were necessary. It is important, therefore, that there be some way to analyze curves taken under these conditions. It has been suggested that the recovery traces be analyzed as exponential curves and a plot of the reciprocal of the apparent T_1 vs observing microwave power be made and extrapolated to zero power to give the true T_1.[14,36,44,45] However, the recovery trace rather quickly departs from exponential form as the power is raised and much of the data taken here could not satisfactorily be analyzed by such means.

An obvious method for analysis of such data is by fitting of curves calculated by numerically integrating the Bloch equations as has been done where the radicals are formed by pulse radiolysis.[8,9] Because the radicals are present at a steady-state concentration many of the modifications introduced, to take account of the chemical reactions[8,9] are not necessary. The equations used here are

$$\dot{u} = -\frac{1}{T_2}u + \Delta\omega v \, , \qquad (1)$$

$$\dot{v} = -\frac{1}{T_2}v - \omega_1 M_z - \Delta\omega u \, , \qquad (2)$$

$$\dot{M}_z = -\frac{(M_z - M_0)}{T_1} + \frac{V M_0}{T_1} + \omega_1 v, \qquad (3)$$

where u and v are the rotating components of the transverse magnetization, $\Delta\omega = \omega - \omega_0$ the difference between the angular frequencies of the exciting microwave field and that at exact resonance, $\omega_1 = \gamma H_1$ where γ is the magnetogyric radio and H_1 the rotating component of the microwave magnetic field, M_0 is the z component of the magnetization at equilibrium, and V is the enhancement factor of the resonance due to CIDEP. These equations are exactly as used in static cases with the addition of the term to take CIDEP into account. The observed ESR signal (absorptive mode) is proportional to the transverse component v. The long-time value of the ESR signal will be just $V + 1$ times the unenhanced signal and from the equation for $\dot{M}_z$ (specifically the coefficient of M_z) it is clear that the time constant will be T_1. Thus, the relaxation time is not affected by the presence of CIDEP. This analysis also pertains when $V < -1$ as for the low-field hydrogen atom line which appears in emission. The term $V M_0/T_1$ is intended to represent specifically the change of magnetization by spin selective disappearance reactions (CIDEP radical-pairs mechanism). However, it can also include magnetization appearing when the radicals are formed. This analysis is valid as long as the chemical lifetimes are much longer than T_1 and T_2. Under the conditions used, the chemical lifetimes were several hundred microseconds thus satisfying this inequality. If the chemical lifetimes were shorter, then loss of magnetization by chemical reaction would have to be considered and shortened relaxation times would occur. In addition, at high concentrations it may be necessary to consider relaxation by Heisenberg spin exchange.

The expected saturation recovery curves were calculated by numerical integration of Eqs. (1)–(3) for suitable values of the parameters. Magnetic field inhomogeneity was taken into account by integrating sets of equations for a number of offsets from the line position ($\Delta\omega$) and adding the contributions with a suitable line shape function as weighting factor. A Gaussian function with a full width at half-height of 56 mG was used for the latter. This value was determined from an absorption spectrum of the H atom taken with a box-car integrator in experiments using pulse radiolysis as the radical source. Most work was done with 21 offset values (symmetrical around $\Delta\omega = 0$) extending to where the weighting function was less than 1% the value at $\Delta\omega = 0$.

As a first step in investigating the saturation recovery traces at higher values of H_1, calculations were done for several values of T_1, T_2, and observing H_1 with the initial conditions $M_x = M_y = M_z = 0$. (High saturating power should allow approach to this condition.) Figure 4 is a plot of such curves for $T_1 = T_2 = 5$ μsec, and it is seen that it is possible to obtain near exponential curves for H_1 < 0. 005 G. Analysis of similar curves leads to the conclusion that for obtaining nearly exponential saturation recovery curves with characteristic times within 10% of "true" T_1 one would use H_1 such that $(\gamma H_1)^{-1} \geq 3T_1$. For $T_2 < T_1$, the saturation recovery curve tends to an exponential form even at higher H_1 values. The rule seems to be that with $H_1 = 0. 001$ G, T_1 values could be estimated with an exponential fit to be better than 10% when
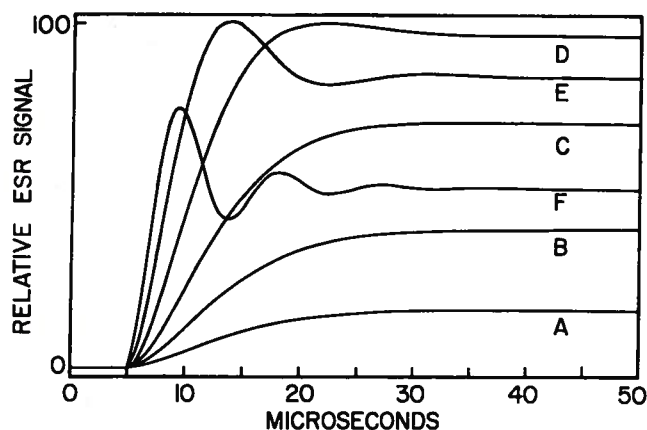
FIG. 4. Saturation recovery traces obtained by numerical integration of Bloch equations with $T_1 = T_2 = 5$ μsec for values of H_1: (A) 0.001; (B) 0.025; (C) 0.005; (D) 0.01; (E) 0.02 and (F) 0.03 G.

