A New Method for Studying Transient Free Radicals by Electron Spin Resonance

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As soon as a free radical is formed its concentration begins to decay as a result of recombination and other reactions and it is impossible to examine by conventional means the whole spectrum, or even one line of it, in a time short compared with the decay. Our new technique consists of monitoring the signal height corresponding to a magnetic field value at a series of times after the radical is formed. This yields a decay curve whose ordinate represents the signal height at the definite magnetic field value as a function of time (Figure 1). The time behaviour of the complete spectrum is obtained by the addition of a large number of observations of this type, each obtained at a different value of the magnetic field which is changed incrementally. The e.s.r. spectrum as a function of field is obtained at a given time as a cross-section of these profiles.

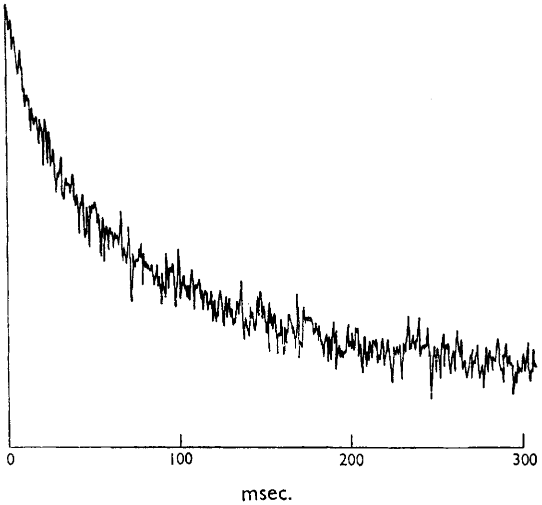

FIGURE 1. *A decay curve obtained at near maximum signal amplitude.*

The experiment has been performed using a Decca *X*-band spectrometer system equipped with a Varian Fieldial II magnet system; 100 Kc./sec. modulation was used. The output was sampled by a Data Laboratories 'Biomac 500' pulse height analyser at 640 μsec intervals. Radicals were produced by a xenon flash tube beside the cavity and each flash was triggered from the 'Biomac' analyser so that the information from 128 flashes at each magnetic field value could be synchronised. After each set of flashes the accumulated data was drawn on a recorder. At present the spectral profiles are derived manually from these traces.

The technique may be demonstrated by observation of the radicals induced in a saturated solution of benzophenone in equal parts of propan-2-ol and 0·1 N-sodium hydroxide. Spectra were taken in steps of 1 gauss near the centre of the spectrum and 2 gauss elsewhere. For the present demonstration purpose the signal was deliberately overmodulated. A typical decay curve is shown in Figure 1. From 20 runs of this type the line shapes were reconstructed as described and 3 of these are shown in Figure 2.

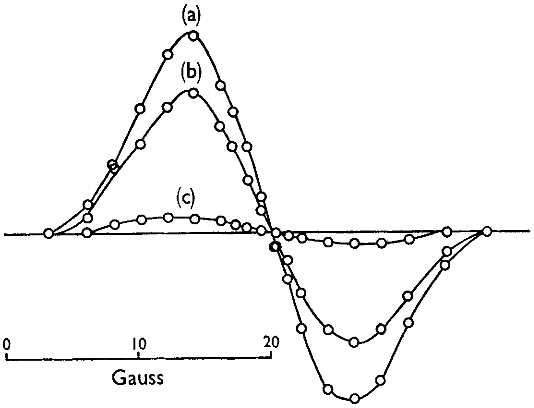

FIGURE 2. *Reconstructed spectra after* (a) *ca.* 5 *msec.,* (b) 16 *msec., and* (c) 176 *msec.*

The technique is capable of giving more detailed information in gases, liquids, and solids at time intervals down to 1 μsec after the radical is formed.

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