Motional Effects in Free Radical Spin Resonance

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Résumé.

Ce travail donne la description de deux effets directs du mouvement molé-culaire sur les spectres de résonance électronique. Le premier est lié à la diffusion des radicaux libres dans le milieu et le changement du spectre résultant de leur interaction avec les autres molécules.

Le second consiste dans une modification de la structure due au fait que le mouvement de rotation de divers groupes à l'intérieur de la molécule est altéré. Dans ce cas, le changement le plus frappant du spectre est celui de la largeur et de la forme des raies, dû à l'« amincissement de mouvement » comme en réso-nance nucléaire.

Dans l'étude du premier de ces effets, une mesure quantitative de l'accroisse-ment et de la diminution d'intensité des divers spectres a été entreprise, et on montre comment une théorie cinétique de premier ordre rend compte convenable-ment des résultats expérimentaux. L'effet d'un changement du mouvement de rotation des groupes « méthyl » est pris comme exemple du deuxième effet où des changement réversibles frappants sont produits dans le spectre du radical isopro-panol par variation de la température de l'échantillon.

I. Introduction.

There are two basic types of molecular motion that produce changes in electron resonance spectra, and can therefore be studied by this method. The first is an actual movement of free-radical molecules through the medium as a whole, and the second is a change in their own internal motion, such as the quenching of the rotation of a methyl group about a carbon-carbon axis. In the first case the active free-radical will interact with the other molecules that it meets as it diffuses through the medium, and new radical species will be formed with their own characteristic hyperfine structure. In the second case the coupling between the molecular orbital of the unpaired electron and the various protons of the radical will be altered, and a significant change in its own hyperfine pattern will be pro-

duced. It is therefore possible, by making a careful analysis of the observed hyperfine structure, and its change with time, to obtain information on both the kinetics of radical interaction, and the internal motion of the molecules themselves. This paper summarises the results obtained on one particular radical system in which both of these two types of motion can be observed and studied quantitatively.

The system chosen has been the interaction of hydroxyl radicals with isopropanol molecules. The former are employed as the initial radical species since it is relatively easy to produce them in quite large concentrations throughout the volume of the specimen tube by the action of U.V. irradiation on hydrogen peroxide [1, 2]. The isopropanol molecules were chosen as the bulk medium since the isopropanol radical, which is formed when a proton is abstracted by an hydroxyl radical, possesses a sevenline hyperfine pattern which can be identified very easily [3]. It will be seen in the analysis of the results which follow that the reaction between the hydroxyl radicals and the isopropanol molecules, as the former move through the medium, can be represented quantitatively by a first order kinetics. The change in the internal motion of the isopropanol radicals when the temperature of the specimen is altered, can also be followed from the changes which occur in the hyperfine pattern of their electron resonance spectra. It may be noted that all these experiments were performed between 77° K and 110° K, and the viscosity of the alcohol glasses at these temperatures is such that the hydroxyl radicals can diffuse slowly through them but the larger isopropanol radicals remain trapped in the glass matrix.

II. Experimental Technique.

Most of the work has been carried out with a 3 cm-wavelength spectrometer, although some of the measurements have been repeated at 1.25 cm wavelength to distinguish between hyperfine splittings and g-value variations. High-frequency magnetic field modulation at 100 Kc/s [4] has been employed to overcome the low-frequency crystal noise, and the resulting spectra are plotted out as first-derivative curves by a pen-recorder following phase-sensitive detection.

The resonant cavity, which contains the specimen under investigation is cooled by immersion in a bath of liquid nitrogen. Rectangular cavities operating in the H_{014} mode have normally been employed, and these are fed

by a section of thin-walled waveguide, backed by plastic material to give mechanical strength, which acts as an effective " heat break ". A method of irradiation " in situ " has also been developed in which a beam of ultra-violet irradiation is focussed onto the specimen tube as it rests in the cavity at liquid nitrogen temperatures. The initial formation of the radicals and their subsequent secondary reactions can then be monitored continuously by the spectrometer.

The radical reactions under investigation take place in frozen alcohol solutions containing a small amount of hydrogen peroxide. If 3650 Å radiation is employed the hydrogen peroxide will be decomposed at a fairly rapid rate, but no other radicals will be formed as the primary acts of photolysis. The hydroxyl radicals are relatively mobile, even at 77° K, however, and attack the isopropanol molecules to form the secondary radicals, and the growth of these secondary radicals can then be studied kinetically. In the specimens investigated about 10^{-6} to 10^{-5} mole of hydrogen peroxide was added to the pure isopropanol, and deep-freezing such mixtures usually produced glasses of reasonable structure.

