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Nuclear Magnetic Resonance in Radicals and in Radical Reactions

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The present review examines papers devoted to the application of NMR to the study of the electronic structure of radicals, their solvation by various solvents, and the kinetics of radical reactions. The characteristic features and experimental difficulties of the NMR of radicals in the solid and liquid phases are examined as are the possibility of obtaining data on the mechanism of the delocalisation of the unpaired electron over large distances in the radicals themselves and in their complexes with solvents. It is shown how relaxation methods involving measurement of T_1 and T_2 and the dynamic polarisation of the nuclei have given information on the correlation times characterising the intensity of molecular motions in a liquid, and the energetics of these motions. The theoretical basis of these methods is examined. The last section gives the theory of the use of NMR spectra to measure the rates of various fast reactions. The results of the study of the kinetics of electron transfer and radical substitutions taking place with zero activation energy are discussed. The bibliography contains 61 references.

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INTRODUCTION

The application of nuclear magnetic resonance to the study of radicals and radical reactions is a new and interesting example of the physical approach to the solution of chemical problems concerning the electronic structure of radicals, their reactivities, and their specific interactions with various molecules. These three aspects make up the contents of the present review. Chief attention is paid to the physicochemical aspects of the phenomena; purely physical aspects which are not of significant importance for chemistry are examined only briefly or not at all.

NMR in radicals gives detailed information on the properties of the molecular orbitals of the unpaired electron and on the mechanism of its delocalisation. The NMR method can give unique data on weak donor–acceptor interactions between radicals and surrounding molecules, on the dynamics of complex-formation equilibria, and on the participation of the unpaired electron in donor–acceptor interactions and the mechanism of its delocalisation in the complex.

Of greatest interest is the possibility of using the NMR method to measure the rates of fast reactions of electron transfer and also radical substitutions, taking place with zero activation energy. This range of problems will subsequently be examined in more detail. We shall restrict ourselves to organic radicals; paramagnetic ions and their complexes with organic ligands will not be considered.

I. NMR AND DELOCALISATION OF THE UNPAIRED ELECTRON IN RADICALS

The molecular orbital of the unpaired electron in radicals usually includes various atomic orbitals of many atoms in the radical. If the nuclei exhibit magnetic moments, the energy of the magnetic electron-nuclear or hyperfine interaction (HFI), measured by the method of electron paramagnetic resonance (EPR), in principle makes it possible to determine the magnitude of the spin density ρ_i. For angle-dependent atomic orbitals (p, d, etc.), ρ_i is determined from the dipole–dipole HFI, and for atomic s orbitals, ρ_i is determined from the isotropic or contact HFI.

A very important characteristic of the behaviour of an unpaired electron, in addition to the magnitude of ρ_i, is the sign of ρ_i, which determines the orientation of the electron spin in the atomic orbital with respect to the orientation of the total spin: $\rho_i > 0$ if these orientations coincide, and $\rho_i < 0$ if they are opposed. The EPR method at best can give only the relative signs of ρ_i (in the study of the EPR of radicals in diamagnetically dilute single crystals[1], or in solutions[2]). The sign of the HFI constants characterises the mechanism of the delocalisation of the unpaired electron over the radical or the mechanism of the "population" of the atomic orbitals—a very important manifestation of electron–electron interactions in the radical.

Let us now consider NMR in a radical. Let us assume that the unpaired electron is situated at an atom with nuclear spin I; the energy levels of the nucleus in a constant magnetic field H_0 with allowance for only the isotropic HFI are then given by the expression

$$E_i = -\gamma_n H_0 m_i + a_i \gamma_e m_s m_i, \qquad (1)$$

where γ_e and γ_n are the gyromagnetic ratios of the electron and the nucleus, m_s and m_i the quantum numbers of the projections of the electron and nuclear spins on the field direction (m_i takes values from $-I$ to $+I$), a_i the constant of the isotropic HFI

$$a_i = \frac{8\pi}{3}\gamma_e\gamma_n|\psi(0)|^2 \qquad (2)$$

and $|\psi(0)|_i^2$ the density of the unpaired electron at a point of the nucleus. The first term in Eqn. (1) corresponds to the Zeeman energy of the nucleus, and the last to the energy of the isotropic HFI.

The magnitude of the local field created by the unpaired electron at a point of the nucleus is $a_i/2(\gamma_e/\gamma_n)$ and for free radicals usually amounts to 10^3–10^4 Oe. This HFI is now not a perturbation of the nuclear Zeeman levels and it displaces considerably the frequency of the nuclear-resonance absorption, so that it becomes non-observable. If, however, the correlation time, that is, the duration of existence of the local field due to the HFI, becomes much shorter than the period of the Larmor precession of the nucleus in this field, this leads to a decrease in the mean value of the local field. In this instance the second term in Eqn. (1) has the form $a_i\gamma_e\langle m_S\rangle m_i$, where $\langle m_S\rangle$ is the mean value of m_S. The value of $\langle m_S\rangle$ is determined by the populations of the electron-spin states $m_S = \pm\frac{1}{2}$. In the high-temperature approximation, when the Zeeman energies are much less than kT, we have

$$\langle m_s\rangle = \sum_{m_s} N_{m_s}m_s \Big/ \sum_{m_s} N_{m_s} \simeq -\frac{\gamma_e H_0}{4kT} \qquad (3)$$

where N_{mS} represents the populations of the states m_S.

For the energy of the transitions $\Delta m_S = 0$, $\Delta m_i = \pm 1$, corresponding to the NMR spectrum we obtain the expression

$$\Delta E = \gamma_n H_0 - a_i\gamma_e(\gamma_e H_0/4kT), \qquad (4)$$

or, converting to the magnitude of the magnetic field at resonance

$$H = H_0 - a_i(\gamma_e/\gamma_n)(\gamma_e H_0/4kT),$$

where H_0 is the resonance field in the absence of HFI. The difference $\Delta H = H - H_0$ is the magnitude of the paramagnetic shift

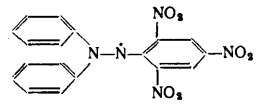
$$\Delta H = -a_i(\gamma_e/\gamma_n)(\gamma_e H_0/4kT). \qquad (5)$$

Thus the fluctuating magnetic field created by the unpaired electron at a point of the nucleus brings about a displacement of the resonance frequency of this nucleus, whose magnitude and sign are determined by the magnitude and absolute sign of the constant a_i. It is necessary only that the frequency of the fluctuations in the local field be much greater than the frequency of the Larmor nuclear precession in this field. It is evident that the paramagnetic shift of the NMR in radicals is analogous to the Knight shift of the NMR in metals, due to the contact HFI of the nuclei with the conductivity electrons[3].

The condition for observability of the paramagnetic shift is that the duration τ of the existence of the local field of the HFI should be short compared with the period of the nuclear precession in this field, that is, $\tau \ll a_i^{-1}$, where a_i is expressed in frequency units. Since the spin-lattice relaxation time T_1 in radicals is usually large, this mechanism cannot ensure that the condition $T_1 \ll a_i^{-1}$ is satisfied; the most important part is taken by the mechanism of the electron–electron exchange interactions taking place in concentrated solid or liquid solutions of the radicals. This corresponds to the mutual reorientation of neighbouring electron spins with exchange frequency ω_{ex}; in crystals of the radicals $\omega_{ex} \simeq 10^{10}$–$10^{11}$ s^{-1}, that is, the electron changes its orientation 10^3–10^4 times within the period of the nuclear precession. This is sufficient to average the local fields created by the HFI, except for the small residual fraction obeying the Boltzmann distribution; it is this HFI which is responsible for the paramagnetic shift.

1. NMR of Radicals in the Solid Phase

NMR in diphenylpicrylhydrazyl (DPPH)



has been studied in most detail.

From the structure of the radical it follows that there are four groups of equivalent protons, and in the NMR spectrum these should correspond to four lines with integral intensities in the ratio 1 : 2 : 2 : 1, proportional to the number of protons of each kind. In the first experiments, however, only two strongly overlapping lines were observed[4] and only later was it possible to resolve the spectrum completely[5]. The NMR spectrum of polycrystalline DPPH, taken in the form of the 1 : 1 complex with benzene, is shown in Fig. 1*a*. It can be seen that in addition to the four expected lines there appears in the centre an additional line which is not displaced and which corresponds to complexed benzene. If benzene is replaced by deuteriobenzene, the intensity of this line decreases sharply; there remains only a small peak which apparently corresponds to diamagnetic impurities in the radical (Fig. 1*b*). Replacement of the *meta*-protons in the picryl group by deuterium showed that the resonance of these protons is displaced considerably to low fields (Fig. 1*c*).

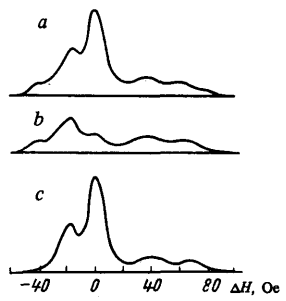


Figure 1. NMR spectra of polycrystalline DPPH at 4.2°K. *a*) DPPH in its 1 : 1 complex with benzene; *b*) DPPH in its complex with deuteriobenzene; *c*) DPPH with deuterium in the picryl group.

On the basis of these data, and also from calculations of the spin densities by the valency bond method, and from the intensities in the spectrum, it was assumed that the resonance of the *meta*-protons is displaced to low fields, and that the resonance of the *ortho*- and *para*-protons is displaced to high fields; the paramagnetic shifts and HFI constants a_H, calculated from Eqn. (5), are given in Table 1.

In view of the approximate nature of the theory and the experimental errors, the agreement is fairly good. Thus at the hydrogen atoms in the *ortho*- and *para*-positions of the phenyl rings, the spin density is negative, whereas it is positive in the *meta*-positions. These conclusions were confirmed in later work; it was shown that the

dependence of the paramagnetic shift on the magnetic field intensity and on temperature obeys Eqn. (5) satisfactorily[6].

