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An Improved Technique for Recording Transient Electron Spin Resonance Spectra

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WE present preliminary results obtained using an improved technique for recording the e.s.r. spectra of transient photolytically generated free radicals. Flash-photolysis methods are used with e.s.r. spectroscopy. Unlike steady-state irradiation,[1] this gives direct information about radical species and decay processes at different times after the flash.

The test sample is placed in a slotted microwave cavity of a conventional spectrometer and irradiated with 50 *J*, 100 μsec. flashes from a Xenon tube at a rate of one flash every 1·5 sec. At a fixed magnetic field the spectrometer output describes the radical decay curve (the radical lifetime must be much smaller than the time between flashes). After each flash the output is monitored by six different sampling channels, each with an open time of 1·5 μsec. (much smaller than the radical lifetime), and with the sampling times suitably distributed over the decay curve. The 1·5 μsec. pulses from each channel are stretched to last until the next flash. The magnetic field is then swept slowly and linearly in the usual way, taking ten minutes to traverse a complete spectrum. The output from each channel is thus a normal e.s.r. display and represents the spectrum for a particular time interval after the flash. A typical set of spectra is shown in Figure 1.

Suitable sampling circuits were not available commercially and special circuitry had to be designed. The photolysing flash is monitored by a photo-diode, and the output from the diode used to trigger simultaneously the monostable delay pulse generators of each of the sampling channels. The trailing edge of each delay pulse, which is set to occur at a different time for each channel, is arranged to trigger a separate monostable 1·5 μsec. sampling gate pulse generator. Each sampling gate is a simple shunt transistor switch, with the gate pulse fed to the base. The pulse stretcher following each sampling gate consists of two successive diode–capacitor pulse

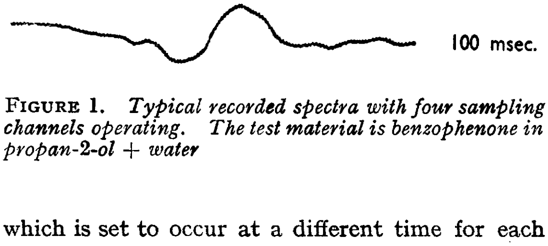

FIGURE 1. *Typical recorded spectra with four sampling channels operating. The test material is benzophenone in propan-2-ol + water*

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stretching circuits, suitably isolated, and finally a series transistor-switched holding circuit. 500 Kc./sec. was chosen for the frequency of field modulation of the spectrometer to allow a large band-width (50 Kc./sec.) and a short response time (6·5 μsec.). A 30 cm. aluminium ellipsoidal reflector is used to focus the light. Full details of the instrumentation are to be published shortly.

Successful results were obtained from the photolysis of benzophenone in propan-2-ol + water, which produces the ketyl radical anion.[2] The "observed" rate constant for the disappearance of both species is determined by the pH. Samples were prepared from 'AnalaR' reagents and degassed by the freeze–pump–thaw technique to a pressure of 10^{-4} torr. Initially a single line of width 7·5 gauss was recorded at a signal : noise ratio of 30 : 1. Reduction of the field modulation revealed hyperfine structure but the noise was too large for quantitative assessment. Decay measurements were made with various values of pH for lifetimes down to 5 msec. and were found to follow accurately second-order kinetics. Figure 2 compares measured rate-constants with those obtained by Beckett and Porter[2] using conventional flash-photolysis and optical spectroscopy. The discrepancy between the two sets of results is comparable with the error in measuring the high pH values.

Piette[3] used shuttered u.v. lamps, single-channel sampling and digital signal averaging (C.A.T.) to record transient e.s.r. spectra. We believe our method to be superior to theirs on at least five counts:

(i) shuttering light loss is avoided,

(ii) flash lengths (10 μsec.) and sampling times can be shorter,

(iii) signal : noise $\sim$ flash energy $\times \sqrt{\text{number of averaged measurements}}$, so a few high-energy flashes are better than many of low energy,

(iv) analogue sampling circuits are cheap,

(v) the presentation is more convenient.

The present instrument can be used to record the spectra of radicals with rate constants as large as $k_1 = 10^5$ sec.$^{-1}$ and $k_2 = 10^9$ l. mole^{-1}. sec.$^{-1}$. These values have been extrapolated from the present measurements using the expression:

$$\text{signal : noise} \sim M_{\text{max}}/k_1^{\frac{1}{2}} \text{ or } (M_{\text{max}}/k_2)^{\frac{1}{2}}$$

where M_{max} is the maximum radical concentration, here 10^{-4} M, and the signal : noise ratio is 30 : 1 for $k_2 = 10^6$ l. mole.$^{-1}$ sec.$^{-1}$. Consideration is now being given to techniques which will improve the signal : noise ratio. These include the use of a double-pulsed flash tube[4] for enhancement of u.v. radiation and of a microwave parametric amplifier.

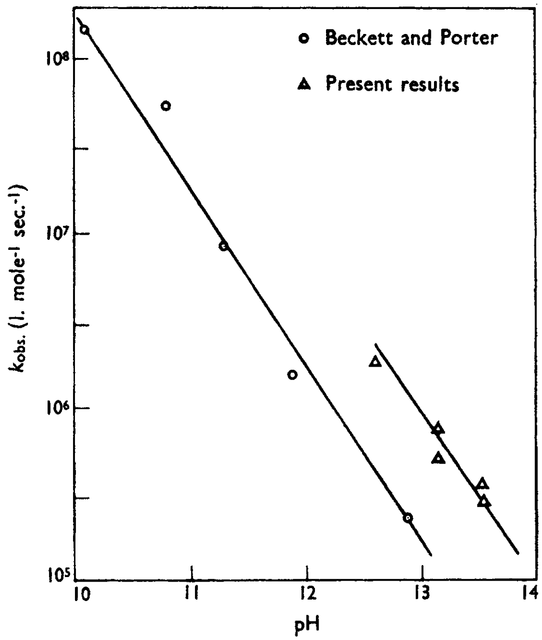

FIGURE 2. *Second-order rate constants for the disappearance of the ketyl radical anion.*

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