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Magnetic Effects in Chemical Reactions

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The Review discusses in what elementary chemical reactions the intrinsic angular momentum of electrons and nuclei is conserved and in what reactions it is not conserved, how weak electron-nuclear magnetic interaction and an external magnetic field influence the conservation of angular momentum and what are the consequences of this effect, and what magnetic effects occur in chemical reactions, as well as the conditions for their development and detection. Conditions are formulated for the non-conservation of the intrinsic angular momentum of electrons and nuclei in chemical reactions. The bibliography contains 36 references.

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I. INTRODUCTION

Chemical processes, i.e. transformations of some molecules into others, are always accompanied by regrouping of nuclei and rearrangement of electron shells. The most important characteristic of such transformations is their energy. In the analysis of chemical processes and the reactivity of reactant species, therefore, it is right to pay maximum attention to the energy aspect. However, it must always be borne in mind that electrons and many nuclei possess intrinsic angular momenta, and the laws of their conservation can exert a marked influence on the direction of chemical reactions and hence on their energetics. Wigner's rule on the conservation of the total electron spin of a reactant system was formulated comparatively long ago, but it is not always satisfied.

The angular momentum of electrons and nuclei is conserved in elementary chemical reactions involving substitution, dissociation, recombination, addition, disproportionation, and electron transfer. If, however, long-lived states, in which transitions are possible between states differing in spin multiplicity, are established in chemical reactions, the angular momentum of electrons and nuclei is not conserved. This leads to the remarkable consequences of magnetic effects in chemical reactions, the

most striking of which—chemical polarisation of nuclei, enrichment of magnetic isotopes in chemical reactions, and the effect of a magnetic field on the rates of chemical reactions—are discussed in the present Review.

II. ORIGIN OF MAGNETIC EFFECTS

In most molecules the intrinsic angular momenta (spins) of the electrons balance: i.e. the electrons are coupled. Chemical reactions may take place either without change of spin in the electron-pairs or with uncoupling of the electrons. In the former case the spins in the electron-pairs remain balanced; in the latter case unbalanced individual electron spins appear. The former reactions are classified chemically as heterolytic, and the latter as homolytic or radical.

Magnetic effects must obviously be sought in reactions of the second type, because they involve the production of magnetic moments of electrons, which interact strongly among themselves, with the magnetic moments of the nuclei, and with external magnetic fields. Under certain conditions all these interactions lead to non-conservation of the electronic and the nuclear spin of the reactant system, to the appearance of magnetic effects in chemical reactions. We shall now consider what these effects are and under what conditions they develop.

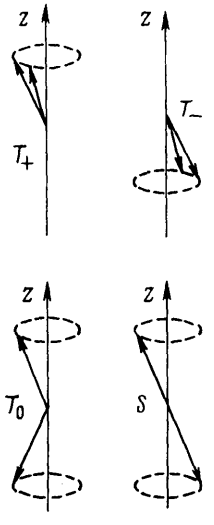


Figure 1. Orientation and precession of electron spins of a radical-pair in an external magnetic field in the z-direction.

In order to understand the origin of magnetic effects in radical reactions it is sufficient to consider as model a simple radical-pair ($HR^{1}\cdot$, $R^{2}\cdot$) in which one radical $HR^{1}\cdot$ contains only one magnetic nucleus (the proton), while the other radical $R^{2}\cdot$ has none. Let the g-factor of the first radical be g_1, and that of the second radical g_2: i.e. the Zeeman energies of the electrons of these radicals in a magnetic field H are $g_1\beta H$ and $g_2\beta H$. We suppose that hyperfine magnetic interaction between electron and proton also occurs in the radical $HR^{1}\cdot$, its energy being am, where $m = \pm\frac{1}{2}$ is the projection of the spin of the proton in the direction of the external magnetic field and a is the electron–proton hyperfine interaction constant. Finally, non-magnetic exchange interaction J occurs between the unpaired electrons of the radical-pair; it forms part of the electrostatic interaction, and is distinguished from the usual Coulombic interaction only in its dependence on the electron spin. Exchange electrostatic forces which depend on the spin of the electrons must be postulated in order to satisfy one of the fundamental principles of quantum mechanics—the Pauli principle.

The spins of the two unpaired electrons in a radical-pair may be oriented in such a way that their vectors must be either added or subtracted, to give a total spin of either unity or zero. Because of the occurrence of exchange interaction the energies of these two states are not the same but differ by the amount J. The state with zero spin is a singlet (S); the state with unit electron spin is termed a triplet (T), since the total electron spin may be oriented in a magnetic field in three different ways with projections of +1, 0, and −1 for the total spin vector in the field direction. These three substates T_+, T_0, and T_- differ in their Zeeman energies, which are respectively $g\beta H$, 0, and $-g\beta H$, where $g = \frac{1}{2}(g_1 + g_2)$. The scheme of orientation of electron spins in a radical-pair is shown in Fig. 1, and the energy levels of the states corresponding to these orientations are indicated in Fig. 2.

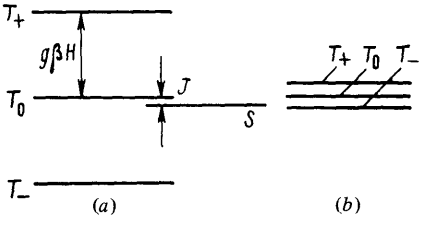


Figure 2. Energy levels of a radical-pair in a magnetic field: *a*) strong; *b*) weak.

We shall now suppose that the radical-pair is in a triplet state. Such a pair must undergo a transition to a singlet state before it is able to recombine to give the reaction product. Thus the probability of recombination (or disproportionation), with the formation of molecular products having zero total electron spin, is proportional to the probability of triplet–singlet transition. The latter probability is proportional to the square of the matrix element calculated from the spin wave functions of state S and T and the spin Hamiltonian $\mathcal{H}$ of the pair:

$$p_{T\text{-}S} \sim |\langle T|\mathcal{H}|S\rangle|^2. \qquad (1)$$

The Hamiltonian $\mathcal{H}$ defines the interactions of electrons and nuclei in the pair:

$$\mathcal{H} = \beta H(g_1S_1 + g_2S_2) - J(^1/_2 + 2S_1S_2) + aIS_1, \qquad (2)$$

where the first term represents the Zeeman interaction of the electrons, the second term the exchange interaction, the third term the hyperfine interaction between electron

and proton in the $HR^{1\cdot}$ radical, S_1 and S_2 are the spins of the first and second electrons, and I is the spin of the proton. The matrix element for the transition T_0–S is

$$\langle T_0|\mathcal{H}|S\rangle = {}^1/_2(\Delta g\beta H + am) \qquad (3)$$

in which $\Delta g = g_1 - g_2$ and $m = \pm\frac{1}{2}$ (for the proton). The matrix elements for transition from states T_+ and T_- to state S are

$$\langle T_+(-{}^1/_2)|\mathcal{H}|S(+{}^1/_2)\rangle = -({}^1/_8)^{1/_2}a, \qquad (4)$$

$$\langle T_-(+{}^1/_2)|\mathcal{H}|S(-{}^1/_2)\rangle = ({}^1/_8)^{1/_2}a. \qquad (5)$$

(The procedure for calculating such matrix elements will be found in greater detail in Ref. 1).

The expressions $(\pm\frac{1}{2})$ in Eqns. (4) and (5) denote the projections of the spin of the proton; triplet–singlet transitions from states T_+ and T_- are obviously allowed only in the presence of hyperfine electron–nuclear interaction, and are necessarily accompanied by reorientation of the nuclear spin: $T_+(-\frac{1}{2}) \rightarrow S(+\frac{1}{2})$ and $T_-(\frac{1}{2}) \rightarrow S(-\frac{1}{2})$. Thus it is important for transitions from T_+ and T_- states to the S state that hyperfine interaction should involve a single electron–nucleus system; the change in electron spin accompanying the triplet–singlet transition will then be balanced by a change in the nuclear spin.

Thus a triplet–singlet transition is accompanied by a change in the total electron spin and is therefore forbidden. However, if the unpaired electrons attached to the components of a radical-pair differ in their Zeeman energy and if hyperfine interaction links electronic and nuclear spin systems, the prohibition on such a transition is partly removed. This partial elimination of spin prohibitions is the cause of the magnetic effects.

Before analysing magnetic effects we note that the mean exchange interaction is small in radical-pairs in a liquid, and the exchange energy can be neglected (proofs of this statement will be given later). Therefore in strong magnetic fields, when the Zeeman energy $g\beta H$ is large, the T_+ and T_- levels are remote from S, and the main contribution to triplet–singlet mixing is made by transitions between contiguous T_0 and S levels. In weak magnetic fields $g\beta H$ is small, all three levels T_+, T_0, and T_- are situated close to the level of the singlet state, and transitions from all the triplet substates are important for triplet–singlet mixing (Fig. 2). We shall now enumerate the principal magnetic effects.