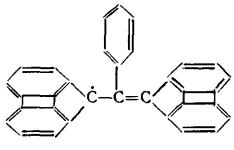
In DPPH, as in most other aromatic radicals, the unpaired electron is a π-electron and its molecular orbital is made up from the orbitals of the nitrogen atoms and the π-orbitals of the carbon atoms of the aromatic system. The isotropic HFI at the protons attached to these carbon atoms appears as a result of σ–π configurational interaction, that is, partial unpairing of the electrons of the C–H bond; the signs of the spin density at the carbon atom and the hydrogen atom attached to it are opposite. This means that in DPPH there is positive spin density at the carbon atoms in the *para*- and *ortho*-positions, and negative spin density at the carbon atoms in the *meta*-positions. Thus the unpaired electron in DPPH is delocalised over the π-system of the radical; its density ρ at the carbon atoms in the rings can be determined from the familiar McConnell relationship[7] $a_H = Q\rho$, where $Q = 23.7$ Oe,[8] and the constants of the isotropic HFI at the neighbouring protons are determined either from the EPR spectra (without signs), or from NMR data, as for DPPH (Table 1).

Table 1. Paramagnetic shifts and HFI constants in DPPH.

Position of protons	ΔH, Oe	a_H, Oe (experiment)	a_H, Oe (theory) (Ref.5)
Picryl (*meta*)	−38	+2.4	+2.55
Phenyl (*meta*)	−16	+2.1	+1.55
Phenyl (*ortho*)	+37	−2.3	−2.94
Phenyl (*para*)	+62	−3.9	−2.74

An interesting feature is that the central line in the NMR spectrum of DPPH, corresponding to the protons of the benzene in the complex with DPPH, is not displaced, that is, the spin density at the atoms of the ligand in the complex is very low, although the complex itself is fairly stable.

The NMR spectrum of 1,3-bis(biphenylene)-2-phenylallyl:



shows some structure even at 77°K. At 4.2°K, two lines are clearly observed; one of these is displaced to high fields by 15 ± 1 Oe, and the other, whose intensity corresponds to ~ 70% of the total intensity of absorption, remains almost unshifted[9].

The EPR spectrum of this radical contains 9 lines with splitting 2.2 Oe. It is not known which protons produce this splitting; nevertheless, it is possible to divide all the protons in the radical into two groups: 8 protons with HFI constant 2.2 Oe, and the other 13 protons with very slight splitting. Since the radical is present in the crystal as the 1 : 1 complex with benzene, the NMR spectrum should contain two lines—one displaced (from the 8 protons) and one which is not displaced (from the 13 + 6 = 19 protons). The observed NMR spectrum shows complete agreement with these ideas. At the protons giving an HFI constant of 2.2 Oe, the spin density is negative (paramagnetic shift to high fields), that is, at the carbon atoms to which these protons are attached, the density of the unpaired π-electron is positive and is much greater than the density of the unpaired electron at the other carbon atoms.

The NMR spectrum of the pyrene radical-anion, in addition to a line which is not displaced and which corresponds to the diamagnetic original substance, contains three displaced lines[10]. The signs and magnitudes of the HFI constants are given in Table 2, which also gives for comparison the values of the same constants obtained by the EPR method; the agreement is very good.

Table 2. Paramagnetic shifts and HFI constants in the pyrene radical-anion.

ΔH, Oe	a_H(NMR)	a_H(EPR)
−35.1	+1.26	(+) 1.09
+79.1	−2.79	(−) 2.08
+140.5	−4.88	(−) 4.75

The NMR spectrum of the tri-*p*-chlorophenylammonium radical-cation at 77°K consists of two poorly resolved lines with equal intensity, one of which is displaced by 2.3 Oe to low fields, whereas the other is displaced by 3.9 Oe to high fields. These lines evidently correspond to the *ortho*- and *meta*-protons, on which the spin densities have positive signs[9].

In addition to the study of these radicals, attempts have also been made to study NMR in the polycrystalline tetramethyl-*p*-phenylenediamine radical-cation (Wurster's cation), but definite results could not be obtained[9]. This is apparently due to the fact that at fairly high temperatures the paramagnetic shifts are small, and at low temperatures the crystal is converted into an antiferromagnetic state[11].

2. NMR of Radicals in Liquids

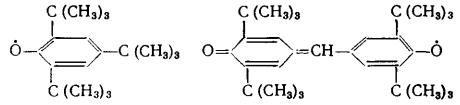
Until now we have examined the paramagnetic shift due only to the isotropic HFI. The anisotropic part of the HFI also produces a shift, whose magnitude and sign are determined by the magnitude and sign of the anisotropic HFI constant; the latter can be found from the paramagnetic shifts in single crystals of radicals. In polycrystalline specimens, the anisotropic HFI leads to marked broadening of the lines; it is for this reason that paramagnetic shifts in polycrystalline specimens can be observed only at very low temperatures, when the magnitude of the shift is greater than the width of the lines. In liquids, the anisotropic HFI is averaged by the molecular motion, and the NMR lines become much narrower.

The condition for observation of the paramagnetic shift is satisfied only in concentrated solutions of radicals. The width of the lines is determined by both the dipole and scalar relaxations (see Section II) and is usually proportional to a^2; the condition for obtaining very narrow lines $\omega_S^2 \tau_{ex}^2 \ll 1$ is difficult to satisfy for solutions of radicals,

in contrast to the situation for paramagnetic ions, where the electronic relaxation times T_{1e} are often small and $\omega_S^2 T_{1e}^2 < 1$.

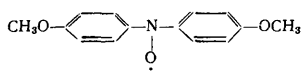
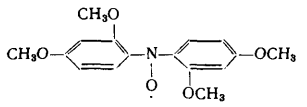
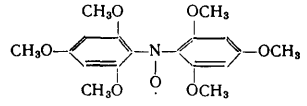
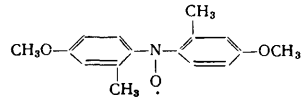
Most studies have naturally been carried out with stable radicals. This, however, does not restrict the possibilities of using the method for the main task—the investigation of the mechanism of delocalisation of electrons in many-electron molecular systems.

In the NMR spectra of 2,4,6-tris-t-butylphenoxyl and Coppinger's radical:



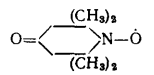
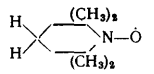
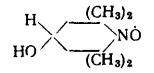
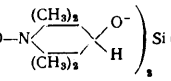
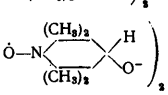
recorded at 20° in C_6D_6, the lines of the *o*-t-butyl protons are displaced to low fields relative to the same protons in the corresponding molecules, that is, there is positive spin density at these protons; the HFI constants are +0.071 Oe and +0.049 Oe respectively, and show good agreement with the constants obtained by the EPR method (0.072 Oe and 0.049 Oe)[12]. Calculation of the spin density in these radicals shows that in the *ortho*-positions of the rings there is positive π-electron density, that is, the signs of the spin densities at the carbon atoms in the *ortho*-position and the *o*-t-butyl protons are the same; this apparently means that the chief part in delocalisation of the unpaired electron on the protons of the t-butyl groups is played by the hyperconjugation mechanism (further proof of this is given below, in section II).

Table 3.

Radical	HFI constants for the protons of the CH_3 and OCH_3 groups, Oe	
	para-position	*ortho*-position
	+0.223	—
	+0.180	+0.100
	+0.120	+0.084
	+0.075	+0.160

In aromatic nitroxide radicals (Table 3) the sign of the constant a_H on the protons of the *ortho*- and *para*-substituents also coincides with the sign of the π-electron spin density on the corresponding carbon atoms of the aromatic rings; this means that the unpaired electron appears in the atomic orbitals of the CH_3 and OCH_3 hydrogen atoms due to a hyperconjugation mechanism[13]. The values of a_H for OCH_3 in a series of radicals (Table 3) gradually decrease; this may be due to a decrease in the spin density in the rings as a result of the twisting due to steric interaction of the *ortho*-substituents[14]. The relationship between the constants a_H for OCH_3 in the *ortho*- and *para*-positions, and also between a_H for OCH_3 and CH_3 is the same as that usually observed in EPR for radicals of this type[15]. Extremely interesting characteristic featues of the delocalisation of an unpaired electron in a σ-system are observed in aliphatic nitroxide radicals[16,17]. The HFI constants in some of these radicals are given in Table 4.

Table 4.

No.	Radical	HFI constants for the protons, Oe			
		β-CH_3	β-CH_2	γ-CH	other protons
I		—0.1	0		
II		—0.2	—0.4	+0.15	
III		0 and —0.43	—0.32 and —0.46	+0.08	
IV		0 and —0.43	—0.31 and —0.46	+0.08	~0
V		0 and —0.4	—0.29 and —0.5	+0.09	

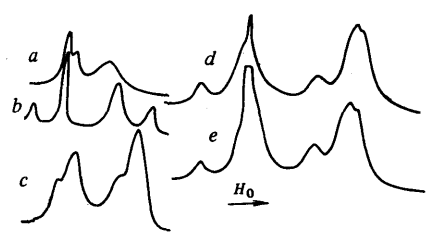


Figure 2. NMR spectra of radicals: I at 50°C (*a*); II at 36°C [16] (*b*); III at 25°C (*c*) and 60°C (*d*); IV at 60°C (*e*). Spectra recorded at 100 mHz (see Table 4).