The total resonance absorption due to the specimen at any given time was determined by graphical double-integration, and the number of radicals was determined by comparison with a doubly-integrated curve from a standard free radical sample observed under identical conditions. The standard samples are formed by diluting ground charcoal with an inert filler, and are themselves cross-calibrated with diphenylpicrylhydrazyl.

III. CHANGE OF SPECTRUM DUE TO DIFFUSION
AND RADICAL REACTION.

The results obtained when the isopropanol-hydrogen peroxide mixture was continuously irradiated with 3650 Å at 110° K are shown in figure 1. It is seen that the initial resonance signal consists of an asymmetrical singlet, due to the OH radical, but that this gradually changes as it grows, until eventually all of the absorption is accounted for by the seven-line pattern of the isopropanol radical [2, 3]. This seven-line pattern arises from an equal interaction of the unpaired electron with the six protons of the two methyl groups of the $(CH_3)_2 . \overset{*}{C} . OH$ radical [3].

The kinetics of the whole of this radical reaction can be represented as follows:

1st step.   Photo-dissociation of hydrogen peroxide.

$$H_2 O_2 + h\nu \longrightarrow 2.\overset{*}{O}H . \tag{1}$$

The 3650 Å irradiation can only photolyse the hydrogen peroxide and hence hydroxyl radicals can be the only primary radicals formed. Let the kinetic constant for this photolysis be k_1. Ie. If n is the number of hydrogen peroxide molecules present at time t after the start of the radiation

$$-\frac{dn}{dt} = k_1 . n . \tag{2}$$

The value of k_1 will depend on such parameters as the light intensity, geometry of the specimen in the cavity, as well as the quantum efficiency of the photodissociation.
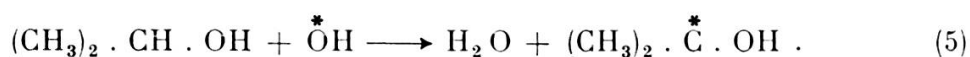
If n_0 is the initial number of hydrogen peroxide molecules in the specimen, the number left after time t will be

$$n_t = n_0 \cdot e^{-k_1 t} \tag{3}$$

and the number of $\overset{*}{O}H$ radicals formed (n_a') will be:

$$n_a' = 2n_0 \left(1 - e^{-k_1 t}\right) . \tag{4}$$

2nd step.   Hydrogen abstraction by $\overset{*}{O}H$.

$$(CH_3)_2 . CH . OH + \overset{*}{O}H \longrightarrow H_2 O + (CH_3)_2 . \overset{*}{C} . OH . \tag{5}$$

The chemical evidence on reactivity supports the deductions from a large number of electron resonance results on different alcohols, that the hydroxyl radical nearly always removes a proton attached to the carbon atom rather than that of the hydroxyl group. Let the kinetic constant for this reaction be k_2. If n_b is the total number of isopropanol radicals that have been formed at time t it follows that