(i) It follows from Eqns. (3)–(5) that the probability of triplet–singlet transitions and hence the probability of reaction depend on the nuclear spin of the radical. As a consequence the recombination products are enriched (or impoverished) in nuclear spins of a certain orientation: i.e. a non-equilibrium population of Zeeman nuclear levels is produced in the reaction products. Such non-equilibrium population or pumping of Zeeman levels results in a non-equilibrium orientation or polarisation of nuclei in the molecules generated from the radical-pairs. This phenomenon of chemically induced magnetic polarisation of nuclei was discovered by Fischer and Bargon and independently by Ward and Lawler in 1967, and has become widely known[2,3].

(ii) It follows also from Eqns. (3)–(5) that the probability of recombination depends on the hyperfine electron–nuclear interaction energy. Isotope effects should be observed in the rates of recombination of the components of radical-pairs, since the nuclei of isotopes possess different magnetic moments and hence have different hyperfine interaction constants.

(iii) The dependence of the probability of recombination of radicals on the hyperfine interaction energy (or on the magnetic moment of the nuclei) makes possible the selection and enrichment of magnetic isotopes in chemical reactions. This effect is purely magnetic in origin, so that a method of isotope enrichment that can be based on it differs fundamentally from other methods (e.g. the selective dissociation of chemical bonds by laser illumination, which utilises the isotope effect on vibration frequencies due to the difference in mass between isotopes[4]).

(iv) Another consequence of Eqn. (3) is that the probability of recombination of the radicals forming a pair depends on the strength of the external magnetic field (provided that the radicals have different g-factors, i.e. that $\Delta g \neq 0$). This gives rise to quite definite and soundly based ideas on the causes and the physical mechanisms of the influence of an external magnetic field on the direction and the rates of chemical reactions. In the case of radical reactions a magnetic field affects the rate of triplet–singlet conversion and changes the probability of recombination. This mechanism is readily generalised to cover any reactions involving species in higher spin states, with a larger number of unpaired electrons (e.g. iron and copper ions, molecular oxygen, etc.). In such cases the magnetic field also influences the probabilities of intersystem transitions between states differing in spin multiplicity (doublets, triplets, quartets, quintets, etc.) in reactant-pairs, and consequently changes the probabilities of chemical reactions.

Each of these four effects will be discussed further. Before proceeding to their detailed analysis, however, we can usefully extend the key equations (3)–(5) to cover any pair of radicals with any number of nuclei. The spin Hamiltonian of such a generalised pair is

$$\mathcal{H} = \beta H(g_1S_1 + g_2S_2) - J({}^1/_2 + 2S_1S_2) + \sum_i a_iS_1I_i + \sum_j a_jS_2I_j \quad , \qquad (6)$$

where I_i is the spin of the ith type of nucleus in the first radical, I_j is the spin of the jth type of nucleus in the second radical, and a_i and a_j are the corresponding hyperfine interaction constants. The matrix element of triplet–singlet mixing for a transition from the T_0 state is

$$\langle T_0|\mathcal{H}|S\rangle = {}^1/_2\left(\Delta g\beta H + \sum_i a_im_i^a - \sum_j a_jm_j^b\right), \qquad (7)$$

where the m_i^a are the projections of nuclear spins of the ith kind in the first radical, the m_j^b are the projections of nuclear spins of the jth kind in the second radical, and the summation covers all nuclei in both radicals. The three terms in Eqn. (7) are respectively the difference in the Zeeman energies of the electrons, the sum of the hyperfine interaction energies in the first radical, and the corresponding sum in the second radical of the pair. The matrix elements of triplet–singlet mixing from states T_+ and T_- are

$$\langle T_+, m_i - 1|\mathcal{H}|S, m_i\rangle = -({}^1/_8)^{1/_2}a_i[I_i(I_i+1) - m_i(m_i-1)], \qquad (8)$$

$$\langle T_-, m_i + 1|\mathcal{H}|S, m_i\rangle = ({}^1/_8)^{1/_2}a_i[I_i(I_i+1) - m_i(m_i+1)]. \qquad (9)$$

As with the model one-proton radical-pair (Eqns. 4 and 5), triplet–singlet transitions from states T_+ and T_- are obviously allowed only in the presence of hyperfine electron–nuclear interaction, and are accompanied by reorientation of the nuclear spin of the ith kind: in a T–S transition the nuclear spin increases ($m_i - 1 \rightarrow m_i$); in a T_-–S transition the nuclear spin diminishes ($m + 1 \rightarrow m_i$).

The probabilities of all these transitions are proportional to the squares of the matrix elements (7)–(9). It is readily seen that Eqns. (3)–(5) are particular cases of the general equations (7)–(9): they are obtained with $m_i = \pm\frac{1}{2}$, i.e. for a one-proton radical-pair.

III. CHEMICAL POLARISATION OF NUCLEI

1. Physical Mechanisms of the Chemical Polarisation of Nuclei

The chemical polarisation of nuclei has acquired great popularity, with accounts of its theory and chemical applications in several books and reviews[2,3,5-7]. For this reason only a brief discussion will appear here of the evolution of ideas in this field, of the current state of the theory, and of chemical applications of the phenomenon.

We shall first discuss the mechanisms by which nuclear polarisation is produced. As noted above, the main contribution to triplet–singlet conversion of a radical pair is made in strong magnetic fields by transitions from the T_0 state. Equation (3) shows that, if $\Delta g > 0$ and $a > 0$, the probability of triplet–singlet transition is greater in a radical-pair having $m = +\frac{1}{2}$ than in a pair having $m = -\frac{1}{2}$. This means that pairs having a proton oriented in the direction of the field undergo triplet–singlet conversion more rapidly and hence recombine more rapidly: i.e. the products of recombination (or disproportionation) are enriched with positively polarised nuclei. On the other hand, radicals that have avoided recombination in the radical-pair and have escaped into space contain an excess of protons oriented against the field, and these radicals confer on their conversion products a negative nuclear polarisation. Thus T_0–S transitions in radical-pairs involve a selection of radicals according to their nuclear spins: chemical reactions lead to selection, to a sorting of radicals (and hence of molecules produced from them) according to their nuclear-spin states.

It is readily seen that, if the sign of Δg or a is changed in Eqn. (3), the sign of the nuclear polarisation also changes. For the same reason the sign of the polarisation is reversed if the precursor of the molecules is not a triplet but a singlet pair, when the reverse singlet–triplet conversion of the pair takes place. It is easy to predict from Eqn. (3) the sign of the chemical polarisation of nuclei as a function of those of Δg and a and the spin state of the radical-pair. Kaptein[8] suggested for this the convenient form

$$\Gamma = \mu\varepsilon\,\Delta g a \qquad (10)$$

known as Kaptein's rule, in which $\mu = +1$ if the precursor of the molecule is a triplet pair, $\mu = -1$ if the precursor is a singlet pair, $\epsilon = +1$ for a product of recombination or disproportionation, $\epsilon = -1$ for conversion products of radicals outside a pair, Δg and a determine the signs of these quantities $\Gamma > 0$ corresponds to positive polarisation (A, absorption in the nuclear magnetic resonance spectra by molecules having polarised nuclei), and $\Gamma < 0$ corresponds to negative polarisation (E, emission in the n.m.r. spectra).

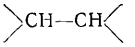
Integral polarisation of a given group of nuclei arises only when $\Delta g \neq 0$. If $\Delta g = 0$, an unusual type of polarisation often appears, which is characteristic of groups of nuclei having spin–spin interaction. In this case the components of the spin multiplet, appearing at high and low fields, correspond to polarisation of different signs; this type of polarisation is termed the multiplet effect or multiplet polarisation.

It is easy to show that multiplet polarisation is produced by the same mechanism as is integral polarisation, i.e. by the dependence of the rate of triplet–singlet transitions in radical-pairs on the nuclear spin of the radicals. Let us consider a simple pair of radicals

each of which contains one proton; the pair is initially in a triplet state, and also has $\Delta g = 0$. Equation (7) then simplifies to

$$\langle T_\bullet | \mathcal{H} | S \rangle = {}^1/_2 (a_1 m^a - a_2 m^b). \qquad (11)$$

If $a_1 < 0$ and $a_2 < 0$, pairs having proton orientations $m^a = \frac{1}{2}$, $m^b = -\frac{1}{2}$ and $m^a = -\frac{1}{2}$, $m^b = \frac{1}{2}$ will obviously pass into the singlet state more rapidly, so that



molecules, in which the two protons have opposite spin orientations, will predominate in the product of recombination. The scheme of population of nuclear-spin levels in such a molecule is shown in Fig. 3, where the arrows denote n.m.r. transitions, which lead to a multiplet effect AE (the components of the spin multiplet correspond to positive polarisation at low field, and to negative polarisation at high field).