The NMR spectra of some of these radicals are given in Fig. 2. In radicals I and II the protons of all the β-CH_3 groups are equivalent and give a single line in the NMR spectrum; the protons of the β-CH_2 groups are also equivalent. In the radicals and polyradicals III–V, the NMR signal of the protons of the β-CH_3 groups consists of two lines which are displaced considerably relative to one another. The HFI constants for these radicals differ considerably from one another for both the β-CH_3 groups and the β-CH_2 groups. This means that these groups are nonequivalent: for two of them, the constants a_H are close to

zero, and for the other two the values lie between −0.38 Oe and −0.42 Oe. The mean value of these constants corresponds exactly to the HFI constant for the β-CH_3 protons in radical II. The spatial configurations of the aliphatic rings in radicals III–V are evidently fixed, and the frequencies of the inversion transitions (of the "chair"–"boat", "chair"–"chair" type etc.) are small compared with the difference in the HFI constants of the protons of the non-equivalent β-CH_3 groups. In radical II the frequencies of these inversions are high so that the averaged HFI constant for all the β-CH_3 protons is observed.

A similar picture is observed for the protons of the β-CH_2 groups; here also they are non-equivalent in radicals III–V, but in radical II they are equivalent with a mean value for the HFI constant equal to half the sum of the HFI constants of the non-equivalent protons of the β-CH_2 groups.

These results show that the unpaired electron is delocalised over the angular orbitals, that is, by a hyperconjugation mechanism (at least on the β-carbon atoms). The presence of a π-electron on the C atom in CH_3 was also proved by the EPR method[18]; it was found that the sign of the constant $a_{^{13}C}$ for CH_3 coincides with the sign of the π-electron spin density $\rho^{\pi}_{^{13}C}$ for the same ^{13}C atom. If it is assumed that the signs of a_H and $\rho^{\pi}_{^{13}C}$ coincide (this assumption is justified by EPR spectroscopy), it follows that there is negative π-electron spin density on the β-carbon atoms. It should be noted that at the N atom the spin density is positive and large: $\rho^{\pi}_N \simeq 0.8$.[19] It is at present difficult to resolve unambiguously the problem of the mechanism of the appearance of negative spin density on β-CH_3 and β-CH_2. It is also not clear why $a_H > 0$ at the protons of the γ-CH group, in contrast to the situation for all other protons of the aliphatic ring. One reasonable explanation can be found in the assumption that there is direct spatial overlap of the γ-CH sp^3 hybrid orbitals and the π-orbital of the nitrogen atom; evidence for this is provided by the fact that a_H for γ-CH in radicals III–V is smaller by a factor of almost two than a_H for γ-CH_2 in radical II.

Recently, considerable attention has been paid to the use of the NMR method to study paramagnetic solutions of aromatic hydrocarbons in the presence of alkali metals. The radical-anions formed take part in fast electron exchange with neutral molecules of the aromatic hydrocarbons; the characteristic time of this reaction is the correlation time of the averaged isotropic HFI. The observed paramagnetic shift is similar in character to that in the examples examined above, and the magnitude of the shift is given by Eqn. (5), in the right-hand side of which appears a new factor f_M—the mole fraction of the ion-radicals (see section III for more details).

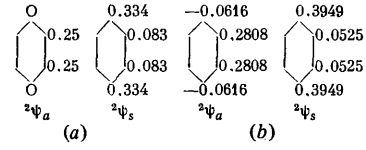
The signs and magnitudes of the isotropic HFI constants on the protons of the alkyl groups in the radical-anions of 1- and 2-alkyl substituted naphthalenes have been determined[20] (Table 5). For the α-protons, the signs of the HFI constants were determined from the NMR spectra, and their absolute values were found from the EPR spectra.

The NMR spectra of the p-xylene and p-diethylbenzene radical-anions[21,22] showed that the spin density on the α-protons of the alkyl groups is negative ($a_{CH_3} = -0.083$ Oe in the p-xylene anion and $a_{CH_2} = -0.050$ Oe in the p-diethylbenzene anion). Calculations show that the isotropic HFI for these protons appears as a result of hyperconjugation. (This can also be seen from the experimental data: the value of a for CH_2 in the p-diethylbenzene anion is less than that for CH_3 in the p-xylene anion—this situation is characteristic of the delocalisation of an electron over the angular orbitals.) This means that the sign of the spin density for CH_3 and CH_2 in these anions is the same as that of the spin density on the carbon atoms to which these groups are attached. This raises the problem of how the negative spin density appears on these carbon atoms.

Table 5. HFI constants at the α-, β-, and γ-protons of the substituents in naphthalene radical-anions.

Substituent	HFI constants × 10^3, Oe				Substituent	HFI constants × 10^3, Oe			
	α	β	γ	δ		α	β	γ	δ
1-CH_3	+3860				2-CH_3	+1810			
1-C_2H_5	+3240	− 74			2-C_2H_5	+1130	+32		
1-n-C_3H_7	+2670	−212	+64		2-n-C_3H_7	+1080	−2	+27	
1-n-C_4H_9	+2800	−155	+45	+35	2-n-C_4H_9	+1050	—	—	+20

The xylene anion can be regarded as a weakly perturbed benzene system. The degeneracy of the ground state of the benzene anion is removed by the perturbing influence of the two CH_3 groups but the splitting between the levels remains very small. EPR studies show that in 1- and 1,4-substituted benzene anions the lowest antibonding orbital is antisymmetric with respect to reflection in a plane perpendicular to the plane of the molecule and passing through the two CH_3 groups. The other orbital, which is symmetric, should have a slightly higher energy. The distribution of the spin density for each of these two orbitals is shown in the scheme below:



(a) (b)

Since the unpaired electron occupies the lowest antisymmetric orbital $^2\psi_a$, its density at carbon atoms 1 and 4 should be equal to zero, so that the HFI splitting for the CH_3 protons should also be equal to zero. Since this splitting is not equal to zero, however, Bolton and coworkers[23] proposed three possible mechanisms which might lead to the observed effect: (a) vibronic or electronic-vibrational interactions between the symmetric and antisymmetric states; (b) thermal excitation, which with increase in temperature increases the spin population of the symmetric state; and (c) configuration interaction between the ground and excited states $^2\psi_a$ and $^2\psi_s$; mechanisms (a) and (b) should make a positive contribution to the HFI constant. Thus mechanism (c) apparently determines the sign of the HFI constant.

For a quantitative estimate of all these contributions, it is necessary to examine the results of the calculation of the spin density at all the carbon atoms in the $^2\psi_a$ and $^2\psi_s$ states[24]. These results [with allowance for the configurational interaction according to mechanism (c) and the inductive influence of the CH_3 groups] are given in scheme (b). If it is assumed that the splitting for the CH_3 in the p-xylene anion is proportional to ρ_1 (or ρ_4) with proportionality constant +25 Oe, the magnitude of this splitting should amount to −1.50 Oe. Experiment gives only −0.1 Oe, that is, the sum of the positive contributions of mechanisms (a) and (b) compensates almost completely

the contribution of mechanism (c). Thus the splitting for CH_3 is almost independent of temperature, if it is assumed that the contribution of mechanism (b) is very small and that the chief part is played by the competing mechanisms (a) and (c).

In the mono-substituted radical-anions of toluene, ethylbenzene, and cumene, the spin density on the α-protons is positive and depends markedly on temperature; this is indicated both by the NMR spectra of the anions and by EPR studies of these anions[22]. Here, the main contribution to the splitting is apparently made by mechanism (b); from the temperature dependence of the splitting at CH_3 in the toluene anion it was found that the energy gap between the $^2\psi_a$ and $^2\psi_s$ states amounts to 2.8 kcal mole^{-1}.[19]

Although the NMR method makes it possible to measure the absolute values of the HFI constants (at fairly small values of ~ 0.1–0.01 Oe), and also in a number of instances to improve the assignment of these constants made from EPR studies of the radicals, its chief role is nevertheless the determination of the signs of the HFI constants. It is for this reason that the NMR method has played an exceptional role in the development of the theory of isotropic HFI and has made an important contribution to ideas regarding the mechanisms of the delocalisation of the unpaired electron in radicals.

II. NMR AND THE SOLVATION OF RADICALS

In the condensed phase, radicals very often form complexes of the donor–acceptor type with molecules of the surrounding medium. This complex formation alters considerably the reactivity of the radicals[25], so that the study of the nature of the electronic interactions in the complex of the radical with the solvent molecules (for the sake of brevity these will subsequently be described arbitrarily as ligands) is of considerable interest. If the molecular orbital of the unpaired electron in the complex also includes the orbitals of the ligand, that is, if the unpaired electron is delocalised over the ligand, an isotropic HFI, whose magnitude and sign are determined by the mechanism of delocalisation of the electron, appears at the magnetic nuclei of the ligand. This HFI of the solvent nuclei can be detected by the NMR method, from the paramagnetic shifts or from the anomalies in the ratios of the nuclear relaxation times T_1/T_2 (single-frequency methods) or from the magnitude and sign of the dynamic polarisation of the nuclei (two-frequency methods). We shall examine briefly all these methods, and we shall analyse the "chemical" information obtained up to the present by these methods.

1. Paramagnetic Shifts of Solvent Nuclei in the Presence of Radicals

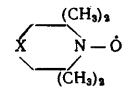
The solvation of paramagnetic species, in particular organic radicals, may be accompanied by delocalisation of the unpaired electron over the molecules of the solvent and the appearance of an isotropic HFI at the nuclei of the solvent. As with radicals, this HFI leads to a paramagnetic shift of the solvent nuclei, whose magnitude and sign are determined by the HFI constants. The only difference from the situation for radicals is in the mechanism of the averaging of the HFI aIS: in radicals, averaging of the spin fraction of the HFI takes place as a result of exchange interaction, but the condition for the observation of paramagnetic shifts of solvents is the modulation of a with a frequency τ_e^{-1} such that $a^2\tau_e^2 \ll 1$; the mechanism of the modulation of a is usually associated with the formation and decomposition of complexes of the radical with solvent molecules. The expression for the paramagnetic shift has the form (its derivation is given in section III):

$$\Delta H = -af(\gamma_e/\gamma_n)(\gamma_e H_0/4kT);$$

$f = nN/N_0$ is the mole fraction of the solvent molecules in the complex with the radicals, N the number of molecules of the radical species, N_0 the number of solvent molecules per unit volume, and n the coordination number of the solvate.