$T_1 < 20$ μsec and $T_2 \lesssim T_1 < 15$ μsec; and with $H_1 = 0.0025$ G, $T_1 \lesssim 10$ μsec; $T_2 < T_1 < 5$ μsec. The conditions $H_1 = 0.001$ and 0.0025 G correspond to observing microwave power levels of approximately 0.14 and 0.25 mW, respectively, with our sample cavity which has a Q between 1500 and 2000.

These studies on solutions to the Bloch equations suggest that the best procedure would be to obtain an estimate for T_1 by fitting an exponential to the saturation recovery curve obtained at low microwave power levels and then to utilize that value as a starting approximation in fitting calculated curves to experimental ones obtained at higher microwave power levels. The amplitude of the microwave magnetic field at the sample H_1 (average) can be obtained from the period of Torrey oscillations, which are usually observed at high values of H_1, when $\gamma H_1 > \frac{1}{2} (T_1^{-1} - T_2^{-1})$. Such measurements of H_1 together with the estimates of T_1 obtained from observations at low microwave power levels, were used as starting approximations and values of T_2 were obtained by fitting the rate at which the Torrey oscillation decayed away. Better values for T_1, T_2, and H_1 at various observing microwave power levels were found by several sequences of adjusting the values for better fit.

The saturation recovery traces of the 1, 2 dicarboxylvinyl radical, obtained by the radiolysis of acetylene dicarboxylate ion at pH ~ 11.0, were used for the first estimates of H_1. Figure 5(a) is the saturation recovery trace of the low field line (see later) of the radical taken at about 0.1 mW of the observing power and it is seen that $T_1 \sim 9.5$ μsec from a fit to an exponential form.
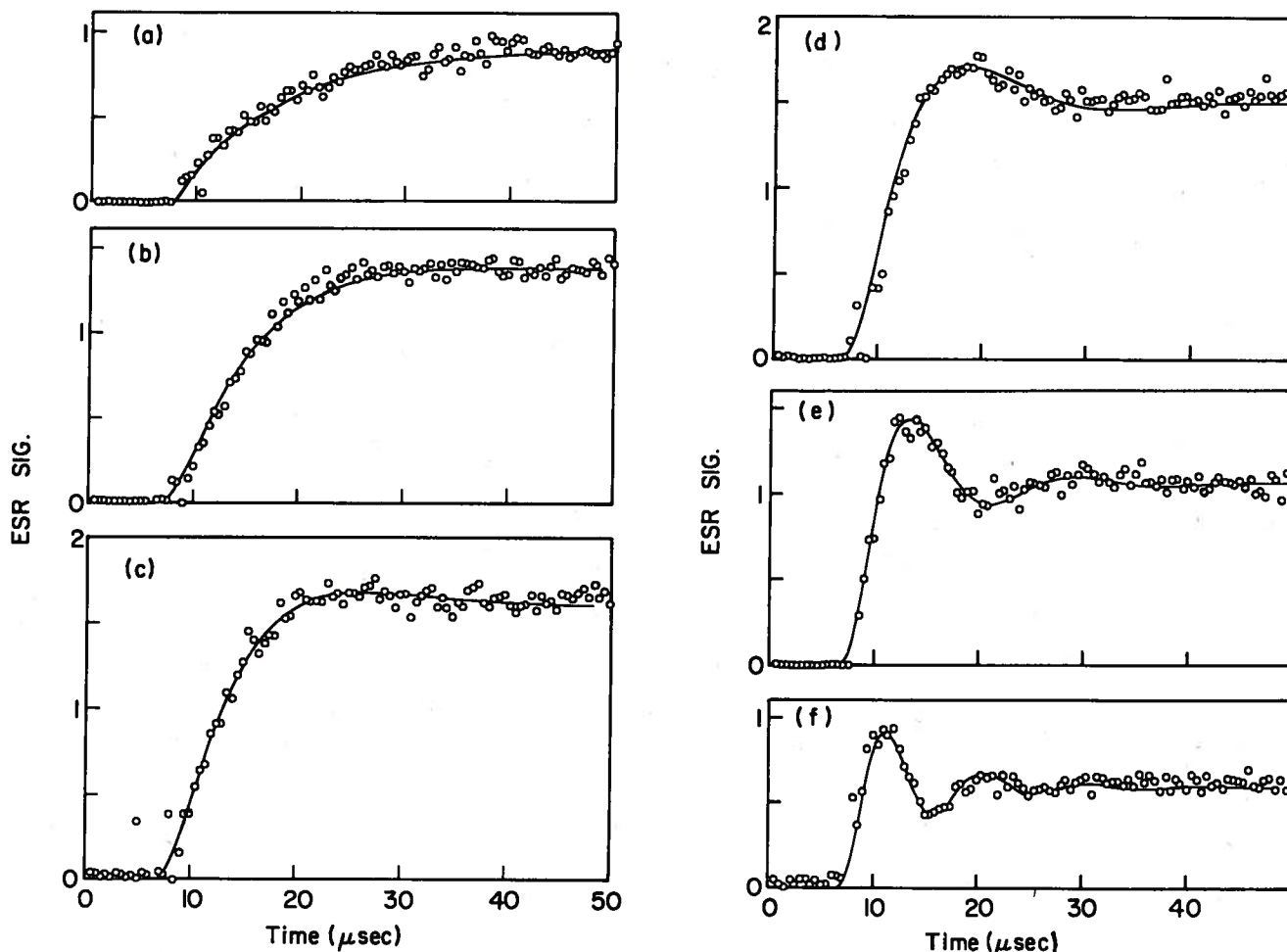