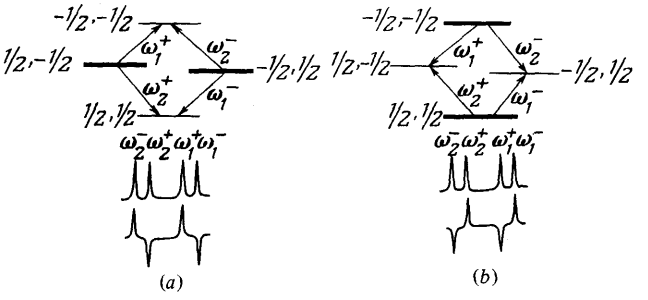


Figure 3. Multiplet effect in a fragment >CH–CH< of a molecule generated from a triplet pair: *a*) AE; *b*) EA.

It is readily seen from Eqn. (11) also that, if the sign of one of the hyperfine interaction constants is changed (e.g. $a_1 > 0$, $a_2 < 0$), the populations of the levels and the sign of the multiplet effect are changed (Fig. 3*b*). These properties are readily predicted from Eqn. (7) for any case. A convenient formula for such prediction was proposed by Kaptein[8]:

$$\Gamma_{ME} = \mu\varepsilon a_i a_j J_{nn} \sigma_{ij}, \qquad (12)$$

where μ and ϵ have the same significance as in (10), a_i and a_j are hyperfine interaction constants, J_{nn} is the spin–spin interaction constant of the nuclei in the molecule (only the signs of these quantities are important here), $\sigma_{ij} = 1$ if the nuclei i and j are present in the same radical

of the pair, and $\sigma_{ij} = -1$ if they belong to different radicals. The multiplet effect has the sign of EA when $\Gamma_{ME} > 0$, and that of AE when $\Gamma_{ME} < 0$.

Thus Eqns. (3) and (7) define the signs of the integral and multiplet polarisation produced in strong fields when transitions from the T_0 state are mainly responsible for the triplet–singlet conversion of the pair. These equations have been obtained by quantum-mechanical calculation. It is not difficult to show that the same result—the dependence of the rate of triplet–singlet conversion on the nuclear spin—can be obtained from classical physics.

We shall demonstrate this on the model one-proton pair ($HR^{1}\cdot$, $R^{2}\cdot$). The orientations of the electron spin vectors of the pair are indicated in Fig. 1. These vectors are known to precess about the z-axis (the direction of the external magnetic field). In order that the transition $T_0 \rightarrow S$ should occur the vectors must be "unwound" relative to each other by 180°: i.e. it is necessary that the difference of phase in the precession of the two electrons should be π. The frequency of precession of the first electron is $g_1\beta H \pm \frac{1}{2}a$ depending on whether the spin of the proton is directed with or against the field. That of the second electron is $g_2\beta H$. The corresponding frequency differences between the two electrons are $\Delta g\beta H \pm \frac{1}{2}a$. In order that the transition $T_0 \rightarrow S$ should take place it is necessary that

$$(\Delta g\beta H + {}^1/_2 a)\, t_\alpha = \pi \text{ (proton with the field)}$$
$$(\Delta g\beta H - {}^1/_2 a)\, t_\beta = \pi \text{ (proton against the field)},$$

where t_α and t_β are the transition times in a pair having nuclear spins α and β. If Δg and a have the same sign, we obviously obtain $t_\alpha < t_\beta$: i.e. radical-pairs in which the proton is oriented in the direction of the field pass into the singlet state and recombine more rapidly. The triplet–singlet conversion of pairs in which the proton is oriented against the field lags behind, and such pairs have a greater chance of dissociating. The result is the selection of radicals according to nuclear-spin states—in agreement with the quantum-mechanical equations (3) and (7).

From the classical picture of a triplet–singlet conversion it is not difficult to estimate the conversion time

$$t_{T_0 \text{-} S} \simeq (\Delta g\beta H + am)^{-1}$$

for a one-proton pair, or in general

$$t_{T_0 \text{-} S} \simeq \left(\Delta g\beta H + \sum_i a_i m_i^a - \sum_j a_j m_j^b\right)^{-1} \quad . \tag{13}$$

With the usual values of the g-factors and the hyperfine interaction constants in organic radicals this time amounts to $\sim 10^{-9}$–10^{-8} s.

In weak magnetic fields the contribution by T_0–S transitions to the integral polarisation becomes negligible, because the difference $\Delta g\beta H$ between the Zeeman energies is small in weak fields. This is accompanied by increased contributions to the polarisation by T_+–S and T_-–S transitions, which entail reorientation of nuclear spins—in conformity with Eqns. (4), (5) and (8), (9).

In contrast to T_0–S transitions, in which the z-component (projection) of the total electron spin remains unchanged, so that the nuclei do not change their orientation, T_+–S and T_-–S transition are accompanied by a change in the z-component of the electron spin and reorientation of the nuclear spins. In fact, T_0–S transitions in radical-pairs involve merely a sorting-out of nuclear spins according to orientation, whereas in T_+–S transitions a fresh orientation of the nuclei is established. For this reason the chemically induced polarisation of nuclei shows considerable differences between weak and strong magnetic fields (for greater detail see Refs. 2, 3, 5, and 6).

2. Main Stages in the Development of the Chemical Polarisation of Nuclei

The discovery of the phenomenon itself must be regarded as the first stage in the development of the chemical polarisation of nuclei; as already stated above, it was made simultaneously and independently by two groups of investigators. It is surprising that this occurred accidentally in both cases: the actual investigations in which the new phenomenon was discovered were on an extremely trivial plane, which is quite instructive from a methodological point of view.

The first attempt to explain the phenomenon in terms of the Overhauser effect was unsuccessful. The four chief experimental criteria of the chemical polarisation of nuclei—the dependence of polarisation on the type of chemical reaction, establishment of the phenomenon in the products of cage recombination, unusually large polarisation coefficients, and finally the multiplet effect—do not fit into the framework of the Overhauser effect.

The second stage began in 1969, when Kaptein and Oosterhoff[9] and independently Closs[10] almost simultaneously suggested that chemical polarisation of nuclei appeared in radical-pairs on triplet–singlet transitions, whose probability depends on the nuclear spin. This idea and the qualitative explanation of the phenomenon based on it have been examined above. We shall now consider the quantitative theory of the chemical polarisation of nuclei.

The probability that a molecule will be formed in the nuclear spin state ab is the integral of the product of three probabilities:

$$P_{ab} = \int_0^\infty \varepsilon\, |c_{S,ab}(t)|^2\, \mathrm{f}(t)\, \mathrm{d}t \quad . \tag{14}$$

Here $|c_{S,ab}(t)|^2$ is the probability that the pair will pass into a singlet state by time t (if the initial state of the pair were a triplet) or remain in the singlet state by this time (if the initial state of the pair were a singlet), i.e. the probability that the pair will be by time t in a singlet state and will be ready for recombination. The function $\mathrm{f}(t)$ represents the lifetime distribution of the pairs: $\mathrm{f}(t)dt$ is the probability that the pair will survive to time t and be destroyed by time $t + dt$. The coefficient ϵ denotes the probability that a pair that has survived from time t and is by then in a singlet state, i.e. completely prepared for recombination, will finally recombine (or disporportionate).

The quantity $|c_{S,ab}(t)|^2$ is obtained by solving the time-dependent Schrödinger equation with the time-independent Hamiltonian of the pair (6). It is supposed that only the spin functions of the pair vary with time, these being produced by the superposition of the wave functions of singlet and triplet states. The quantity $c_{S,ab}(t)$ is essentially a coefficient of the singlet component of the spin function of the pair, and its square a contaminant of the singlet state. If the pair were initially in a triplet state, in strong magnetic fields we have

$$|c^T_{S,ab}(t)|^2 = (\mathscr{H}^2_{ab}/D^2_{ab}) \sin^2 D_{ab} t, \tag{15}$$

where

$$\mathscr{H}_{ab} = \langle T_0 | \mathscr{H} | S \rangle = \frac{1}{2}\left(\Delta g\beta H + \sum_i a_i m_i^a - \sum_j a_j m_j^b\right) \tag{16}$$

is a matrix element of T_0–S mixing (Eqn. 7) and

$$D_{ab} = (\mathcal{H}_{ab}^2 + J^2)^{1/2} . \quad (17)$$

If the initial state of the pair is a singlet, then

$$|c_{S,ab}^S(t)|^2 = \frac{1}{n} - \frac{\mathcal{H}_{ab}^2}{D_{ab}^2} \sin^2 D_{ab} . \quad (18)$$

The subscript ab denotes the nuclear spin state of the pair, where a and b represent the sets of nuclear spins of the first and second radicals respectively and n is the total number of nuclear spin states of the radical-pair (and of the molecule generated from the pair). Equation (18) is obtained from the condition for normalisation: the total probability of finding the pair in the nuclear spin state ab is $1/n$, independently of whether the pair exists at the given moment in a singlet or a triplet state.