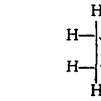
These complexes are essentially ideal models for studying the mechanism of delocalisation of the unpaired electron. Unfortunately, very little work has yet been done on the paramagnetic shifts of solvents in the presence of organic radicals.

Richards and coworkers[26] observed the paramagnetic shift of the fluorine nuclei of C_6F_6 in the presence of tris-t-butylphenoxyl; a_F is positive and amounts to ~ 4 Oe. The paramagnetic shifts of the protons of a series of solvents have been studied in the presence of nitroxide radicals



with X = CH_2, CO, or CHOH [27] (Table 6).

Table 6.

Solvent molecule	HFI constant for the protons, Oe			
	OH	α-CH	β-CH	other protons
H_2O	−0.56			
HOD	−0.56			
$\bar{O}H$	−1.27			
CH_3OH	−0.485	+0.066		
CH_3CH_2OH	−0.363	+0.058	+0.025	
$(CH_3)_2CHOH$	−0.363	+0.044	+0.013	
$(CH_3)_3COH$	—		0.01	
$(CH_2OH)_2$	−0.264	+0.074		
$PhCH_2OH$	−0.52	+0.055		
$CH_2{=}CH{-}CH_2OH$	—	+0.033	+0.055	
CH_3COOH	−0.435		0	
$HCCl_3$				−0.396
H_2CCl_2				−0.088
$(CH_3CH_2)_2NH$		+0.033	+0.018	−0.051
		+0.04		−0.3

The HFI appears at the protons in the molecules of those solvents which take part in donor–acceptor interactions (of the hydrogen bonding type) with the radical (Table 6). Analysis of the HFI shows a number of characteristic features of the delocalisation of the unpaired electron in the solvate complex. Firstly, at the protons forming a hydrogen bond with the paramagnetic centre of the radical, the spin density is always negative. Secondly, at the α- and β-protons the HFI constant is positive and its magnitude decreases along the aliphatic chain. Comparison of the HFI constants for the α- and β-protons in a series of alcohols shows that at the α- and β-carbon atoms the unpaired electron is situated in angular orbitals (apparently quasi-π-orbitals) and it appears in such orbitals by a hyperconjugation mechanism. This mechanism

assumes the presence of positive π-electron spin density on the atomic orbitals of the oxygen or nitrogen in alcohols or amines; this possibly results from direct overlap of the π-orbitals of the radical and the atomic orbitals of the O and N atoms in the complex. The negative spin density on the protons taking part in hydrogen bonding then arises by a spin polarisation mechanism (as in the $\gg$CH fragment). An interesting feature is that in $\overline{\text{O}}$H, where direct overlap of the orbital of the unpaired electron with the orbitals of the O atom should be greater than in other instances, the HFI constant at the H atom is also much greater. At the protons of the amino-group, on the other hand, this constant is very small; here the negative spin density, produced by the spin polarisation mechanism, apparently compensates to a considerable extent the contribution of the positive density from the unpaired electron in the NH orbitals, partly hybridised with the electron pair of the nitrogen†.

2. Single-frequency Relaxation Methods for Studying the Solvation of Radicals

The kinetics of the change in nuclear magnetisation in NMR are usually defined by two kinetic constants: the spin-lattice or longitudinal relaxation time T_1, characterising the rate of the approach of the z component of the nuclear magnetisation to the equilibrium corresponding to the Boltzmann population of the nuclear Zeeman levels, and the transverse relaxation time T_2, determining the rate of the approach of the total x and y components of the magnetisation to zero, that is, the approach to dephasing of the nuclei (z is the direction of the external magnetic field). Physically, longitudinal relaxation corresponds to inversion of the nuclear spins (exchange of energy takes place between the spin system and the lattice). The transverse relaxation is related both to the longitudinal relaxation and to the presence of local magnetic fields which alter the frequency of precession of each spin and lead to dephasing of the nuclei; complete dephasing corresponds to zero values of the x and y components of the magnetisation of the complete spin system.

A physical model of nuclear relaxation in a liquid was proposed by Bloembergen and coworkers[28] as early as 1948. It was based on the fact that the disordered molecular motion of the species in a liquid leads to fluctuations of the local fields produced by the dipole–dipole interaction of the nuclei. A contribution to T_1 is made only by the x and y components of the fluctuating field, whereas contributions to T_2 are made not only by these fluctuations but also by the z components of the local field. The usual method for calculating T_1 and T_2 involves the determination of spectroscopic densities, that is, the Fourier transforms of the correlation functions describing the dipole–dipole interaction modulated by the molecular Brownian motion. T_1 contains the spectroscopic densities $J(\omega)$ and $J(2\omega)$, where ω is the Larmor precession frequency of the nuclei, and T_2 also contains $J(0)$, corresponding to the dephasing of the nuclei in the local fields created by the fluctuating z component.

Nuclear relaxation in the presence of paramagnetic species is described in principle in the same way. The dipole–dipole electron–nuclear interaction operator has the form

$$H' = \gamma_e\gamma_n \frac{ISr^2 - 3(Ir)(Sr)}{r^5}.$$

In polar coordinates, this can be represented in the more explicit form

$$H' = \gamma_e\gamma_n(A+B+C+D+E+F),$$

where γ_e and γ_n are the gyromagnetic ratios of the electron and the nucleus, I and S the spin operators of the nucleus and the electron, r the distance between the electron and the nucleus, and the operators A–F have the forms:

$$A = r^{-3}(1-3\cos^2\theta)I_zS_z,$$
$$B = -\frac{1}{4}r^{-3}(1-3\cos^2\theta)(I_+S_- + S_+I_-),$$
$$C = -\frac{3}{2}r^{-3}\sin\theta\cos\theta\, e^{-i\varphi}(I_zS_+ + I_+S_z),$$
$$D = -\frac{3}{2}r^{-3}\sin\theta\cos\theta\, e^{i\varphi}(I_zS_- + I_-S_z),$$
$$E = -\frac{3}{4}r^{-3}\sin^2\theta e^{-2i\varphi}I_+S_+,$$
$$F = -\frac{3}{4}r^{-3}\sin^2\theta e^{2i\varphi}I_-S_-,$$

where $I_\pm = I_x \pm iI_y$, $S_\pm = S \pm S_x \pm iS_y$, and the spatial parts of the operators are the spherical functions Y_2^0, $Y_2^{\pm1}$, and $Y_2^{\pm2}$. T_1 contains the spectroscopic densities $J(\omega_I - \omega_S)$, $J(\omega_I)$, and $J(\omega_I + \omega_S)$, corresponding to the correlation functions of the operators B, C, and D, and E and F, and T_2 also contains $J(0)$ and $J(\omega_S)$, corresponding to the operators A, C, and D.

Since in liquids with low viscosity the correlation time of the molecular motions τ_C is small (10^{-11}–10^{-12} s), we have $\omega_I^2\tau_C^2 \ll 1$ and $\omega_S^2\tau_C^2 \ll 1$, when all the spectroscopic densities become independent of ω and equal to $J(0)$ and $T_1 \simeq T_2$ (these become equal to the extent to which the inequality $\omega_S^2\tau_C^2 < 1$ is satisfied). This is the case of strong narrowing, when relaxation of the transverse components of the magnetisation takes place only by spin-lattice relaxation. Relaxation in the presence of most paramagnetic ions obeys this theory; equality of T_1 and T_2 is effectively observed.

An anomaly in the ratio T_1/T_2 was first observed for the protons of water in solutions of Mn^{2+} and Gd^{3+} salts, where it was found that $T_1/T_2 > 1$; this phenomenon was subsequently observed in aqueous solutions of a number of other ions.

Bloembergen[29] attributed this anomaly in the ratio T_1/T_2 to the presence of isotropic HFI of the solvent nuclei with the unpaired electron of the paramagnetic species. This interaction may take place in the complex formed by the paramagnetic species with the solvent molecules as a consequence of the finite density of the unpaired electron at the nuclei of the solvent.

The isotropic interaction aIS can be represented by the operator $H'' = aI_zS_z + \frac{1}{2}a(I_+S_- + I_-S_+)$, where the first term, whose spin part corresponds to the spin part of the operator A of the dipole interaction, makes a contribution to $J(0)$ (secular part), and the second term, with spin part similar to the operator B, makes a contribution to $J(\omega_I - \omega_S)$.

For the contribution of the interaction H'' to the relaxation to be significant, it is necessary to have mechanisms leading to time modulation of H''. Two main mechanisms of such modulation can be pictured. Firstly, change in the constant a with correlation time τ_e, which has the significance of the lifetime of the complex formed by the

† The structure of the complexes and the mechanisms of the delocalisation of the unpaired electron in complexes with hydrogen bonding and in π-complexes have been discussed in more detail elsewhere [59].