FIG. 5. Saturation recovery traces at different observing microwave powers for the low field line of 1,2-dicarboxylvinyl radical. Circles are experimental points. The solid line in (a) is a least-square exponential fit with $T_1 = 9.0$ μsec. In (b)–(f) the solid line is a fit to the Bloch equations with the following parameters: $T_1 = 9$ μsec; $T_2 = 8.5$ μsec; $H_1 = 0.004$ (b); 0.007 (c); 0.012 (d); 0.022 (e); 0.034 G (f).
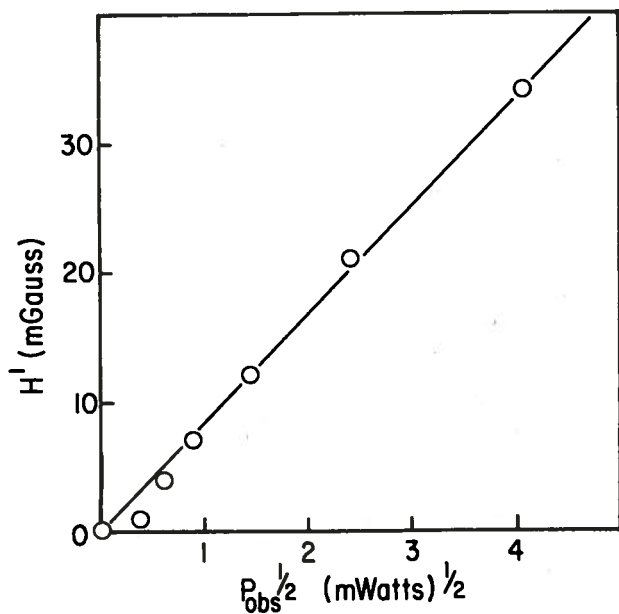
FIG. 6. A plot of (observing microwave power)$^{1/2}$ vs H_1. The values of H_1 were determined from ESR time profiles as described in the text.

Figure 5(f) is the saturation recovery trace of the same line at 16.5 mW of observing microwave power and the fit is for $T_1 = 9$ μsec; $T_2 = 8.5$ μsec, and $H_1 = 0.036$ G. Figures 5(b), (c), (d), and (e) are fits with the same T_1 and T_2 but different H_1 values (0.004, 0.007, 0.012, 0.022 G corresponding to observing powers P_{obs} of 0.36, 0.80, 2.08, 5.80 mW, respectively). Figure 6 shows that the H_1 values thus determined depend on $(P_{obs})^{1/2}$ in the expected way. This method was used frequently to follow any changes in H_1 caused by the deterioration of the "Q" of the cavity because of irradiation, and changes in sample cells or samples (e.g., change of pH, solvent etc.).