The theory was originally based on a static model of the pair, in which

$$f(t) = \frac{1}{\tau} \exp(-t/\tau), \quad (19)$$

where τ is the lifetime of the radical-pair. From Eqn. (14) together with (15) and (19) we find that the probability of formation of a molecule in the nuclear spin state ab from a triplet pair is in this case

$$P_{ab} = 2\varepsilon\mathcal{H}_{ab}^2\tau^2/(1 + 4D_{ab}^2\tau^2). \quad (20)$$

This quantity is essentially the population of the state ab in the molecule: the coefficient of nuclear polarisation in the transition ab–$a'b'$ is the difference between those of states ab and $a'b'$ related to the equilibrium, Boltzmann difference between the populations of these states. Similarly, it is easy to calculate the populations in molecules generated from singlet pairs, by substituting Eqns. (18) and (19) in (14), a variant known as the Closs–Kaptein–Oosterhoff theory.

With reasonable lifetimes $\tau \simeq 10^{-12}$–10^{-11} s for the pairs this theory gave calculated polarisations that were too small. Experimental values far exceeded those predicted theoretically (examples of calculations will be found in Ref. 4). The reason for such a discrepancy is obvious: as shown above (§III, 1) the duration of a triplet–singlet transition is 10^{-9}–10^{-8} s, in comparison with which the lifetime of a pair is too short and insufficient for triplet–singlet conversion of the pair and the accompanying selection of radicals according to nuclear spins.

The third stage in the development of the theory of the chemical polarisation of nuclei was initiated by the publications of Adrian [11-13], who suggested a dynamic model of a radical-pair, in which the radicals are able to diffuse into space, diverge, and again return to the initial pair after completing diffusion migrations. The probability of return gradually diminishes with increase in length of the diffusion path, so that the probability of the radicals meeting again decreases with increase in this length and hence in the duration of diffusion. However, a longer path entails a longer time of triplet–singlet evolution and hence greater efficiency of selection of radicals according to nuclear spins. In the dynamic model

$$f(t) = mt^{-3/2} \quad (21)$$

a function used by Noyes [14] to interpret the kinetics of liquid-phase reactions. It has recently received direct experimental support from flash photolysis in the picosecond range [15].

From Eqns. (21) and (14) we find that the population of the nuclear spin state ab in a molecule generated from a triplet pair is

$$P_{ab}^T = \pi^{1/2}\varepsilon m(\mathcal{H}_{ab}/D_{ab})^2 |D_{ab}|^{1/2} . \quad (22)$$

In order to calculate the population in a molecule generated from a singlet pair we must bear in mind that the majority of the pairs recombine immediately after formation (primary recombination), and radicals separate only from the remaining pairs, diffusing away, returning, and again meeting (secondary recombination). Only pairs that have undergone secondary recombination are subject to singlet–triplet evolution, and only in them is nuclear polarisation produced. For the population of the nuclear spin state ab in a molecule generated from a singlet pair we can therefore write

$$P_{ab}^S = \frac{\alpha}{n} + (1-\alpha)\int_0^\infty \varepsilon |c_{S,ab}^S(t)|^2 f(t)\,dt . \quad (23)$$

The first term in (23) represents the probability of primary recombination, and the second term the population produced in pairs that have undergone secondary recombination. It is noteworthy that α and ϵ are similar in physical meaning and probably in magnitude (~0.5–0.8); the slight difference between them is that α relates to a primary pair, in which the radicals may be separated by foreign molecules (e.g. in the decomposition of acyl peroxides $R^1CO.O.O.CO.R^2$ a CO_2 molecule separates the pair of radicals $R^1\cdot$ and $R^2COO\cdot$), whereas ϵ defines the probability of recombination in a contact pair. Substituting (18) in (23), we obtain the population

$$P_{ab}^S = \frac{\alpha}{n} + (1-\alpha)\left[\frac{1}{n}\int_0^\infty \varepsilon f(t)\,dt - \pi^{1/2}\varepsilon m(\mathcal{H}_{ab}/D_{ab})^2 |D_{ab}|^{1/2}\right] . \quad (24)$$

The first two terms are not well defined, but this has no significance, since only the difference between the populations is important for calculating the polarisation, and these terms do not enter into this difference.

If a molecule is produced by chance encounters of independently generated radicals, its precursor is a pair whose initial state may equally probably have been singlet or triplet T_0 (such pairs are said to be uncorrelated). Some of the singlet pairs undergo primary recombination, and the remainder singlet–triplet evolution and secondary recombination. All those pairs that have been in a T_0 state undergo the reverse, triplet–singlet evolution. The nuclear polarisation produced in these pairs is the net result of such complicated evolution and can be calculated without difficulty [3] (for uncorrelated pairs $\epsilon = \alpha$).

The introduction of a dynamic model of a pair into the chemical polarisation of nuclei immediately solved several theoretical difficulties. Quantitative agreement between theory and experiment improved markedly. The physically unreal model of a static pair, in which the radicals were fixed at a definite distance for an unnaturally long time, became unnecessary. Quantitative calculations were simplified, for it became clear that the greatest contribution to the polarisation was made by long diffusion paths with the long time required for successful T–S evolution. It is on such paths that the radicals diverge far apart, so that the exchange energy of the electrons J can be neglected with good approximation. It is easily seen that Eqns. (22) and (24) then simplify to

$$P_{ab}^T = \pi^{1/2}\varepsilon m |\mathcal{H}_{ab}|^{1/2} , \quad (25)$$

$$P_{ab}^S = \frac{\alpha}{n} + \frac{(1-\alpha)}{n}\int_0^\infty \varepsilon f(t)\,dt - (1-\alpha)P_{ab}^T . \quad (26)$$

It immediately became possible to dispense with (which was entirely justified physically) a fairly inconvenient and indeterminate theoretical parameter.

Even with a dynamic model of the pair, however, difficulties remained in the theory of the chemical polarisation of nuclei. Firstly, the function $f(t)$ does not take into account the finite lifetime of the radicals (more correctly, it assumes that the radicals exist for an indefinite time). Secondly, theory does not reproduce the dependence of the polarisation on the magnetic interaction energy: it predicts that the polarisation will be proportional to $|\mathcal{H}_{ab}|^{\frac{1}{2}}$—see Eqns. (25) and (26)—whereas proportionality both to $|\mathcal{H}_{ab}|^{\frac{1}{2}}$ and to $\mathcal{H}^2_{ab}$ has been found experimentally. The overcoming of these difficulties constituted the fourth stage in the development of the chemical polarisation of nuclei, which characterises the current state of the theory.

3. Current State of the Theory

In order to correct defects in the dynamic model of a pair the modified function

$$f(t) = m^{-3/2} \exp(-t/\tau) \tag{27}$$

has been suggested[16,17], where τ is the characteristic lifetime of the radical, the time of its conversion into another radical (by decomposition or substitution), as a result of which the initial pair disappears and is replaced by a new pair. The function $f(t)$ in the form (27) describes an exponential distribution of diffusion paths with respect to length (and duration).

Substituting (27) in (14) and calculating the difference between the populations of the nuclear spin states ab and $a'b'$ in a molecule generated from a triplet pair, we obtain

$$P^T_{ab} - P^T_{a'b'} = \pi^{1/2}\varepsilon m \left\{ [(2\mathcal{H}_{ab})^2 + \tau^{-2}]^{1/4} \cos\frac{\arctan(2\mathcal{H}_{ab}\tau)}{2} - [(2\mathcal{H}_{a'b'})^2 + \tau^{-2}]^{1/4} \cos\frac{\arctan(2\mathcal{H}_{a'b'}\tau)}{2} \right\} = X(\tau) \ . \tag{28}$$

It can readily be shown that in the two limiting cases—short-lived radicals ($\tau \ll \mathcal{H}^{-1}_{ab}, \mathcal{H}^{-1}_{a'b'}$) and long-lived radicals ($\tau \gg \mathcal{H}^{-1}_{ab}, \mathcal{H}^{-1}_{a'b'}$)—Eqn. (28) leads to the formulae

$$P^T_{ab} - P^T_{a'b'} = \pi^{1/2}\varepsilon m\tau^{3/2}(\mathcal{H}^2_{ab} - \mathcal{H}^2_{a'b'}) \ , \tag{29}$$

$$P^T_{ab} - P^T_{a'b'} = \pi^{1/2}\varepsilon m (|\mathcal{H}_{ab}|^{1/2} - |\mathcal{H}_{a'b'}|^{1/2}) \ . \tag{30}$$

Thus with short-lived radicals the polarisation is proportional to the difference between the squares of the matrix elements of triplet–singlet mixing (as in the static model). With long-lived radicals the polarisation is proportional to the difference between the square roots of the matrix elements (as in Adrian's dynamic model). Hence Eqn. (28) is a general expression for the difference in populations, from which the equations of the Closs–Kaptein–Oosterhoff and Adrian theories are obtained as particular, asymptotic solutions.