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solvent molecule with the paramagnetic species; it is assumed that a depends markedly on distance; it is equal to a during the existence of the complex and is equal to zero when the complex decomposes. The relaxation due to this mechanism is called first-order scalar relaxation. Secondly, aIS may be modulated by the longitudinal relaxation of the spin of the electron; the correlation time of the interaction aIS then becomes the electronic relaxation time T_{1e}; this is second-order scalar relaxation. In solutions of organic radicals, T_{1e} is usually large, and the main contribution to the relaxation is made by the modulation of a.[30]

Rigorous examination of both contributions—dipole and isotropic—to the relaxation according to the scheme outlined briefly above gives the following expressions for T_1^{-1} and T_2^{-1} for $\omega_I^2\tau_C^2 \ll 1$:

$$\frac{1}{T_1} = \frac{\gamma_I^2\gamma_S^2\hbar^2 Nn}{10r_0^6 N_0}\left(3\tau_c + \frac{7\tau_c}{1+\omega_S^2\tau_c^2}\right) + \frac{1}{2}\left(\frac{A}{\hbar}\right)^2 \frac{Nn}{N_0}\left(\frac{\tau_e}{1+\omega_S^2\tau_e^2}\right), \quad (6)$$

$$\frac{1}{T_2} = \frac{\gamma_I^2\gamma_S^2\hbar^2 Nn}{20r_0^6 N_0}\left(7\tau_c + \frac{13\tau_c}{1+\omega_S^2\tau_c^2}\right) + \frac{1}{4}\left(\frac{A}{\hbar}\right)^2 \frac{Nn}{N_0}\left(\tau_e + \frac{\tau_e}{1+\omega_S^2\tau_e^2}\right), \quad (7)$$

where τ_C and τ_e are the correlation times of the dipole interaction and the isotropic HFI, N and N_0 the numbers of radical species and solvent molecules in 1 cm³, and n the coordination number of the complex. The first terms in (6) and (7) evidently correspond to the dipole contribution to the relaxation, and the second terms to the contribution of the isotropic HFI. It can also readily be seen that the ratio $T_1/T_2 > 1$ only when the correlation time τ_e is sufficiently large; with this condition, a contribution to T_2 is made by the spectroscopic density $J(0)$ produced by the secular part of the isotropic HFI. In the limit, for $\omega_S^2\tau_e^2 \gg 1$, the second term in T_1^{-1} is equal to zero, and the contribution of this term to T_2^{-1} is $\frac{1}{4}(a/\hbar)^2\frac{Nn}{N_0}\tau_e$.

It is evident that the anomaly in T_1/T_2 is greater, the greater a and τ_e (but τ_e should not be greater than a^{-1}). At small values of τ_e (weak complexes) or in weak fields (ω_S small), we may have $\omega_S^2\tau_e^2 \ll 1$, so that again $T_1/T_2 = 1$; physically, this means that although scalar interaction aIS takes place in the complex, the contribution of the secular terms $J(0)$ in T_2 becomes negligible.

The method involving determination of the ratio T_1/T_2 has found extensive application for the study of the complexes formed by paramagnetic ions with ligands; little work has been done on radicals.

The first paper was published in 1963. Gutowsky and Tai[31] determined T_1 and T_2 for protons in various solvents —chloroform, dioxan, benzene, acetonitrile, water, dichloroethane, tetramethylsilane, and cyclohexane—in the presence of DPPH and the di-t-butylnitroxide radical. T_1^{-1} and T_2^{-1} were linearly dependent on the concentration of radicals, but the ratio T_1/T_2 was found to be constant for all concentrations and equal to 1.1–1.2, that is, its value was very close to unity. For the fluorine nuclei in hexafluorobenzene and 1,3,5-trifluorobenzene, however, T_1/T_2 differed significantly from unity and amounted to 1.40–1.70. These results show that in the complexes formed by fluorine-containing molecules with radicals, the unpaired electron is delocalised over the atomic orbitals of the ligand, the constants of the isotropic HFI at the fluorine nuclei being sufficiently large (10^6–10^7 s^{-1}) to make a secular contribution to T_2. The fact that for the protons $T_1/T_2 \simeq 1$ shows that a_H may be much less than a_F. This makes it very difficult to decide whether the complex has a structure of the π-complex type, or whether there is localised interaction in the complex between the radical and the fluorine atom of the molecule.

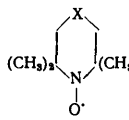
Sagdeev and Molin[32] determined T_1 and T_2 for the protons of biphenyl, naphthalene, nitrobenzene, and nitromethane in the presence of DPPH. They found that the values of T_1/T_2 differ considerably from unity and established a relationship between this deviation and the ionisation potentials of the ligand molecules. Table 7, taken from the work cited[32], illustrates this relationship. The existence of this relationship indicates that there is donor–acceptor interaction in the complexes.

Table 7. Ionisation potentials and HFI constants for protons in the presence of DPPH.

Solvent	T_1/T_2	I, eV	a, s^{-1}	References
Chloroform	1.12	11.42		31
Acetonitrile	1.13	11.96		31
Dichloroethane	1.13	11.1		31
Dioxan	1.15	9.52		31
Benzene	1.16	9.24		31
1,3,5-Trifluorobenzene	1.18	9.15		31
Biphenyl (in CCl_4)	1.42	8.3	$>1.5\cdot10^5$	32
Naphthalene (in CCl_4)	2.15	8.1	$>3.3\cdot10^5$	32
Nitrobenzene	2.3	—	$1.1\cdot10^6$	32
Nitromethane	2.6	—	$3.5\cdot10^6$	32

Paramagnetic shifts were also observed in the last four solvents. The proton lines are displaced to strong fields, that is, there is negative spin density at the protons of the ligands in the complex with DPPH; this is apparently due to a mechanism involving σ–π configurational interaction of the electrons of the C–H bond with the positive spin density of the π-system of the ligand. For CH_3NO_2, the authors cited[32] propose localised interaction of the NO_2 group with the radical, the O–N–O group being similar to the allyl group: the π-electron spin density is positive at the oxygen atoms, and negative at the nitrogen atom; on the CH_3 group the spin density appears as a result of hyperconjugation with the unpaired electron of nitrogen and has the same sign. The HFI constants determined from the magnitudes of the paramagnetic shifts using Eqn. (5) are given in Table 7.

A number of studies have been carried out in solutions of stable nitroxide radicals of the type



The formation of complexes by radicals of this type with the molecules of water, alcohols, and acetic acid was observed by the EPR method[33]; it was shown that a hydrogen bond is formed between the radical and the solvent molecules with the participation of the unpaired electron. The energy of this bond amounts to 2–4 kcal mole^{-1} and the coordination number of the complex is $n = 1$.

The relaxation times of the protons of water in the presence of the nitroxide radical with X = CO have been measured[34]. The ratios T_1/T_2 for various concentrations of the radical are given in Table 8.

At low concentrations of the radicals, T_1/T_2 is much greater than unity, that is, the unpaired electron has a

finite density at the protons of the water molecules taking part in hydrogen bonding with the radicals.

Using the value $a = -0.56$ Oe obtained from the paramagnetic shifts (see p. 804) and $T_1/T_2 = 1.5$, we readily obtain the correlation time $\tau_e = 3 \times 10^{-10}$ s.

Table 8.

Concentration of radical, M	T_1/T_2	Concentration of radical, M	T_1/T_2
$5 \cdot 10^{-3}$	1.7	$5 \cdot 10^{-3}$	1.5
$7.5 \cdot 10^{-3}$	1.5	$7.5 \cdot 10^{-2}$	1.2
10^{-2}	1.6	10^{-1}	1.1
$2.5 \cdot 10^{-2}$	1.5	1.0	1.0

An interesting feature is that at high concentrations of the radical, when the frequency of electron exchange becomes equal to $\sim 10^{10}$ s^{-1}, the ratio T_1/T_2 gradually decreases and reaches unity at a concentration of 1 M. This behaviour of T_1/T_2 can be attributed to the fact that at high frequencies of exchange ω_{ex}, τ_{ex} becomes the correlation time of the isotropic HFI, and if $\tau_{ex} < \tau_e$, $\omega_S^2\tau_{ex}^2$ decreases with increase in concentration; as a result, there is a decrease in the contribution of the secular terms in T_2. This fact provides further proof of the manifestation of HFI at the protons of water in the complex with the radical; it also confirms that τ_e at concentrations in the region of 0.5 M (when the concentration dependence of T_2^{-1} begins to deviate from linearity) is comparable with τ_{ex}, that is, $\tau_e \simeq 10^{-10}$ s^{-1}; this shows good agreement with the value of τ_e calculated above from the values of the paramagnetic shift and the ratio T_1/T_2.

In the presence of the nitroxide radical with X = CH_2 (1 M) the ratio T_1/T_2 for the hydroxyl proton of methanol amounts to 1.23;[35] here, we should apparently observe the same picture as in aqueous solutions of the radicals.

A very interesting paper on the solvation of paramagnetic oxygen molecules in water and alcohols was recently published[36]. Only the dependence of T_1 for the protons in the pure solvents and in solutions saturated with oxygen on the field intensity (or ω_S) was measured. In pure water, T_1 was independent of ω_S; this means that $\omega_S^2\tau_C^2 \ll 1$, that is, the condition for strong narrowing is satisfied. In the presence of dissolved oxygen, T_1 depended on ω_S; this means that in the expression for T_1^{-1} there appears a second term which takes account of the contribution of the isotropic HFI, with correlation time $\tau_e < \tau_C$ and with $\omega_S^2\tau_S^2$ comparable with unity. It can readily be shown that for this example Eqn. (6) can be reduced to the form

$$T_1^{-1} = \alpha\tau_c + B\frac{\tau_e}{1+\omega_S^2\tau_e^2},$$

where α and B are constants, and τ_e and $\alpha\tau_C$ can readily be found by combining the expressions for T^{-1} with different ω_S values. For the complexes formed by oxygen with water molecules, the bond energy, determined from the temperature dependence of τ_e, was found to be 2.5 kcal mole^{-1}; τ_e is of the order of 10^{-11} s. In methanol, the dependence of T_1 on ω_S is very weak, that is, either the complexes formed by oxygen with the alcohol are weak (τ_e is small) or the constant a in the complex is small.

Thus the results of this work provide an elegant and convincing proof of the existence of complexes of oxygen with water molecules, in which there is delocalisation of the unpaired electrons of the oxygen over the atomic orbitals of the ligand.

The work examined above on the study of solvation using the ratio T_1/T_2 essentially exhausts the range of work carried out by this method in solutions of organic radicals. A disadvantage of this method is that it gives no information on the sign of the HFI constant in the complex; its advantage over methods which use measurement of paramagnetic shifts lies in the possibility of determining the kinetic characteristics of the complex—the correlation time τ_e and its temperature coefficient. Thus the two methods effectively supplement one another and give extensive information on the mechanism of the delocalisation of the unpaired electron in a complex; this is illustrated by the work examined above.