$$\frac{dn_b}{dt} = k_2 \left(n_a' - n_b\right) \tag{6}$$

since $(n_a' - n_b)$ is the number of hydroxyl radicals that have not yet reacted with the isopropanol molecules.
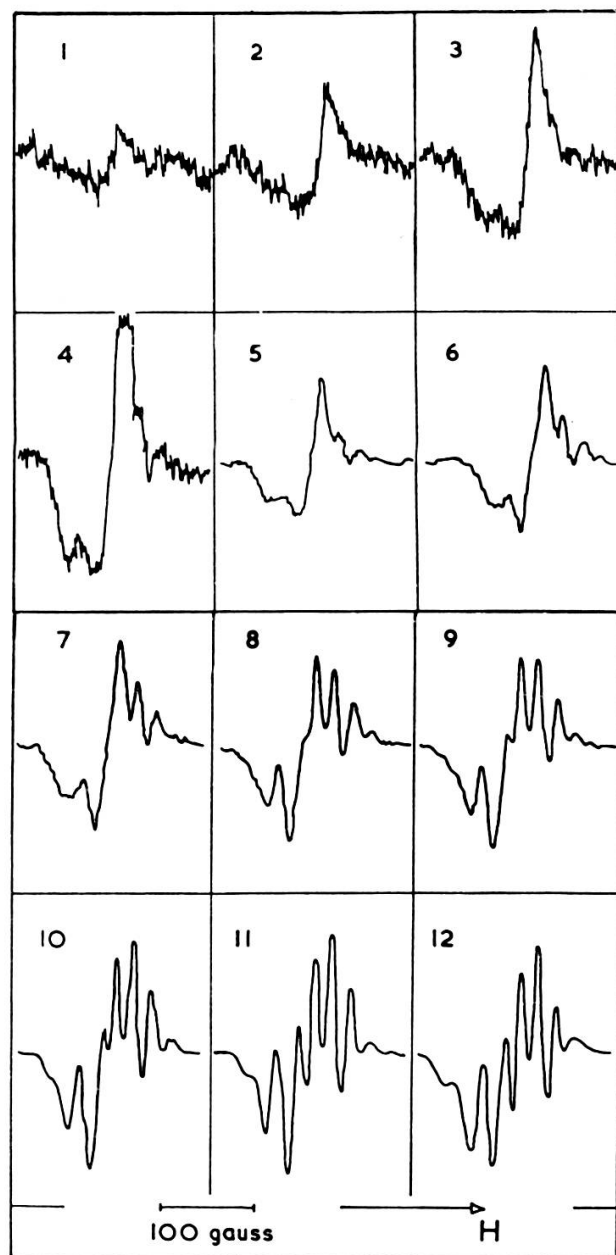
Fig. 1.

Variation of isopropanol spectra with time of irradiation.
Spectra were taken at approximately 10 minute intervals.

Substitution of equation 4 into equation 6 and integration then gives

$$n_b = n_0 \left[1 - \frac{(k_2 \, e^{-k_1 t} - k_1 \, e^{-k_2 t})}{k_2 - k_1} \right] \quad if \; k_1 \neq k_2 \qquad (7)$$

or

$$n_b = 2n_0 \left[1 - (1 + kt) \, e^{-kt} \right] \quad if \; k_1 = k_2 \; . \qquad (8)$$

The general form of these equations are summarised graphically in figure 2, where the variation of n_a', n_b and the actual number of hydroxyl radicals, $(n_a' - n_b)$, are plotted against time.
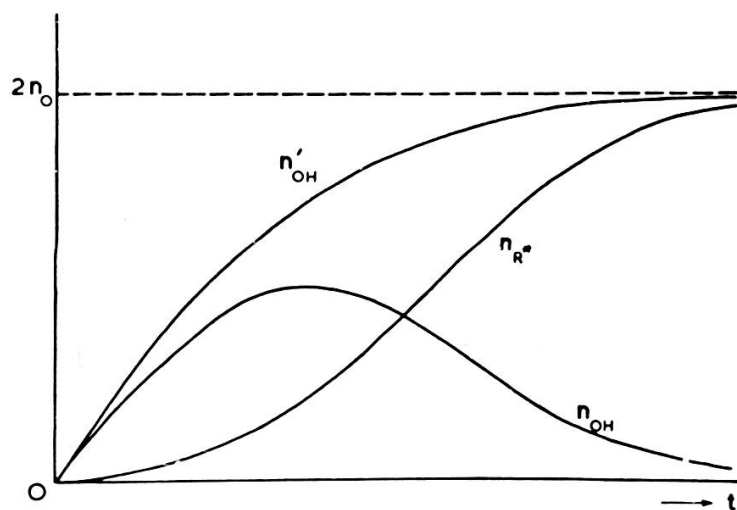

Fig. 2.

Variation of free radical concentration with time of irradiation, as predicted by first-order kinetics.
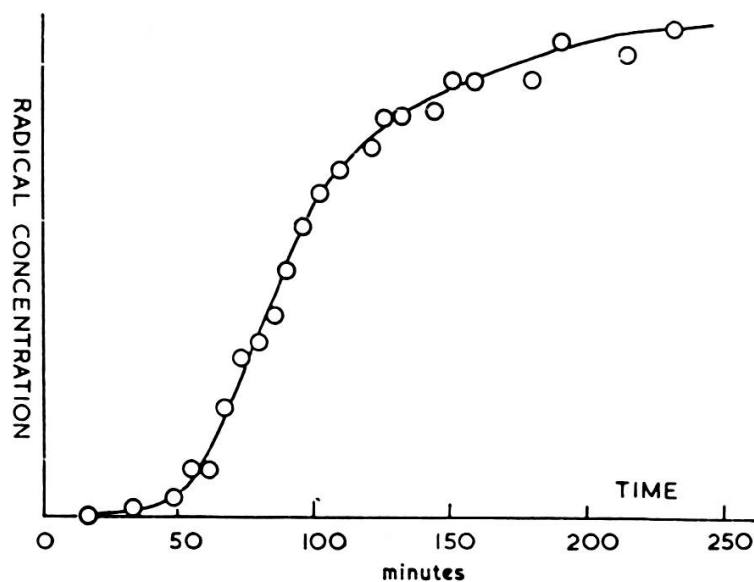

Fig. 3.