Nor is it difficult to deduce expressions for the difference between the populations of nuclear spin states in a molecule generated from a singlet pair or from an uncorrelated pair:

$$P^S_{ab} - P^S_{a'b'} = -(1-\alpha)X(\tau) \tag{31}$$

$$P^U_{ab} - P^U_{a'b'} = {}^1/_2\alpha X(\tau) \ , \tag{32}$$

where $X(\tau)$ has been given by Eqn. (28). It follows also from these equations that the polarisation of molecules generated from triplet and uncorrelated pairs has the same sign but is opposite to the polarisation of molecules from a singlet pair (in agreement with earlier, qualitative predictions). The polarisations from these pairs are in the proportions $1 : \frac{1}{2}\alpha : -(1-\alpha)$ and depend on the probability of primary recombination; in particular, when $\alpha = 0.8$ the proportions are $1 : 0.4 : -0.2$.

An important stage in the development of the chemical polarisation of nuclei and its application to chemistry and chemical kinetics was the establishment of a kinetic theory linking the kinetics of the polarisation with that of chemical reactions[4,18]. The principal equation is

$$\frac{dI}{dt} = E\frac{dI_0}{dt} - \beta(I - I_0), \tag{33}$$

where I is the nuclear magnetisation (or n.m.r. signal) during the reaction and I_0 is the corresponding equilibrium magnetisation (or equilibrium n.m.r. signal). The first term defines the rate of chemical pumping, the rate of establishment of polarisation; while the second term is the rate of its destruction, the rate of relaxation of the non-equilibrium magnetisation to its equilibrium value $\beta = T_{1n}^{-1}$, in which T_{1n} is the nuclear relaxation time in the molecule. Solutions describing the kinetics of chemical reactions occurring under various régimes were obtained from Eqn. (33).[4] The kinetic parameters of the reaction, the nuclear relaxation times, and the polarisation coefficient E could be obtained by comparison with experiment.

This last parameter is of especial interest for the theory; it shows the factor by which the non-equilibrium nuclear polarisation of a molecule at the instant of its generation from a radical-pair exceeds its equilibrium, Boltzmann polarisation (in particular, $E = 1$ for molecules having the equilibrium polarisation). In other words, the coefficient of nuclear polarisation is the ratio of the non-equilibrium difference in population of nuclear spin states to its equilibrium value:

$$E = \langle P_{ab} - P_{a'b'}\rangle / (P^0_{ab} - P^0_{a'b'}) \ , \tag{34}$$

where

$$P^0_{ab} - P^0_{a'b'} = p^0_n = \tanh\frac{\hbar\gamma_n H}{2kT} \ .$$

The coefficient E is determined experimentally from the kinetics of the chemical polarisation of nuclei and applies to a molecule, a molecular group, or a certain nuclear spin transition between states ab and $a'b'$ in the molecule. Populations are calculated and normalised per single radical-pair. In order to determine the polarisation parameters from experimental polarisation coefficients E, therefore, the relation between the coefficient and the populations of nuclear spin states must be established.

Molecules for which the polarisation coefficient has been determined experimentally are generated in various nuclear spin states, with various population differences; some of them contain no excess polarisation at all (e.g. those formed from singlet pairs in primary recombination). For this reason the experimental polarisation coefficient for the ab–$a'b'$ transition is an average value:

$$E_{ab-a'b'} = \sum_i E_i p_i, \tag{35}$$

where E_i is the partial polarisation coefficient for the ith molecular species and p_i the fractional content of these molecules. For example, the mean polarisation coefficient of the transition for a molecule generated from a triplet pair is

$$E^T_{ab-a'b'} = \frac{P_{ab} - P_{a'b'}}{P^0_{ab} - P^0_{a'b'}} \cdot \frac{P_{ab} + P_{a'b'}}{\sum\limits_{ab} P_{ab}} + \frac{P^0_{ab} - P^0_{a'b'}}{P^0_{ab} - P^0_{a'b'}}\left(1 - \frac{P_{ab} + P_{a'b'}}{\sum\limits_{ab} P_{ab}}\right). \tag{36}$$

The first term gives the contribution to the total polarisation by those molecules that have been generated in the nuclear spin states ab and $a'b'$; all the remaining molecules are generated in other nuclear spin states, so that they contribute the equilibrium polarisation to the given transition $ab-a'b'$. The first of the multipliers in the terms in (36) correspond to the partial polarisation coefficients of these molecules, and the second of the multipliers to their partial fraction; ΣP_{ab} is the total probability of generation of a molecule summed over all nuclear spin states. The second term is obviously negligibly small, so that from (28) we have

$$E^{T}_{ab-a'b'} = \frac{X(\tau)}{p_n^0}\,\Phi^{T}\,, \qquad (37)$$

where

$$\Phi^{T} = \frac{(P_{ab} + P_{a'b'})}{\sum\limits_{ab} P_{ab}}$$

is the fraction of molecules that have been generated in states ab and $a'b'$. It can easily be deduced that e.g. for a pair with one proton $\Phi^{T} \simeq 1$, and for a two-proton pair $\Phi^{T} \simeq \frac{1}{2}$. In general, for a polyproton system containing m protons in the pair $\Phi^{T} \simeq 2^{1-m}$. Values of P_{ab} and hence of Φ^{T} can in principle be calculated for any specific system.

Similarly, formula (35) can readily be used to express the experimental polarisation coefficient for the $ab-a'b'$ transition in a molecule generated from a singlet pair:

$$E^{S}_{ab-a'b'} = -\frac{(1-\alpha)X(\tau)}{p_n^0}\,\Phi^{S}, \qquad (38)$$

where

$$\Phi^{S} = \frac{P^{S}_{ab} + P^{S}_{a'b'}}{\sum\limits_{ab} P^{S}_{ab}}$$

$$\sum_{ab} P^{S}_{ab} = \alpha + (1-\alpha)\int_0^{\infty} \varepsilon\, \hat{f}(t)\, dt - (1-\alpha)\sum_{ab} P^{T}_{ab}\,.$$

The exact expression for Φ^{S} is more cumbersome than that obtained with a triplet pair; however, it can be accepted approximately that $\Phi^{S} \simeq 2/n$. If the molecule contains m protons, for example, we have $\Phi^{S} \simeq 2^{1-m}$. In the same way expressions can be obtained for the polarisation coefficient of a molecule from an uncorrelated pair.

The meaning and purpose of these equations lie in the theoretical calculation (in terms of population differences) of nuclear polarisation coefficients and hence, from a comparison of the results with experimental values, determination of the parameters of chemical nuclear polarisation (magnetic parameters of the pair, lifetimes of the radicals). This approach to a quantitative analysis of the phenomenon has several advantages over the simulation of n.m.r. spectra of molecules with polarised nuclei. The chief advantage is that we can disregard relaxation effects in the molecules and their distorting effects on the populations of levels and the chemical nuclear polarisation spectra; the difficulties entailed in allowing for relaxation in the simulation of the spectra led to several errors in the analysis of the chemical polarisation of nuclei (for further details see Ref. 4).

All the theoretical approaches discussed here are essentially semi-empirical, since they involve two hypothesis. Firstly, it is assumed that the spin Hamiltonian of a radical-pair is independent of time, i.e. that the exchange interaction of electrons in the pair is independent of time and hence of the distance between the radicals. Secondly, the molecular dynamics of the pair, described by the distribution of diffusion paths of the radicals and the probability of the latter meeting again after their diffusion separation, is described by the Noyes semi-empirical function, which depends on a power of the time $t^{-\frac{3}{2}}$. These assumptions enable spin dynamics (i.e. the dynamics of the singlet–triplet evolution of the pair) and molecular dynamics (i.e. the dynamics of diffusion displacements) to be treated separately, independently. As has been shown above, the result of their combined action, leading to nuclear polarisation, can be presented in comparatively simple analytical form, convenient for the analysis of experimental data, physically clear, and easily interpreted.