3. Dynamic Polarisation of Nuclei (Two-frequency Methods)

If we have two interacting spin systems—for example, electronic and nuclear—a change in the state of one spin system (at one resonance frequency) produces a change in the state of the other spin system; this change is detected at another resonance frequency. This is the essential feature of two-frequency methods of studying nuclear-nuclear and electronic-nuclear interactions. If we have a dipole interaction in an electron–nucleus system placed in a magnetic field, the component operators may bring about different transitions with a simultaneous change in the orientation of the electronic and nuclear spins, that is, with a change in the characteristic values of the z components of the spin of the electron M and the nucleus m. It can readily be seen from the form of the operator B that it brings about transitions $\Delta M = -\Delta m = \pm 1$ (flip-flop transitions), when there is simultaneous inversion of the electronic and nuclear spins in opposite directions. The operators C and D bring about transitions with $\Delta(M + m) = \pm 1$ (ordinary transitions of the electron or nucleus between their Zeeman levels), and the operators E and F induce transitions $\Delta M = \Delta m = \pm 1$ (flip-flip transitions) with simultaneous inversion of the spins of the electron and the nucleus in the same direction[37].

The Zeeman levels for the particular case of an electron and a proton and the populations of these levels are illustrated in Fig. 3 (it must be noted that for the electron $\gamma_e < 0$ and for the proton $\gamma_n > 0$); we have $N_-/N_+ = \exp(\hbar\gamma_e H/kT)$ and $n_+/n_- = \exp(\hbar\gamma_n H/kT)$.

With saturation of the electronic transitions there is an increase in the number of electron relaxation acts $+1/2 \rightarrow -1/2$; if only flip-flop transitions take place, the nuclear spins undergo inversion in the opposite direction $-1/2 \rightarrow +1/2$, that is, the population of the lower Zeeman level of the nuclear spin system increases sharply, with a corresponding increase in the NMR signal. For complete saturation of the electronic transitions $N_+ = N_-$ and $n_+/n_- = \exp(\hbar\gamma_e H/kT)$, that is, the populations of the nuclear states obey the Boltzmann relationship, but with the Boltzmann factor $\exp(\hbar\gamma_e H/kT)$ instead of $\exp(\hbar\gamma_n H/kT)$, which is observed for statistical equilibrium in the absence of EPR saturation. This means that for complete EPR saturation the effective gyromagnetic ratio of the nucleus γ_n is equal to the gyromagnetic ratio of the electron γ_e. This phenomenon of positive dynamic polarisation of nuclei for EPR saturation is known as the Overhauser effect. It is used in physics as a method of obtaining polarised

nuclei; in chemistry the Overhauser effect is important as a method of studying the nature and mechanism of electron–nuclear interactions in radicals and their complexes with ligands.

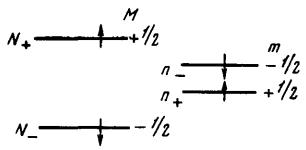


Figure 3. Scheme illustrating the Zeeman levels of the electron and the proton.

If only flip-flip transitions take place, the sign of the nuclear polarisation becomes negative. EPR saturation is then accompanied by an increase in the population of the upper Zeeman level of the nuclear spin system; relaxation of the nuclear spin is accompanied by the emission of the nuclear Zeeman frequency. This negative dynamic polarisation of nuclei is used in the production of microwave generators and amplifiers, or masers.

If we take account of all the transitions and solve the kinetic equations for the populations of the nuclear and electronic Zeeman levels, we obtain an equation relating the nuclear magnetisation $\langle I_z \rangle$ and the electronic magnetisation $\langle S_z \rangle$

$$\frac{\langle dI_z \rangle}{dt} = -\frac{1}{T_1^{II}}(\langle I_z \rangle - I_0) - \frac{1}{T_1^{IS}}(\langle S_z \rangle - S_0)$$

where I_0 and S_0 are the equilibrium values of $\langle I_z \rangle$ and $\langle S_z \rangle$ (in the absence of saturation); the constants T_1^{II} and T_1^{IS} are determined by the spectroscopic densities $J(\omega_I - \omega_S)$, $J(\omega_I)$, $J(\omega_I + \omega_S)$, and $J(\omega_I - \omega_S)$, $J(\omega_I + \omega_S)$ respectively. It can be seen from the equation that the polarisations of the spins I and S are related in such a way that a radiofrequency field with, for example, frequency ω_S, acting on $\langle S_z \rangle$, will also alter $\langle I_z \rangle$. Under steady-state conditions, $d\langle I_z \rangle / dt = 0$ and $\langle I_z \rangle - I_0 = \rho(\langle S_z \rangle - S_0)$, where $\rho = T_1^{IS}/T_1^{II}$.[30] The constant ρ is expressed in terms of the probabilities p, q, and r of the transitions produced by the operators B, C, D, E, and F respectively:

$$\rho = \frac{r - p}{r + 2q + p}.$$

The probabilities p, q, and r are calculated in the usual way via the correlation functions and spectroscopic densities. With the condition of strong narrowing, which is almost always satisfied in liquids, $p : q : r = 2 : 2 : 12$, so that $\rho = -1/2$, that is, for dipole–dipole interaction of the nuclei of the solvent with the unpaired electrons of the paramagnetic species we have negative dynamic polarisation of the nuclei.

The isotropic HFI operator produces only flip–flop transitions and if a contribution to the relaxation is made only by the isotropic HFI, we have $q = r = 0$ and $\rho = -1$, that is, in this instance there is positive polarisation, whose absolute magnitude is twice that of the negative polarisation corresponding to dipole–dipole interaction.

If both interactions make a contribution to the relaxation, ρ is a complex function of these contributions. Complete calculation of the spectroscopic densities for these interactions for $\omega_S^2 \tau_C^2 \ll 1$ leads to the following expression for ρ:[30]

$$\rho = \frac{1 - \tau_e/\sigma\tau_c\,(1 + \omega_s^2\tau_e^2)}{2 + \tau_e/\sigma\tau_c\,(1 + \omega_s^2\tau_e^2)}, \qquad (8)$$

where $\sigma = \hbar^2\gamma_n^2\gamma_e^2/r^6a^2$. It is clear that the magnitude and sign of the constant ρ contains all the "chemical" information regarding the nature of the interaction of the radical with the solvent molecules; it is usually determined experimentally from the dependence of the degree of polarisation on the level of EPR saturation (details can be found in a paper by Richards and White[38]). The magnitude and sign of ρ depend on many parameters—the magnetic field intensity, the isotropic HFI constant, viscosity, and temperature (via τ_C and τ_e).

Positive nuclear polarisation for protons was previously observed only in solutions of the alkali metals in ammonia ($\rho = -1$), in which the strongly solvated electron gives high values of a on the protons[39]. Recently, positive polarisation was observed on the protons of the t-butyl groups in tris-t-butylphenol in the presence of its radical tris-t-butylphenoxyl[40]. In the opinion of the authors cited[40], this is related to the fact that positive polarisation of these protons takes place in the radical, in which, as already noted (section I) there is considerable isotropic HFI at these protons. As a result of the exchange reaction of the radical with the phenol (see below), this polarisation appears in the phenol, and if the characteristic time of the reaction is less than the relaxation time of the protons in the molecule, this polarisation is preserved in the phenol and is detected.

An interesting feature is that in contrast to the situation for the protons of the t-butyl groups, the polarisation of the *meta*-protons in the same radical is negative, although the HFI on these protons is large ($a_H = 1.7$ Oe). This means that the contribution of the scalar relaxation is small, since there is no effective mechanism for the modulation of a (the corresponding spectroscopic densities are small).

This fact is of considerable interest in connection with the problem of the mechanism of delocalisation of the unpaired electron in the orbitals of the CH_3 groups in tris-t-butylphenoxyl. Since a necessary condition for positive polarisation is modulation of the HFI constant, and a mechanism for this modulation may be provided by internal rotation in the t-butyl groups, this means that the unpaired electron is delocalised in the t-butyl groups over the angular orbitals, that is, by a hyperconjugation mechanism. These considerations are also confirmed by data on the dynamic polarisation of ^{13}C nuclei (natural concentration) in the t-butyl groups of this radical—the sign of the polarisation is positive[41]‡.

In the presence of organic radicals it has been possible to observe the contribution of the isotropic HFI only in the polarisation of the fluorine nuclei in fluorine-containing solvents. Thus in solutions of DPPH in 1,3,5-trifluorobenzene[42], $\rho = 0.37$ (at the fluorine nuclei), that is, $-1 < \rho < 1/2$, indicating a contribution by the isotropic HFI to the polarisation of the fluorine nuclei.

‡ In principle, polarisation may be induced by the same mechanism by chemical reactions taking place with the formation of radicals. This was recently confirmed experimentally[60,61]. This is an extremely promising development from the viewpoint of kinetics and mechanism, and also in connection with the possibility of creating a "chemical" maser.

In fluorobenzene in the presence of DPPH, ρ has a value equal to approximately zero at 20°C, that is, the contributions of the dipole–dipole and isotropic interactions to the dynamic polarisation of fluorine are almost identical; with increase in temperature, however, the contribution of the isotropic interaction decreases, that is ρ increases[42]. This means that the temperature dependence of the correlation time τ_e is more marked than that for τ_c.

Eqn. (8) can be written

$$\rho = \frac{1-\alpha}{2+\alpha},$$

where

$$\alpha = \frac{\tau_e}{\sigma\tau_c}(1+\omega_s^2\tau_e^2)^{-1}$$

and

$$\ln\alpha = \ln\frac{\tau_e^0}{\sigma\tau_c^0} + \frac{\varepsilon_e-\varepsilon_c}{RT} - \ln(1+\omega_s^2\tau_e^2).$$

This equation was used by the authors cited[42] to calculate ϵ_e from the dependence of α on $1/T$; it shows satisfactory agreement with experiment. Using the value of ϵ_c found by Gutowsky and Tai[31] (ϵ_c = 2.5 kcal mole^{-1}), the authors cited[42] found that the energy of the bond in the complex formed by DPPH with fluorobenzene amounts to 3.3 kcal mole^{-1}.