In cases such as 2,5-di-t-butyl-p-benzosemiquinone anion, where the signal intensities were high enough to enable good measurements at lower observing microwave power levels and where T_2 is expected to be much smaller than T_1 due to unresolved hyperfine structure, the true value of T_1 was obtained by plotting $1/T_1$ against P_{obs} and determining the extrapolated value of T_1 as $P_{obs} \rightarrow 0$.

We believe that the T_1 values determined by fitting solutions to the Bloch equations are accurate to 10% and T_2 to 25%, since the fitting is not so critically dependent on changes in T_2. A somewhat better accuracy in the determination of T_1 is expected for cases such as 2,5-di-t-butyl-p-benzosemiquinone anion, where fitting of exponential forms and extrapolation to zero microwave power was used.

IV. STUDIES ON SEMIQUINONE ANIONS

The preliminary tests on the system were carried out with relatively long-lived semiquinone anions: 2,5-di-t-butyl-p-benzo-semiquinone anion (2,5-DTBSQ) and p-benzosemiquinone anion (PBSQ). The spin-lattice re-

laxation times T_1 of these had been investigated by one of the authors (BV)[39,41,42] and it was interesting to study whether, with the refinements of the present spectrometer, one could confirm the previous observations. Since the semiquinone anions were not the main targets of the present investigations, our studies were limited to tests of the spectrometer and a few measurements to see whether (1) the separation of free-induction decay from the saturation recovery trace changed the findings of the earlier investigation; (2) measurements at lower observing power and improvements in signal-to-noise ratio because of signal averaging caused any major changes in the values reported earlier; (3) there was any dependence of T_1 on concentration especially at lower concentrations, since earlier findings had found no dependence of T_1 on concentration in the range of free radical concentration of 10^{-2}–10^{-3} M.

A. 2,5-DTBSQ

Since 2,5-DTBSQ ($g = 2.0046$; $a(2H) = 2.14$; $a(9H) = 0.06$ G) could easily be prepared, test runs on this free radical were used as checks for the operation of the entire system. The ESR spectrum is a triplet and the line-widths depend on the free radical concentration which could easily be varied from 10^{-2}–10^{-5} M. At about 10^{-2} M even the triplets are not well-resolved but at concentrations below 10^{-5} M even the small splitting by the t-butyl protons is partially resolved at low microwave power and with the exclusion of oxygen.[47] All the measurements were confined to samples prepared by the air oxidation of alkaline, alcoholic solutions of the corresponding hydroquinone to obtain radical concentrations between 10^{-3} and 10^{-4} M, where the triplets were well resolved but the hyperfine splittings from the t-butyl protons were not evident. In such cases it was seen that the free-induction decay is insignificant (Fig. 7) leading to the conclusion that the earlier results,[39,41,42] where no special care was taken to eliminate effects of free-induction decay, are free from this possible source of error. Plots of measured $(T_1)^{-1}$ as a function of P_{obs} were made for each of the three ESR lines (Fig. 8). Straight lines through the data extrapolated, in each case, to the same value of $(T_1)^{-1}$ but the slope of the line was greater for the central line. That T_2 (the inverse of this slope) is smaller for the central line is in agreement with earlier findings.[48] The common extrapolated value of T_1 is 11.5 ± 0.5 μsec at 290 K (cf. 8.5 ± 1 μsec at 290 K reported earlier[41]). It is clear, that although effects of free-induction decay are small for 2,5-DTBSQ the previously reported values of T_1 might still suffer from two possible sources of error: dependence of T_1 on the microwave power level and errors from fitting of exponential curves to noisy signals. The latter problem is known to lead to inaccurate determinations of characteristic times.[49] Within experimental error we have not noticed a dependence of T_1 on the free radical concentration (which was varied between 10^{-3} and 10^{-4} M).