However, the hypothesis that spin and molecular dynamics are independent is in general incorrect. The diffusion of the radicals in the pair modulates the mutual orientation of and the distance between the radicals, and consequently modulates the exchange potential. The latter in turn influences the rate of triplet–singlet evolution. Through the exchange potential the molecular dynamics thus has a strong influence on the spin dynamics and hence on the polarisation produced.

A rigorous, non-empirical theory should consider spin and molecular dynamics together, i.e. should solve the problem of the singlet–triplet evolution of a pair with a time-dependent spin Hamiltonian, which in turn controls the molecular dynamics and is a random function of time. Such a non-empirical approach has recently been developed by Freed and Pedersen[19], who have obtained an exact solution of the problem of the $S-T_0$ evolution of a pair and have calculated both nuclear and electron polarisation. It is significant that these authors have used the physically most real model, in which the energy of exchange interaction depends exponentially on the distance between the radicals, while the time dependence of the inter-radical distance is determined by random diffusion and is described by Liouville's stochastic equation. Numerical solution gave polarisation coefficients as functions of various parameters (diffusion coefficients, hyperfine interaction energies, differences in Zeeman energies, parameters of the exchange potential). The problem of the influence of the Coulombic and exchange potential on molecular-diffusion dynamics and on the polarisation has also been solved.

The results of the Freed–Pedersen theory are important in all respects, in particular for the chemical polarisation of nuclei, as the rigorous theory has confirmed the main principles and physical ideas of the semi-empirical theory. Moreover, it has shown that the postulated independence of spin and molecular dynamics does not present a difficulty and does not distort at all seriously the true physical picture of the phenomenon. The physical reason for the insensitivity of the spin dynamics to the exchange potential is that the singlet–triplet evolution is a slow process, so that during its progress the radicals of the pair are able to separate to considerable distances, at which their exchange energy can be neglected. In other words, the main contribution to the singlet–triplet evolution of a pair and to the consequent nuclear polarisation is made by long diffusion paths, on which the exchange potential is negligible. This constitutes an important difference between nuclear and electron polarisation: the former is produced in long-range diffusion paths, whereas short-range spin dynamics makes the major contribution to the establishment of electron polarisation.

The practical (or rather technical) advantage of the semi-empirical theory is that it will give more reliable results, which are simple to interpret physically. The

semi-empirical theory contains several parameters (such as the coefficient m in the Noyes function, the probability of recombination in a contact singlet pair ϵ, and the fraction of primary recombination α), of course, but the number of such empirical parameters in the non-empirical theory is no less and even greater. Comparison of the two theories indicates that the semi-empirical theory describes satisfactorily the physics of the phenomenon of chemically induced polarisation of nuclei and gives quite reliable quantitative results. However, this theory requires further development, the empirical parameters must become more accurate, and fresh experiments must be undertaken aimed at further improving and refining the theory.

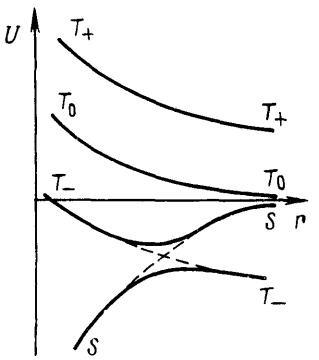


Figure 4. Dependence of energy of spin states of a radical-pair on the inter-radical distance. Full curves show adiabatic reaction paths for recombination (or dissociation) with change in the electron spin; the broken lines represent non-adiabatic paths with conservation of spin.

Besides establishing the physical mechanisms of the non-equilibrium pumping of Zeeman nuclear levels, the chemical polarisation of nuclei has also presented several fundamental results relating to the chemical physics of elementary chemical processes. Firstly, it has confirmed the concepts of the primary and secondary recombination of radicals in a pair and the molecular dynamics of a pair. The quantitative agreement between experiment and theory shows that the function f(t) reproduces quite well the dynamic behaviour of a pair.

Both quantitative agreement with theory and direct experimental results have demonstrated that the intrinsic angular momenta are preserved in elementary radical reactions involving the transfer of atoms (substitutions) and electrons, as well as in the addition of radicals: i.e. such reaction take place with complete conservation of electron and nuclear spins. This is indicated also by the maintenance of spin multiplicity in the transformation of pairs occurring on the decomposition of one of the radicals or on substitution: the resulting new radical-pair retains the spin multiplicity of the old pair. These direct experimental facts, together with the quantitative agreement between theory and experiment, show that the contribution by acts of dissociation and of actual recombination (i.e. "collapse" of the pair) to the establishment of nuclear polarisation is infinitesimal: i.e. these acts occur with conservation of the spins of electrons and nuclei. The behaviour of the energy levels of the dissociating molecule (or, what is the same, the collapsing radical-pair) is shown in Fig. 4. The conservation of the spins of electrons and nuclei as the system moves along the reaction coordinate of dissociation (with increase in the distance r) or recombination (in the opposite direction) shows that the region of quasi-intersection of T_- and S levels (in which $J \simeq g\beta H$) is traversed rapidly, non-adiabatically. For this reason adiabatic effects are insignificant in producing nuclear polarisation[3].

Finally, it must be noted that the spin correlation of electrons, a kind of spin "memory", is preserved in radical-pairs in a liquid for a long time ($\sim 10^{-6}$–10^{-7} s). The spin correlation is lost in the time interval during which the state of the pair passes into those of the individual radicals. This time is found to be sufficiently long for the radicals to separate to great distances, while retaining the spin "memory" and phase relations of the initial pair[3].

The quantitative agreement between theoretical and experimental results shows that the chief interactions responsible for the singlet–triplet evolution of radical-pairs are hyperfine and Zeeman. These are the "strongest" interactions, responsible for the non-conservation of electron and nuclear spins in radical-pairs; all other interactions (spin–orbit, spin-rotation, etc.) usually play a subordinate role (although, as we shall see later, these interactions are sometimes extremely significant).

4. Chemical Applications of the Chemical Polarisation of Nuclei

The detection of chemical nuclear polarisation has become a new and powerful method for investigating the mechanisms of chemical reactions, a new and sensitive method of detecting radicals and radical processes, on which much has already been written[3,7,20] and which has made the phenomenon widely known and popular in chemistry. However, it must be clearly understood that the observation of nuclear polarisation in a reaction still does not mean that a radical mechanism is fundamentally involved. Several recent experimental results indicate that the phenomenon often arises either entirely in side-reactions or in a process resembling the main process but constituting only a small part of the latter. Thus investigation of the chemical nuclear polarisation in the thermal isomerisation of 2-alkoxyquinoline N-oxides has shown[21] that the proportion accounted for by a radical mechanism is 0.2–0.7.

Chemical nuclear resonance of phosphorus-31 has shown that organic phosphites react with hydroperoxides by two competing mechanisms—radical and non-radical (molecular or ionic)—where the former reaction path, which induces polarisation of phosphorus-31 nuclei, constitutes only a minute fraction (10^{-2}–10^{-4}).[22] In the corresponding reactions catalysed by transition-metal ions it has also been established that the radical path is secondary[23]. Application of the same technique to the reactions of ozone with organic phosphites indicates that radical ozonolysis amounts to only about 5%, the main reaction probably involving biradical states in which nuclear polarisation is not produced[24]. Investigation of the chemical polarisation of nuclei in the products of the fairly unusual reaction of tetra-alkylammonium salts with carbon tetrachloride suggests[25] that it has either an ionic or a nucleophilic mechanism and is accompanied by the

formation of unstable intermediate compounds, which initiate secondary radical reactions in which the observed polarisation is produced.

Analysis of the chemical polarisation of carbon-13 in the reaction of quinone diazide with cyclohexylamine reveals strong polarisation of the nuclei in an unstable intermediate triazen[26]. It is concluded that this is formed in non-radical stages of the reaction, and that is polarisation results from subsequent reversible decomposition of the triazen by a radical mechanism.

A common feature of the above examples is that the radical mechanism leading to nuclear polarisation either does not predominate or plays an altogether subordinate part. An entirely new aspect of this technique is the separation of radical and non-radical mechanisms, and sometimes even frank discrediting of radical stages and their role in the reactions.

Chemical nuclear polarisation is the only kinetic method which will distinguish competition between radical and non-radical mechanisms, especially if they yield the same products. It becomes possible not only to distinguish these mechanisms but also to estimate their competition. Thus, if a given product is formed by two paths with constants k_1 and k_2 and polarisation coefficients E_1 and E_2, the observed polarisation coefficient is

$$E = (E_1k_1 + E_2k_2)/(k_1 + k_2) = E_1p_1 + E_2p_2 , \qquad (39)$$

where p_1 and p_2 are the fractions of the two reaction paths. If the second path is non-radical, $E_2 = 1$ and the second term can be neglected. Having calculated E_1 theoretically, we can then easily find p_1 and p_2 (for greater detail see Ref. 3).