Experimentally observed variation of isopropanol radical concentration with time.

The actual values of k_1 and k_2, and the units along the axes will depend on the conditions of the particular experiment, and may be found by plotting the experimentally observed curves, and then making a best fit between these and those of figure 2. In practice the intensity of the isopropanol spectrum can be measured the most accurately, since there is no overlap of its outer hyperfine peaks, on the high field side, with the OH spectrum. The intensity of these peaks may therefore be taken as proportional to the number of $(CH_3)_2$. . $\overset{*}{C}$. OH radicals present. The quantitative analysis of the traces in figure 1 has been made in this way and is summarised in figure 3. Different values for k_1 and k_2 can then be substituted into the theoretical equations [7] or [8] and a best fit with the observed curve can be obtained. The theoretical curve for which $k_1 = 0.03$ min^{-1} and $k_2 = 0.04$ min^{-1} is found to lie very close to that shown in figure 3, apart from a small shift along the time axis which is probably due to the " warming up " period of the mercury lamp. It would therefore appear that a simple theory, based on first-order kinetics, gives a good approximation for free-radical formation by a diffusion process through such frozen media.

IV. CHANGE OF SPECTRUM WITH INTERNAL MOTION.

The other type of motion that can be studied by an analysis of electron resonance hyperfine patterns is the internal motion of the groups within the molecule. The rotation of the CH_3 groups of the isopropanol molecule about their carbon-carbon bond directions furnishes a good example of this. At relatively high temperatures the three protons will be rotatiug rapidly around this axis, whereas, as the temperature is lowered, this group rotation will be prevented or restricted. Such restriction of methyl rotation will be reflected by a change in the observed hyperfine pattern of the resonance spectrum. This arises from the fact that the hyperconjugative overlap with the orbit of the unpaired electron will only take place for protons in positions parallel to the $2p_\pi$ orbits of the attached carbon atom. If the methyl group is rotating at a rate faster than the frequency splitting of the spectrum, all three protons will pass through equivalent positions in turn, and hence will be equally coupled to the unpaired electron's orbit. If the motion of the group is restricted, however, it is possible that only two, or one, of the protons will be in the correct position to interact, and the number of hyperfine components will thus be correspondingly reduced.

A good example of this change in spectra is shown in figure 4, which is for the isopropanol radical at two different temperatures. Figure 4 (*i*) is the spectrum observed at 110° K and consists of the seven lines discussed before. The fact that there is equal coupling to all six methyl protons shows that both methyl groups must still be rotating at 110° K. Figure 4 (*ii*) is the spectrum from the same compound but at 77° K, and a marked change in the hyperfine pattern is evident. The integrated absorption curve of this spectrum is shown at the top of figure 5, and it is seen to consist of six lines with a slight central plateau. This indicates that the electron interaction is now primarily with five, instead of six, protons.

This type of situation might occur if the actual rotation of both methyl groups were quenched, and, instead, the protons in each group executed jumps between three equilibrium positions. One of the methyl groups would then be expected to have two of its protons in positions parallel to the carbon $2p_\pi$ orbital, with the third in its null plane. The other methyl group would have its equilibrium positions rotated with respect to this, however, to avoid close proximity with protons of the first group, and all three of these protons could therefore interact with the carbon $2p_\pi$ orbital. An alternative explanation of the six-line spectrum is that the rotation of both methyl groups is quenched, giving an interaction with only four protons, but at the same time the rotation or exchange of the hydroxyl protons is also quenched. This proton would then also couple with the unpaired electron to give a total of five interacting protons and hence a six-line spectrum.

If one proton becomes less effective under one of these possible quenching processes, the spectrum will consist of six lines, produced by the five equally coupled protons, each split into two by any residual interaction with the odd proton. The detailed shape of the hyperfine pattern at 77° K can then be explained if the residual interaction is taken as 9 gauss, while the interaction with the five equally coupled protons is 22 gauss.