Richards and coworkers[26,43] observed positive nuclear polarisation of fluorine in a number of fluorine-containing solvents—C_6F_6, *p*-difluorobenzene, CF_3–CCl_3, $CFCl_2$–CF_2Cl, fluorine-containing alcohols, perfluoroacetone, and hexafluoroethane—in the presence of DPPH, tris-t-butylphenoxyl, and semiquinone radicals. This shows that in the complexes formed by the fluorine-containing molecules with the radical there is strong isotropic HFI, associated with the appearance of spin density on the fluorine nuclei of the ligand.

The dynamic polarisation of ^{31}P nuclei in phosphites and phosphates in the presence of tris-t-butylphenoxyl was recently studied[44]; the sign of the polarisation is positive, that is, the radical also forms complexes with phosphorus-containing esters, in which the isotropic HFI at the phosphorus nucleus is large. The polarisation is greater in phosphites than in phosphates. The authors cited attribute this to the fact that in the phosphites the phosphorus atom has a free $3s^2$ pair, so that there is an increase in the isotropic HFI in the complex.

A large number of papers have been devoted to the dynamic polarisation of protons in the presence of organic radicals, but they are of slightly less interest from the viewpoint of "chemical" information. In most instances in these systems $\rho = 1/2$, that is, the main contribution to the polarisation is made by dipole–dipole interactions. These papers, however, contain a large amount of information on the correlation times τ_c and ϵ_c, characterising the intensity of the molecular Brownian movement in various liquids; this is of considerable interest for the kinetic theory of liquids[45,46].

Until now we have been considering those two-frequency methods in which EPR saturation at microwave frequency has led to changes in the populations of the Zeeman levels of the nuclear spin system and these changes have been detected at the NMR radiofrequency. At the present time, increasing use is being made of another version of the two-frequency method—electron–nuclear double resonance—for the study of organic radicals. The essential features are as follows. For saturation with a microwave frequency, the EPR signal decreases. If the radiofrequency is now altered slowly, it is found that at values corresponding to the resonance of a given type of nuclei, by flip–flop or flip–flip transitions, a change takes place in the populations of the electronic Zeeman levels and the EPR signal at this frequency also changes (it increases or decreases to a greater extent, depending on which transitions play the most important role). Thus in this instance detection takes place at the microwave frequency, and the NMR radiofrequency is used as a probe for the electron–nuclear interaction. This method, discovered by Feher[47], has been used successfully for a considerable time to study the structure of paramagnetic centres in crystals; only a few papers[48,49] have been devoted to the study of organic radicals in liquids. A significant advantage of double resonance is the considerable simplification of the EPR spectra and the high accuracy of the determination of the HFI constants. For example, in triphenylmethyl, which contains three kinds of magnetically non-equivalent hydrogen nuclei, the EPR spectrum consists of 196 lines of hyperfine structure, whereas the double resonance spectrum contains only six lines[49]; the double resonance spectrum of triphenylphenoxyl contains seven lines instead of 4050.[50] The most valuable feature of double resonance in radicals in single crystals, however, is that it makes it possible to determine the absolute signs of the hyperfine interaction constants. An example is provided by the determination of the signs of the HFI constants on the β-protons in the radical HOOC–$\dot{C}$H–CH_2COOH.[51]

III. NMR AND THE KINETICS OF RADICAL REACTIONS

In recent years the theory has been developed and NMR has been successfully applied, for the study of the kinetics of radical reactions, in particular electron exchange and radical substitution taking place with transfer of a hydrogen atom. The attractions of the NMR method for these purposes include not only the possibility of studying fast reactions (with rate constants of 10^8–10^9 litre mole^{-1} s^{-1}) but also, and this is most significant, the fact that this method makes it possible to study the kinetics of reactions taking place with zero heat change, that is, elementary reactions with the same initial and final states; it is extremely difficult to study the kinetics of these reactions by classical methods, although it is these reactions which are of greatest interest for the theory of reactivity. Another extremely important aspect is that it becomes possible in principle to study electronic interactions in the activated complex.

The use of the method is based on the broadening of the NMR signals from the nuclei in the molecules which are taking part in the exchange of electrons or hydrogen atoms:

$$P + D \overset{k}{\rightleftarrows} D + P \qquad (9)$$

where P is the paramagnetic species (ion or radical), and D is the diamagnetic ion or molecule. Each elementary act of this reaction leads to a change in the magnetic field acting on the resonance nuclei of the corresponding molecules, since as a result of this reaction these nuclei are found at one moment in the paramagnetic species, when they are acted on by the field of the unpaired electron, and at another moment in the diamagnetic molecule. Thus the nuclei are acted on by paramagnetic "pulses" whose intensity and frequency influence the shape and width of the NMR lines. To study the kinetics of these reactions it is possible to use the line width for any nucleus of a molecule taking part in the reaction, where there is an isotropic HFI.

In general, for reaction (9), an expression for the paramagnetic broadening of the NMR lines can be obtained either by solving Bloch's kinetic equations for the magnetisation or by means of relaxation matrices [52]

$$\Delta T_2^{-1} = \frac{f_P \tau_P a^2/4}{1 + f_D \tau_P^2 a^2/4 + 2\tau_P T_{1e}^{-1}}, \quad (10)$$

where ΔT_2^{-1} is the paramagnetic broadening; $\Delta T_2^{-1} = T_{2,PD}^{-1} - T_{2,D}^{-1}$, where $T_{2,PD}^{-1}$ and $T_{2,D}^{-1}$ are the widths of the NMR lines in the presence and absence of the paramagnetic species P; f_P and f_D the mole fractions of P and D; τ_P the lifetime of the paramagnetic species; T_{1e} the electronic longitudinal relaxation time; and a the isotropic HFI constant at the nuclei whose resonance is observed. Experimentally, it is possible to realise conditions under which Eqn. (10) is simplified. Two cases are known, described by the terms "strong pulse" and "weak pulse".

Let us examine the first—the strong pulse. For this to be realised, the following conditions are necessary.

Firstly, the lifetime of the paramagnetic species should be much shorter than the lifetime of the diamagnetic species, that is, $\tau_P \ll \tau_D$. Since $\tau_D = 1/k(P)$, and $\tau_P = 1/k(D)$, this condition requires that $(P) \ll (D)$; this is readily satisfied, and $f_D \simeq 1$.

Secondly, it is necessary that $\tau_P^2 a^2 \gg 1$. Since the frequency of precession of the nucleus in the field of the unpaired electron is equal to $a/2$, this nucleus comes out of phase with the other nuclei in the molecule D, if the paramagnetic "pulse" lasts longer than one period corresponding to the precession frequency a, that is, if $\tau_P \gg 1/a$. This means that either a or τ_P should be sufficiently large for the nuclei to come completely out of phase during the period for which the unpaired electron is in the molecule; the paramagnetic broadening on the nuclei will be the same and independent of a. For the same reason it is necessary that the electronic relaxation time or electronic exchange time $T_{1e} \gg 1/a$, that is, $T_{1e}^2 a^2 \gg 1$, so that all the nuclei are able to come out of phase before the electron alters its orientation. In this instance neither relaxation of the electron spin nor electron exchange influence the broadening. The last two conditions can be combined into one, namely, $a^2\tau^2 \gg 1$, where $1/\tau = 1/\tau_P + 1/T_e$. For the "strong pulse" case, the transverse relaxation time is determined essentially by τ_D, since $\tau_D \gg \tau_P$ and when time τ_D has elapsed (after D is converted into P) the nuclei come out of phase almost immediately. Since $a^2\tau^2 \gg 1$, the experimental criterion for realisation of the "strong pulse" case is preservation of the hyperfine structure of the EPR spectrum of the paramagnetic species.

The condition $a^2\tau^2 \gg 1$ may be satisfied, although the hyperfine structure is not observed, if $T_{1e} > T_{2e}$, where T_{1e} and T_{2e} are the longitudinal and transverse electronic relaxation times. This is due to the fact that the width of the EPR lines, determined by T_{2e}, may become greater than the splitting.

When these conditions are satisfied, Eqn. (10) becomes

$$\Delta T_2^{-1} = k(P)(D) \quad (11)$$

by means of which k can readily be found from the magnitude of the broadening and the known concentrations (P) and (D). Since the condition $\tau_P^2 a^2 \gg 1$ is most readily satisfied for large values of τ_P or small values of k, the "strong pulse" case corresponds to a slow reaction. This was first analysed by McConnell [53].

Let us now consider the second case—the "weak pulse" case—which is realised under the following conditions.

Firstly, as before, $\tau_D \gg \tau_P$. Secondly, $\tau_P^2 a^2 \ll 1$ or $\tau_P \ll 1/a$, that is, the lifetime of the paramagnetic species, during which the nuclei are exposed to the local field of the unpaired electron, is less than the period of the Larmor precession of the nucleus in this field, leading to its averaging and the production of a paramagnetic shift. A result of the reaction is modulation of the HFI constant and the consequent scalar relaxation, described above.

Here, a necessary condition is that $\tau_P \ll T_{1e}$, for if $\tau_P \gg T_{1e}$ the correlation time of the isotropic HFI becomes the electron spin relaxation time T_{1e}, which is not related to the reaction and the study of the kinetics of the reaction itself becomes meaningless.