An important role in the mechanisms of radical reactions is often played not only by radicals (and hence radical-pairs) but also by biradicals. It is sensible to distinguish between biradicals having dynamic exchange, in which the exchange interaction is usually weak, from radical centres joined by flexible molecular bridges, so that they are able periodically to move together and apart. As a consequence, such biradicals often behave in chemical reactions like radical-pairs. Biradicals with static exchange, on the other hand, usually have a rigid molecular frame, so that the exchange interaction in them is not modulated by molecular movements and remains constant. The Table shows what nuclear polarisation can in principle be expected in strong and weak fields for reactions involving radicals and biradicals.

Character of nuclear polarisation in radical-pairs and biradicals.

Field	Radical-pairs, and biradicals with dynamic exchange	Biradicals with static exchange
Strong	$S-T_0$ (integral and multiplet)	$S-T$ (integral, with $g\beta H \approx J$)
Weak	$S-T_0$ (multiplet) $S-T$ (integral)	

In order that $S-T_-$ transitions should make a significant contribution to nuclear polarisation it is necessary that the S and T_- levels should have approximately the same energy, i.e. that $g\beta H \simeq J$. Hence it follows that their contribution arises in shorter diffusion paths than that by $S-T_0$ transitions. In biradicals with static exchange, where the exchange energy J is fixed, the polarisation has a "resonance" character and appears in a magnetic field corresponding to the condition $g\beta H \simeq J$. It is thus possible by means of chemical nuclear polarisation to measure the energy of exchange interaction in biradicals having different structures. Interesting examples of this type have been given in Closs[6].

In conclusion let us consider in what reactions chemical nuclear polarisation can be observed and whether any predictions can be made. No definite answer can be given, but several considerations may be adduced. First of all, it is necessary that radicals should be generated in the reaction, either in the main or in a secondary reaction path. "Chemical" intuition is necessary to predict this, but experience shows that this is not infallible: the phenomenon is often observed unexpectedly, where radical mechanisms have not been suggested.

Further, high rates of chemical pumping, comparable with the rates of nuclear relaxation, are necessary for the certain observation of chemical nuclear polarisation. It is good if the reaction takes 3–5 min, and still better if it occurs within seconds. However, this condition is desirable but not necessary: even in slow reactions such polarisation can be observed provided that the polarisation coefficients are sufficiently large. In the decomposition of acyl peroxides, for example, intense polarisation has been observed for an hour and more without additional supply of reactant. A quite strict condition can be formulated: in order that a maximum should be observed on the kinetic curves of chemical nuclear polarisation (and this is the clearest and most unambiguous criterion of detection), the condition

$$|E|k - \beta > 0 \quad \text{or} \quad |E|kT_{1n} > 1$$

must be satisfied. Furthermore, these three fundamental parameters—the polarisation coefficient, the reaction rate constant, and the nuclear relaxation time in the molecule—determine the detectability of the polarisation, while the above relation among them is a criterion of its experimental observation.

IV. ISOTOPE EFFECTS IN RECOMBINATION

As shown in Section III, the probability of triplet–singlet conversion in a radical-pair depends on the energy of hyperfine electron–nuclear interaction. For this reason isotope effects should be observed in the recombination of radicals in pairs. Their magnitude can easily be calculated by means of Eqns. (14) and (23).

We shall consider as illustration the simple example of the recombination of hydrogen and deuterium atoms with the trichloromethyl radical. We suppose for simplicity that the initial states for recombination are triplet pairs and assume that the lifetime of the radicals $\tau \gg \mathcal{H}_{ab}^{-1}$. The probability of recombination can then be calculated from Eqn. (25). We compute the ratio of probabilities as

$$\frac{P_{CHCl_3}}{P_{CDCl_3}} = \frac{\sum_{ab} \pi^{1/2} \varepsilon m |\mathcal{H}_{ab}^{H}|^{1/2}}{\sum_{ab} \pi^{1/2} \varepsilon m |\mathcal{H}_{ab}^{D}|^{1/2}} . \qquad (40)$$

The summation covers all states having $m_H = \pm\frac{1}{2}$ for hydrogen and $m_D = 0, \pm 1$ for deuterium, while

$$\mathcal{H}_{ab} = \langle S|\mathcal{H}|T_0\rangle$$

is defined by Eqn. (7). In weak magnetic fields, when $\Delta g\beta H \ll a$, we find from Eqn. (40) with $a_H = 506$ and $a_D = 77$ oersteds that

$$P_{CHCl_3}/P_{CDCl_3} \simeq 1.75 .$$

In general, when $\Delta g\beta H$ is comparable with the hyperfine interaction, the effect should depend on the strength of the magnetic field.

Isotope effects in the recombination of any radicals from any pair of precursors can readily be calculated in a similar manner. The largest effects must be expected in recombination from triplet pairs, and the smallest from singlet pairs. It would be interesting to compare predicted and experimental effects if any exist.

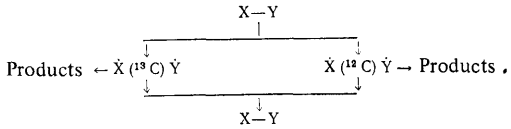
V. ENRICHMENT OF MAGNETIC ISOTOPES IN CHEMICAL REACTIONS

As has been shown earlier—Eqns. (3)–(5) and (7)–(9)—the probability of triplet–singlet transitions in a radical-pair, and hence the probability of recombination, depend on the energy of hyperfine interaction. It depends also on the magnetic moment of the nucleus, since this energy is unambiguously linked with the magnetic moment of the nucleus by the well known Fermi relation

$$a = \frac{8\pi}{3}\mu_e\mu_n |\psi(0)|^2,$$

where μ_e and μ_n are the magnetic moments of the electron and the nucleus, while $|\psi(0)|^2$ is the density of electrons on the nucleus. Thus the probability of a chemical reaction should depend on the magnetic moment of the nucleus, so that chemical reactions can be used for the selection and enrichment of magnetic isotopes, as well as their isolation from non-magnetic isotopes.

This idea can easily be illustrated by a simple example in which triplet pairs are generated chemically (by thermal or photochemical dissociation) from a molecule X–Y:



We suppose that one of the radicals (e.g. X·) contains a carbon nucleus. Radical-pairs containing the magnetic carbon-13 isotope will undergo more rapid triplet–singlet conversion than will pairs containing the non-magnetic carbon-12 isotope. Therefore the former pairs will become singlets more rapidly and recombine more rapidly with the formation of the original X–Y molecules, whereas the triplet–singlet conversion of the latter pairs will lag and such "non-magnetic" pairs will have less chance of recombining. Thus molecules of the initial substance X–Y will be enriched with the magnetic isotope, while the conversion products will be depleted of this isotope.

It is easy to suppose that, if singlet pairs are generated from X–Y, the reverse singlet–triplet evolution of the pairs will result in depletion of the magnetic isotope from the initial molecules, and enrichment of the decomposition products. However, this process will be far less efficient in selecting isotopes, since the majority of the singlet pairs recombine without singlet–triplet conversion (primary recombination), and only a small proportion of singlet pairs undergo singlet–triplet evolution leading to selection of the isotopes. The recombination of triplet pairs is always preceded by triplet–singlet conversion, so that such pairs are most effective in selection. Uncorrelated pairs, formed by the chance encounters of independently generated radicals, occupy an intermediate position with respect to efficiency of isotope selection.

Considering now the quantitative theory of isotope enrichment for the same model pair from X–Y, we suppose that the pair (X·, Y·) is initially in a triplet state and that transitions from the T_- state make the major contribution to its triplet–singlet conversion. The content of the magnetic carbon-13 isotope in the molecule formed from the pair will then be

$$\delta_{S-T_-} = \frac{P^{^{13}C}_{S-T_-}\delta_{^{13}C}}{P^{^{12}C}_{S-T_-}\delta_{^{13}C} + P^{^{12}C}_{S-T_-}\delta_{^{13}C}}, \qquad (41)$$

where $P^{^{13}C}_{S-T_-}$ and $P^{^{12}C}_{S-T_-}$ are the probabilities of $S-T_-$ transitions in pairs containing carbon-13 and carbon-12 respectively, while $\delta_{^{13}C}$ and $\delta_{^{12}C}$ are the contents of these isotopes in the initial molecules that have not yet undergone chemical change. The numerator of (41) is the probability of formation of X–Y molecules from pairs containing carbon-13; the denominator defines the total probability of the generation of X–Y molecules both from "magnetic" and from "non-magnetic" pairs; and their ratio is the isotopic content of carbon-13 in X–Y molecules formed after recombination. The probabilities of $S-T_-$ transitions are proportional to the squares of the matrix elements of these transitions (Eqns. 5 and 9). On substituting them in (41), we obtain

$$\delta_{S-T_-} = \frac{\delta_{^{13}C}\left[\sum_i \langle T_-|\mathcal{H}|S\rangle_i^2\right]_{^{13}C}}{\delta_{^{13}C}\left[\sum_i \langle T_-|\mathcal{H}|S\rangle_i^2\right]_{^{13}C} + \delta_{^{12}C}\left[\sum_i \langle T_-|\mathcal{H}|S\rangle_i^2\right]_{^{12}C}}, \qquad (42)$$

where

$$\left[\sum_i \langle T_-|\mathcal{H}|S\rangle_i^2\right]_{^{13}C}$$

is the sum of the squares of the matrix elements over all nuclear spin states of the "magnetic" radical-pair; the second term in the denominator is the corresponding sum for the "non-magnetic" pair.