These interactions are denoted as a' and a respectively in the theoretical reconstruction shown in figure 5 (*ii*). It is interesting to note in this connection that the splitting between the seven lines of the spectrum at 110° K is given by $a'' = 20$ gauss, and that the relation

$$5a + a' = 6a''$$

is accurately obeyed. This implies that the amount of unpaired spin density interacting with the protons is conserved throughout the process.
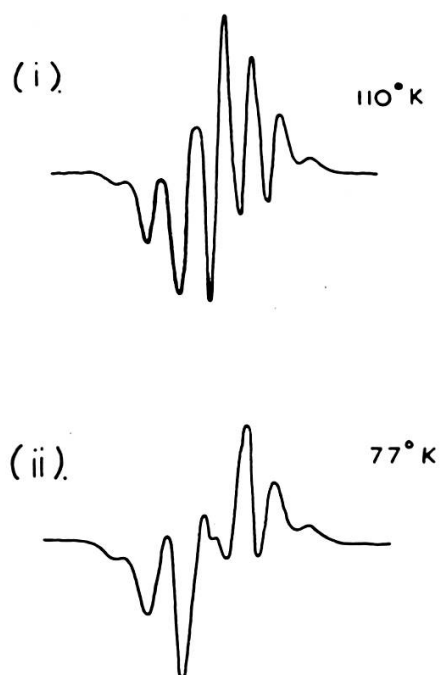
Fig. 4.

Spectra of isopropanol radical, at (*i*) 110º K and (*ii*) 77º K
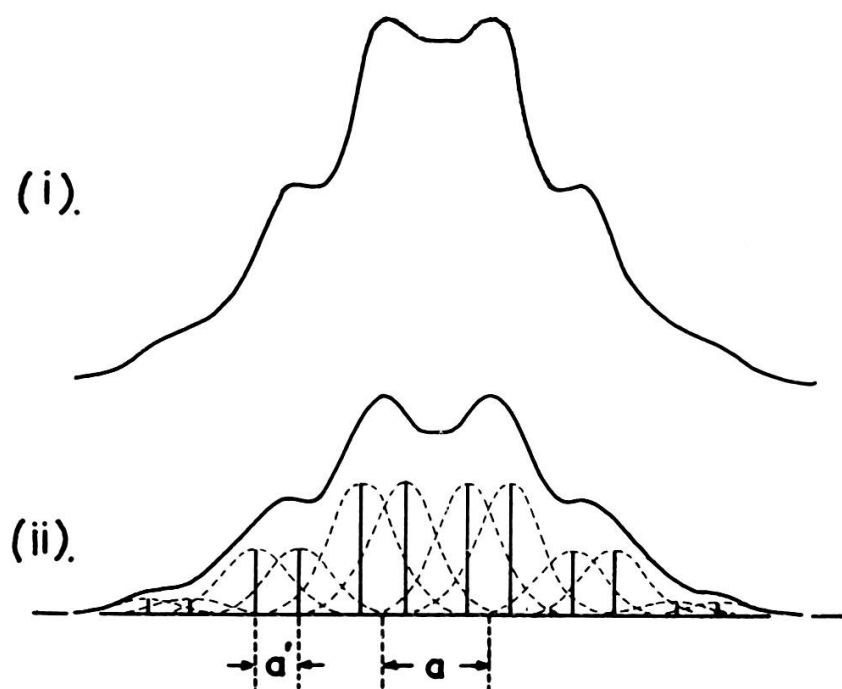

Fig. 5.

Reconstruction of isopropanol spectrum at 77º K.

(*i*)   Observed absorption;
(*ii*)   Theoretical Reconstruction.

It has been suggested that the difference between the spectra at the two temperatures might be due to different radicals being formed at the two temperatures. This hypothesis can be eliminated, however, by watching the change in spectra as the specimen is cooled from 110° K to 77° K, and also on rewarming. The change from a seven to a six-line spectrum is found to be quite reversible with temperature proving that the change must be due to a change in internal motion, and not to different radical reactions.

V. Conclusions.

These experiments, performed on a model radical system, have shown that both the motion due to diffusion of the whole radical, and the internal motions of the radicals themselves, can be studied by electron spin resonance. It is possible to carry out a quantitative analysis of the results in both cases, and in the case of the radical reaction a first-order kinetic theory can be formulated and tested.

It is hoped that further measurements at different temperatures and with a variety of radical systems will enable quite detailed kinetic studies of this type to be made.

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