B. PBSQ

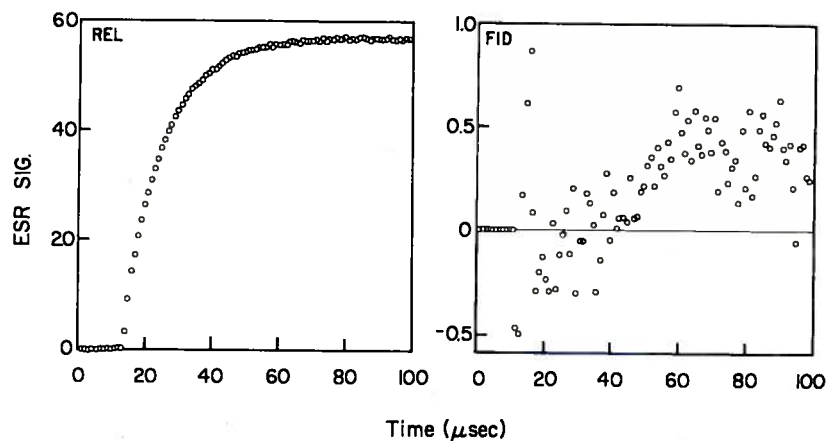The radical PBSQ ($g = 2.0045$; $a(4H) = 2.38$ G) was generated by three different methods in this study: (1)

FIG. 7. Saturation recovery trace and free-induction decay as observed for 2,5-DTBSQ.

Time (μsec)

by air-oxidation of an alcholic, alkaline solution of hydroquinone (10^{-3} M); (2) by photolysis of an N_2O saturated aqueous solution of hydroquinone (10^{-3} M) at pH ~ 11.0; and (3) by continuous radiolysis of an N_2O saturated aqueous solution by hydroquinone (10^{-3} M) at alkaline pH ~ 11.0. Within the experimental errors, no dependence of the T_1 values upon the method of radical production was found. The concentrations of the radicals in the three cases were all about 5×10^{-5} M. Since $T_1 \sim T_2$ for this radical, Torrey oscillations could easily be seen when off resonance and these persisted in the free induction decay even at 100 mG from resonance. The saturation recovery curves did exhibit nonexponential behavior at higher observing powers and fitting of solutions of the Bloch equations as described in Sec. III was employed. All of the five hyperfine lines were examined. The values for the different hyperfine components were found to be the same within limits of experimental error in contrast to the observation by Dobbs who reports a variation of 25% in T_1 among the hyperfine components.[50] The value of T_1 thus observed is 2 ± 0.3 μsec and T_2 = 1.8 ± 0.5 μsec at 290 K. The values reported earlier are ~2 μsec at 298 K,[41] 2.8 μsec at 273 K[51] and 3 μsec at 263 K.[39,51] There was some indication that T_1 may be dependent on concentration, especially in the lower ranges but more systematic investigations are needed before any definite conclusions can be reached.

V. STUDIES ON TRANSIENT FREE RADICALS PRODUCED BY RADIOLYSIS

The radicals studied were those known to give relatively intense spectra or those of special interest such as hydrogen atoms in aqueous solutions. All of the radicals were generated by the radiolysis of corresponding aqueous solutions, *in situ*, in a quartz flat cell placed inside the sample cavity. In the case of chelidonic acid trianion radical, photolysis was also used to generate the radical. The solutions were deoxygenated by bubbling with either nitrogen or nitrous oxide depending on the required chemistry. The measurements were carried out at 290 K as measured at the outlet of the sample tube. The beam current was usually steady within ± 5% during a signal averaging run, which could last as long as 30 min and the flow rates were normally between 0.02 and 0.04 ℓ/min.

A. Hydrogen atom

Hydrogen atoms ($g = 2.0021$; $a = 503$ G) were produced by the radiolysis of nitrogen bubbled solutions of 0.1 M perchloric acid to which t-butanol (0.01 M) had been added.

$$e_{aq}^- + H_3O^+ \rightarrow H \cdot + H_2O .$$
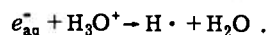
At electron currents of about 10 μA, the apparent steady state H atom concentration, i.e., that calculated from ESR signal heights ignoring the polarization, was about 4×10^{-6} M although the actual concentration was much lower. It was necessary to average at least 40 000 traces to achieve a reasonable signal-to-noise ratio.