If $T_{1e} \simeq \tau_P$, it is necessary to know T_{1e} in order to study the kinetics of the reaction. Since in time τ_P the nuclei with different values for the isotropic HFI constant a_i are able to come out of phase to different extents, the paramagnetic broadening is not the same for all nuclei and is determined by the quantity a_i^2. In this instance, $f_D\tau_P^2 a^2/4 + 2\tau_P T_{1e}^{-1} \ll 1$ and Eqn. (10) becomes

$$\Delta T_2^{-1} = \frac{1}{4}\frac{(P)}{(D)^2} a^2 k^{-1}, \quad (12)$$

from which it is possible to find k if we know a at the nuclei whose resonance is being observed. In contrast to the previous case, the broadening decreases with increase in temperature, since it is inversely proportional to the rate constant k. The condition $\tau_P^2 a^2 \ll 1$ is readily satisfied at small values of τ_P, that is, at large values of k, so that these conditions correspond to fast reaction or fast exchange; it was examined first by Bloembergen [29].

These are the conditions and chief characteristic features of the two extreme limits, which might be described respectively as the limits of deep low-frequency modulation and superficial high-frequency modulation.

The paramagnetic shift produced by reaction (9) has the form

$$\Delta H = -af_P(\gamma_e/\gamma_n)(\gamma_e H/4kT)\left(1 + \frac{f_D\tau_P^2 a^2}{4}\right). \quad (13)$$

For $\tau_P^2 a^2 \ll 1$ ("weak pulse")

$$\Delta H = -af_P(\gamma_e/\gamma_n)(\gamma_e H/4kT), \quad (14)$$

which coincides with the expression for the paramagnetic shift in polycrystalline radicals, where $f_P = 1$, Eqn. (5). Eqn. (14) is also used to determine the constants a from the paramagnetic shifts of a solvent in the presence of radicals forming complexes with the solvent (see section II).

The first report of the use of NMR in the kinetics of organic reactions appeared in 1956. Bruce and coworkers [54] measured the rate constant for electron transfer from tetramethyl-*p*-phenylenediamine to the corresponding Wurster's radical-cation in acetic acid at pH 3.2. In the presence of Wurster's cation, the NMR lines of the solvent (water, acetate ion) undergo very little broadening, whereas the lines of the ring and methyl protons of the reacting diamine undergo broadening equally strongly and in proportion to the concentration of the cation; this shows that the "strong pulse" case is realised, and the constant calculated from Eqn. (11) was found to be 2.5×10^4 litre mole^{-1} s^{-1}.

The kinetics of this reaction were recently studied in detail by the NMR method over a wide pH range in D_2O. [55] The original amine was taken in the form of its dihydrochloride, so that the reaction mixture contained equilibrium quantities of the dihydrochloride, the monohydrochloride, and the free base. The broadening of the lines was the same for the methyl and ring protons of the amine ("strong pulse"). The rate constants showed a marked dependence on pH, decreasing with decrease in pH; this

shows that the tendency to take part in electron transfer differs considerably for the base (the amine) and its salts (the mono- and di-hydrochlorides). If it is assumed that only the free base takes part in electron exchange with the cation-radical, it is possible to calculate the true rate constant for this bimolecular reaction; it was found that over the wide pH range 2.7–6.1, this constant does in fact remain constant and is equal to $(1.5 \pm 0.7) \times 10^8$ litre mole^{-1} s^{-1} at 20°C.

The conclusion that only the free base takes part in electron transfer is also confirmed by data obtained by Johnson[56], who studied the same reaction in acetonitrile, with all the amine in the form of the base. In contrast to the earlier work, where the "strong pulse" case was realised, the broadening of the methyl and ring protons of the amine in acetonitrile was found to be proportional to the square of the HFI constants at these protons (6.76 Oe and 1.97 Oe), and the rate constant determined from Eqn. (12) amounted to $\sim 2 \times 10^8$ litre mole^{-1} s^{-1}; this agrees with the true rate constant determined in the previous paper. Thus in acetonitrile, in which electron exchange takes place rapidly, the "weak pulse" case is realised. A similar difference in the broadening of the NMR lines of different protons was observed in diethyl-*p*-phenylenediamine in aprotonic solvents, and also in the di-cations of ethyl- and methyl-viologen in the presence of their paramagnetic mono-cations; here, the fast exchange case ("weak pulse") applies throughout[56].

An interesting example was observed in a study of the kinetics of electron transfer in *p*-xylene[21] in the presence of its anion-radicals, obtained by the reaction of *p*-xylene with potassium. Since the HFI constants *a* for the ring and methyl protons in the anion differ considerably (5.34 Oe and 0.08 Oe respectively), both cases are realised in electron exchange—"strong pulse" for the ring protons and "weak pulse" for the methyl protons. The broadening of the ring protons increases with increase in temperature, whereas the broadening of the methyl protons decreases—in accordance with Eqns. (11) and (12). For this particular case, Johnson[56] proposed a method for determining *k*, which does not require a knowledge of the concentration of paramagnetic species P. In actual fact, by combining Eqns. (11) and (12) for the broadening of the lines for different protons, one can immediately obtain *k* and the concentration of paramagnetic species (P).

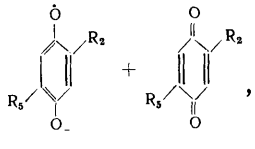
The following expression was obtained for the rate constant for electron transfer in the system formed by *p*-xylene and the *p*-xylene anion[21]:

$$k = 10^{12} \exp(-6200/RT) \text{ litre mole}^{-1} \text{ s}^{-1}.$$

These constants are much smaller than the constants obtained for the same reaction in the absence of potassium (when the anions are obtained by electrolysis). This shows that the constants given above relate to the slower exchange of *p*-xylene with an ion pair:

$$P^-K^+ + D \rightleftarrows D + P^-K^+ .$$

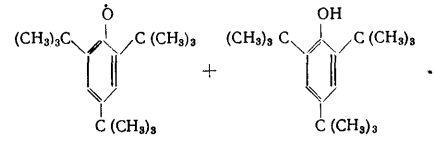
The rate constants for electron transfer in the quinone–semiquinone system



where $R_2 = -CH(CH_3)_2$ or $-OC_2H_5$, and $R_5 = H$ or OC_2H_5, were found to be close to 10^8 litre mole^{-1} s^{-1}.

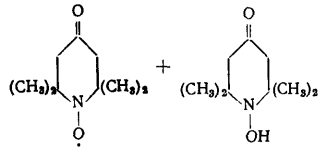
An anomalous ratio $T_1/T_2 > 100$ is observed at the α-proton in $-CH(CH_3)_2$ and at the methylene protons in $-OC_2H_5$; this anomaly may appear for the "weak pulse" case; the correlation time of the isotropic HFI—Eqn. (7)—becomes τ_P.[57]

Radical substitutions have been the subject of only one paper, by Kreilick and Weissman[58], who studied the kinetics of hydrogen atom transfer from tris-t-butylphenol to tris-t-butylphenoxyl:



The reaction was carried out in CCl_4 in the presence of $Si(CH_3)_4$ as internal standard. The NMR of a solution of the phenol in CCl_4 gives four lines: two from the protons of the non-equivalent *o*- and *p*-t-butyl groups and two from the *meta*-protons and the hydroxyl proton. With increase in the concentration of the radical, the lines for the t-butyl and *meta*-protons broaden to equal extents, in proportion to the concentration of radicals ("strong pulse"). The correction for the dipole–dipole electron–nuclear broadening was determined from the broadening of the tetramethylsilane protons; this correction was very small. The constant *k*, determined from Eqn. (11), amounted to 300 litre mole^{-1} s^{-1} at 30°C, and the activation energy for the reaction was 1.0 ± 0.5 kcal mole^{-1}.

In the paper cited, the correction for the dipole–dipole broadening was introduced wrongly (this is pointed out by the authors themselves), since the correlation time τ_C of the dipole–dipole interaction of the tetramethylsilane and phenol protons with the unpaired electron of the radical should be different. In our study of the same reaction[59], the dipole–dipole correction was determined from the broadening of the lines of tris-t-butylbenzene, for which τ_C should be very close to τ_C for tris-t-butylphenol; the constant *k* at 25°C was found to be 400 litre mole^{-1} s^{-1}, which is very close to the constant obtained by Kreilick and Weissman. Moreover, we determined the rate constant for the analogous reaction



from the broadening of the lines of the methyl protons: $k = 130$ litre mole^{-1} s^{-1} at 25°C; here the dipole–dipole correction was determined from the broadening of the lines of the methyl protons of the corresponding amine.

The behaviour of the NMR line of the hydroxyl proton is of greatest interest, since as a result of each act of the reaction, the initial and final states of this proton remain unchanged: it always remains in a diamagnetic molecule, with the exception of the activated complex. For the broadening of its NMR line we can use Eqn. (10), in which $f_P = f_{act}$—the mole fraction of the activated complexes; it can readily be shown that $f_{act} = k(P)\tau_{act}$—also τ_P becomes the lifetime of the activated complex τ_{act}, and *a* is equal to the HFI constant in this complex a_{act}. Then for $\tau_{act} T_1^{-1} \ll 1$ we have

$$\Delta T_2^{-1} = k(P) \frac{\tau_{act}^2 a_{act}^2/4}{1 + \tau_{act}^2 a_{act}^2/4} . \qquad (15)$$

In the paper by Kreilick and Weissman, this equation was used to determine τ_{act} with arbitrary assumptions regarding the magnitude of a_{act} (20 Oe). These estimates of τ_{act} ($\sim 10^{-9}$ s) are hardly meaningful; it is more appropriate to determine a_{act} by giving τ_{act} a definite reasonable value.

There are, of course, fundamental difficulties in this approach. It is necessary first of all that the rate constant k be sufficiently high (fast reactions). Moreover, the formation of the activated complex may be preceded by the formation of ordinary donor–acceptor complexes (for example, by hydrogen bonding), so that a contribution to ΔT_2^{-1} will be made not only by states close to the top of the potential barrier for the reaction but also by these donor–acceptor complexes (this situation apparently was observed in the work of Kreilick and Weissman[58]). Moreover, formula (15) does not take account of the anisotropic HFI, although this interaction itself will produce additional broadening in states lying close to the top of the barrier. All these features make it difficult at present to determine the HFI constants in an activated complex.

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