Eiben and Fessenden[52] reported that the low field ESR line of the H atom in aqueous solution appears in emission in steady-state experiments. The saturation recovery traces of the low- and high-field lines [Fig. 9(a) and 9(b)] under identical conditions, exhibit opposite senses as to be expected from the steady-state signals. The saturation recovery traces were taken at different observing microwave power levels and an estimate of T_1 was obtained from fitting the low-power trace to an exponential. The high-power traces (with oscillations)
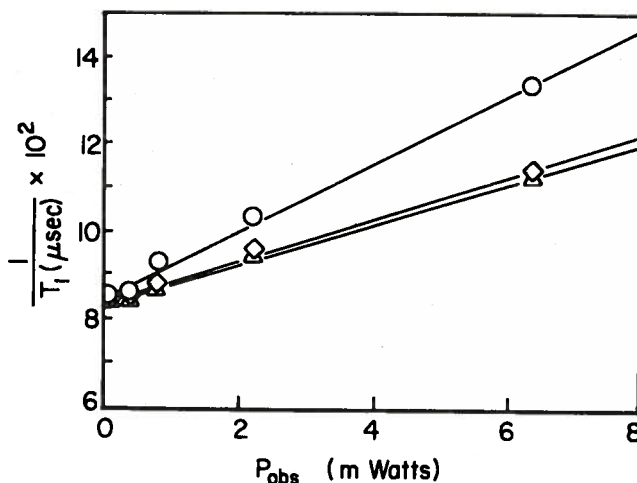

FIG. 8. Plot of (measured T_1)$^{-1}$ vs observing microwave power for 2,5 DTBSQ-(o) central line; ($\diamond$)-high-field line ($\triangle$) low-field line.
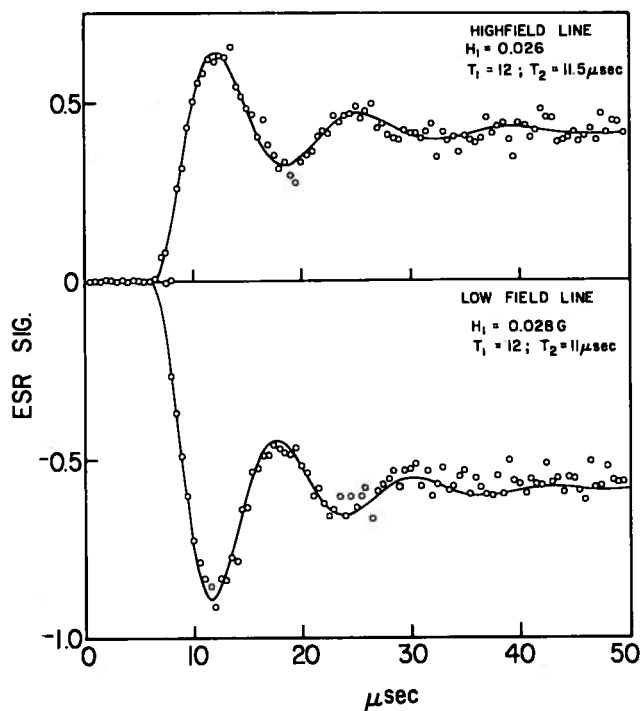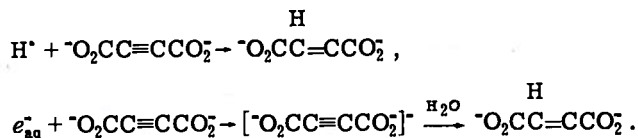
FIG. 9. Saturation recovery traces for the low-field and high-field lines of the hydrogen atom. Circles are the experimental points and the solid lines are the fit to the Bloch equations.

were then used to refine the values of H_1. (There was some decrease in Q caused by the high conductivity of the acid solutions.) Using the estimated T_1 as a starting point and the refined H_1 values, the Bloch equations were fitted to the saturation recovery traces at all the power levels and a better value of T_1 and an estimate of T_2 were obtained. Within experimental limits of error, there were no differences in T_1 and T_2 between the two different hyperfine lines. The values of $T_1 = 13.5 \pm 1$ μsec, $T_2 = 10.5 \pm 2$ μsec so obtained can be compared with the values $T_1 = 20$ μsec and $T_2 = 1.5$ μsec reported by Verma and Fessenden.[9] Those values were obtained by fitting of calculated curves to the H atom ESR signals from pulse radiolysis experiments. The chemical decay periods were typically less than 10 μsec so that the observed curves were not very sensitive to the value of T_1 and any T_1 greater than about 10 μsec would fit that data reasonably well. The small value $T_2 = 1.5$ μsec was adopted[9] to simulate the effects of field inhomogeneity and so does not represent the true T_2. Thus here is no disagreement with the present results for either T_1 or T_2.

B. 1,2-dicarboxylvinyl radical

The 1,2-dicarboxylvinyl radical ($g = 2.00283$; $a(1H) = 49.8$ G) is produced by the radiolysis of solutions of acetylene dicarboxylate anion from both H atom and solvated electron:[8,53]

$$H^{\cdot} + {}^{-}O_2CC{\equiv}CCO_2^{-} \rightarrow \overset{\displaystyle H}{{}^{-}O_2CC{=}CCO_2^{-}},$$

$$e_{aq}^{-} + {}^{-}O_2CC{\equiv}CCO_2^{-} \rightarrow [{}^{-}O_2CC{\equiv}CCO_2^{-}]^{-} \xrightarrow{H_2O} \overset{\displaystyle H}{{}^{-}O_2CC{=}CCO_2^{-}}.$$

The solutions contained 5 mM acetylene dicarboxylate at pH ~ 11 and was deoxygenated by bubbling with N_2. A radical concentration of 10^{-5} M was estimated for a 9 μA electron beam current and averages of at least 20 000 repetitions were used to assure a reasonable signal/noise ratio. This radical was utilized for estimating H_1 values as described in Sec. III since the saturation recovery curves at high observing microwave power levels showed excellent oscillations. Following the procedure outlined in Sec. III, values of $T_1 = 9 \pm 1$ μsec and $T_2 = 7 \pm 2$ μsec were obtained for both transitions. These values are in excellent agreement with $T_1 = T_2 = 7.5$ μsec determined by Verma and Fessenden from pulse radiolysis experiments.[8]

C. Chelidonic acid trianion radical

The chelidonic acid trianion radical[54] [$g = 2.00402$; $a(2H) = 1.2$ G] was formed by the radiolysis of an N_2 bubbled aqueous solution of chelidonic acid (10^{-3} M) at pH ~ 11 which also contained 4.5% acetone and 10% 2-propanol by volume. The trianion radical is formed by electron transfer from $(CH_3)_2\dot{C}OH$.
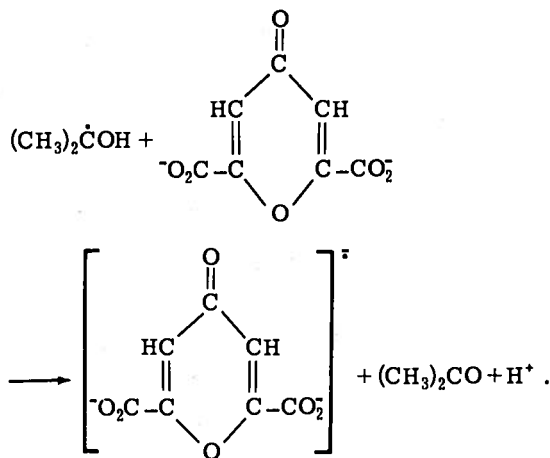
The free-induction decay of this radical exhibits oscillations even at resonance and low observing microwave power levels and we have not been able to account for this fact. The frequency of the oscillations was intermediate between the frequencies corresponding to the linewidth and the line separation and did not depend on whether sodium or potassium hydroxide was added to the aqueous solution to make it alkaline (thus ruling out unresolved hyperfine structure due to the counter ions as a cause for the oscillations). The presence of these oscillations on the free-induction decay prompted us to utilize this compound as a test sample for phase adjustments of the microwave pumping power as described in Sec. II.

The apparent T_1 of this radical, as determined by fitting exponential curves to the experimental traces, was strongly dependent on the observing microwave power level. A plot of T_1 against observing microwave power gave a value for T_1 at zero power of 4.5 ± 0.5 μsec, while fitting of the Block equations gave $T_1 = 5 \pm 0.5$ μsec and $T_2 = 4.5$ μsec for all three lines. Radicals formed during photolysis of the same solution gave similar values for T_1. Both radiolysis at about 6 μA

TABLE I. Relaxation times and concentrations of free radicals.

Radical	Concentration of racical[a]	Relaxation times (μsec)	
		T_1	T_2
1. Hydrogen atom	4×10^{-6} M	13.5 ± 1	11 ± 2
2. 1,2-dicarboxylvinyl radical	8×10^{-6} M	9 ± 1	7 ± 2
3. Chelidonic acid trianion radical	3×10^{-5} M	5 ± 0.5	4.5 ± 1
4. Ascorbate radical ion	4×10^{-5} M	2.3 ± 0.5	1.0 ± 0.3
5. p-Benzosemiquinone anion	5×10^{-5} M	2 ± 0.3	1.8 ± 0.5
6. 2,5-di-t-butyl-p-benzo-semiquinone anion	10^{-3}–10^{-4} M	11.5 ± 0.5	

[a]These are estimates of "apparent" concentration, not taking into account chemically induced electron polarization.

current and photolysis with the 1000 W lamp, as described earlier, produced a radical concentration of about 3×10^{-5} M and most of the traces were obtained with reasonable signal/noise ratio by averaging at least 4000 curves.

D. Ascorbate radical

Since ascorbate radical[55] [$g = 2.00518$; $a(1H) = 1.76$ G; $a(2H) = 0.19$ G; $a(1H) = 0.07$ G] is a relatively long-lived species, one could obtain reasonably high concentrations of the radical ($\sim 10^{-5}$M) by continuous radiolysis with 0.6 μA. A 2.5 mM aqueous solution of ascorbic acid at pH ~ 11 (bubbled

$$R = -CH(OH)CH_2(OH)$$
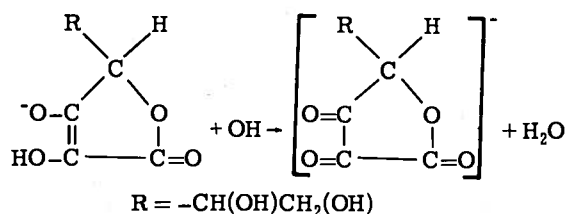
with N_2O) was used. Under our conditions the smallest splitting was not resolved. Measurements of T_1 were carried out on the central lines of the two triplets. The apparent T_2 was expected to be small because of the unresolved hyperfine structure. Extrapolation of plots of the T_1 values obtained by fitting exponential forms to the saturation recovery traces gave a value of T_1 at zero power of 2.7 ± 0.5 μsec for the central lines of both triplets. The curve fitting procedure using traces obtained at various higher observing power levels gave for both transitions $T_1 = 2.3 \pm 0.5$ μsec and $T_2 = 1 \pm 0.3$ μsec.

VI. CONCLUSIONS

Table I summarizes the measurements of T_1 for the free radicals investigated here together with the approximate concentrations of the free radicals. It is interesting to note that within experimental error no differences have been found, between the T_1 values of different hyperfine components of the same free radical. Whether such a variation is expected depends, of course, on the mechanism of relaxation. In most of the cases

the hyperfine constants are small so that modulation of the hyperfine constant by tumbling of the radical is not likely to be a major contribution. Most other mechanisms will effect all lines similarly.

The values of relaxation times determined by this method agree with those determined in other ways where comparison is possible. The values for 1,2-dicarboxylvinyl radical are very close to those determined from the growth of ESR signal in pulse radiolysis experiments. In that case the time scales of relaxation and chemical decay were rather different so agreement is to be expected. The present data for hydrogen atoms are much superior to previous estimates[9] but do not conflict with those conclusions.

The methods described here allow measurement of T_1 for transient free radicals independent of assumptions regarding CIDEP and chemical kinetic parameters and, therefore, increase the reliability of such parameters determined by time-resolved ESR studies. This aspect is particularly important for hydrogen atoms where the relaxation time is long and the reaction rates high. The present methods are restricted by sensitivity considerations to radicals which can be produced at relatively high concentrations so that the signal intensities are large. However, other time-resolved methods will be similarly limited. It should be emphasized that the presence of CIDEP is often an advantage in this method, since it enhances the sensitivity for detection of at least some of the ESR lines as in the cases of H atoms where both lines have ESR signal intensities corresponding to apparent concentrations much higher than the true concentration.

Further application of these methods can be made to investigate the dependence of T_1 and T_2 on free radical concentrations, viscosity, temperature, and nature of solvents. Such a study would provide insight into the nature of solvent–radical and radical–radical interactions as was done in the case of semiquinones.[39,42] Of particular interest is the measurement of relaxation by Heisenberg spin exchange between reactive radicals. A comparison of the rate for this process with that for

chemical reaction will give information on how the exchange interaction varies with radical separation. One should investigate hydrogen atoms more thoroughly and also attempt to measure T_1 and T_2 of deuterium atoms. The study of T_1 and T_2 values of both these atoms as a function of temperature and viscosity would aid our understanding of the motions and interactions that these atoms undergo in liquids such as water. In fact it is surprising that T_1 is as small as 13.5 μsec for the H atom which has an isotropic g factor and hyperfine splitting. Future studies are expected to contribute to our understanding of the mechanisms by which hydrogen atoms relax in aqueous solutions.

ACKNOWLEDGMENTS

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