Considering a numerical example, we suppose a triplet pair (~· C=O, ·CH_2 ~), in which $a_{^{13}C} = 150$ (acyl radical) and $a^H_{CH_2} = 16$ oersteds, with initially the natural isotope content $\delta_{^{13}C} = 0.01$ and $\delta_{^{12}C} = 0.99$. Computing with these values the matrix elements by means of Eqn. (5) or (9) and substituting them in (42), we obtain

$$\delta_{S-T_-} = \frac{[(150/8^{1/2})^2 + 2(16/8^{1/2})^2]\cdot 1\cdot 10^{-2}}{[(150/8^{1/2})^2 + 2(16/8^{1/2})^2]\cdot 1\cdot 10^{-2} + [2(16/8^{1/2})^2]\cdot 0{,}99} \simeq 0.32$$

i.e. the carbon-13 content in the carbonyl group in the ~CO.CH_2~ molecules formed after recombination should have increased more than thirtyfold.

We shall now estimate the contribution of $S-T_0$ transitions to the enrichment of magnetic isotopes. In this case the content of carbon-13 in a molecule generated from a triplet pair by $S-T_0$ transitions is

$$\delta_{S-T_0} = \frac{P^{^{13}C}_{S-T_0}\delta_{^{13}C}}{P^{^{13}C}_{S-T_0}\delta_{^{13}C} + P^{^{12}C}_{S-T_0}\delta_{^{12}C}} . \qquad (43)$$

Again replacing the probabilities of these transitions by the corresponding matrix elements, we obtain

$$\delta_{S-T_0} = \frac{\left[\sum_i \langle T_0|\mathcal{H}|S\rangle_i^2\right]^{^{13}C}\delta_{^{13}C}}{\left[\sum_i \langle T_0|\mathcal{H}|S\rangle_i^2\right]^{^{13}C}\delta_{^{13}C} + \left[\sum_i \langle T_0|\mathcal{H}|S\rangle_i^2\right]^{^{12}C}\delta_{^{12}C}}. \qquad (44)$$

Each of the items in this formula has the same meaning as in Eqn. (42); the sole difference is that the matrix elements are calculated for $S-T_0$ transitions by means of Eqn. (3) for a one-proton pair, or in general by means of Eqn. (7).

However, as we have seen earlier (in analysing the chemical polarisation of nuclei), the probability of an $S-T_0$ transition is proportional to the square of the matrix element only for short-lived radicals: for long-lived radicals the probability is proportional to the square root of the matrix element. This means that Eqn. (44) applies only to short-lived radicals. For long-lived radicals we find from (43) that

$$\delta_{S-T_0} = \frac{\delta_{^{13}C}\left[\sum_i \langle T_0 | \mathcal{H} | S\rangle_i^{1/2}\right]^{^{13}C}}{\left[\sum_i \langle T_0 | \mathcal{H} | S\rangle_i^{1/2}\right]^{^{13}C}\delta_{^{13}C} + \left[\sum_i \langle T_0 | \mathcal{H} | S\rangle_i^{1/2}\right]^{^{13}C}\delta_{^{13}C}} \quad (45)$$

This equation defines the content of the carbon-13 isotope in a molecule generated by an $S-T_0$ transition from a triplet pair of long-lived radicals.

Let us again estimate the contribution made by $S-T_0$ transitions to isotopic enrichment for the same pair (~• C=O, • CH_2~). Substituting the parameters of this pair in Eqn. (7) and confining our attention to weak fields (i.e. neglecting the term $\Delta g\beta H$), we obtain $\delta_{S-T_0} \simeq 0.29$ for short-lived radicals and the value 0.04 if the lifetime of the radicals in the pair $\tau \gg \mathcal{H}_{ab}^{-1}$.

Enrichment should be most efficient in weak fields, where the contribution to triplet–singlet conversion arises from all three triplet substates; in strong fields only the contribution from T_0–S transitions remains. However, this conclusion must not be regarded as generally applicable: situations may occur in which $\Delta g\beta H$ is large, and then in a strong field $S-T_0$ transitions can play an even greater role in the selection of isotopes than do all three transitions taken together in a weak field.

It is easy also to deduce rigorous equations of isotopic enrichment for cases of recombination in uncorrelated pairs as well as in singlet pairs. It must be borne in mind merely that in singlet pairs primary recombination takes place without isotopic enrichment, so that the isotope content must be averaged over molecules formed by primary and by secondary recombination. Clearly, the greater the probability of primary recombination the smaller the mean isotopic enrichment. For this reason, as has already been noted, the efficiency of selection of isotopes is low in singlet pairs compared with triplet pairs of the same structure.

The above numerical estimates of isotope enrichment apply to cases in which each initial X–Y molecule has undergone only one chemical change, only one act of decomposition. We shall term this the first stage of enrichment. Molecules that have passed through the first stage and are enriched with the magnetic isotope can obviously undergo fresh chemical change and become still more enriched in a second stage; and so on. In fact, with increase in the degree of chemical conversion the quantity of substance X–Y remaining will diminish, but its isotope content will continually increase in proportion to the extent of conversion.

To calculate this effect we suppose that X–Y decomposes at a constant rate (e.g. on photochemical initiation) according to the scheme

$$XY \underset{k}{\overset{n_\nu}{\rightleftarrows}} XY^T \xrightarrow{\varphi} (\dot{X}\dot{Y})^T \begin{cases} \xrightarrow{\tau^{-1}\theta} XY \\ \xrightarrow{\tau^{-1}(1-\theta)} \text{Products} \end{cases}$$

The excited triplet state of the molecule XY breaks down at a constant rate φ to form the triplet pair $(X^\bullet, Y^\bullet)^T$, which either recombines again to XY or breaks down and is converted into products; n_ν is the number of quanta absorbed, k the rate constant for deactivation of the triplet state, and $\tau^{-1}\theta$ the constant representing "collapse" of the pair to the original molecule; and θ denotes that fraction of the rate constant that depends on magnetic interactions in the pair. The scheme for conversion of the same molecule XY* containing a magnetic isotope is of the same form, except that the corresponding "collapse" constant is $\tau^{-1}\theta^*$. From the above equations it is easy to express their ratio in terms of the matrix elements of singlet–triplet mixing. If T_-–S transition make the major contribution to enrichment, for example, we have

$$\theta^*/\theta = \left[\sum_i \langle T_- | \mathcal{H} | S\rangle_i^2\right]^{^{13}C} \Big/ \left[\sum_i \langle T_- | \mathcal{H} | S\rangle_i^2\right]^{^{13}C}.$$

Analysis of the kinetic scheme for the concentration variation of "magnetic" molecules XY* and "non-magnetic" molecules XY yields the equations

$$[XY^*] = [XY^*]_0 - \frac{n_\nu \delta_{^{13}C}\varphi}{k+\varphi}(1-\theta^*)t, \quad (46)$$

$$[XY] = [XY]_0 - \frac{n_\nu \delta_{^{13}C}\varphi}{k+\varphi}(1-\theta)t. \quad (47)$$

Since $\theta^* > \theta$, it follows by formal kinetics that a mixture of XY and XY* molecules is enriched with the "magnetic" molecules XY*. The degree of enrichment can be defined as the ratio

$$\delta = \frac{[XY^*]}{[XY]+[XY^*]}.$$

Substitution from (46) and (47) yields

$$\delta(t) = \frac{\delta_{^{13}C}[XY]_0 - \frac{n_\nu \delta_{^{13}C}\varphi}{k+\varphi}(1-\theta^*)t}{[XY]_0(1+\delta_{^{13}C}) - \frac{n_\nu \delta_{^{13}C}\varphi}{k+\varphi}(1-\theta^*)t - \frac{n_\nu \delta_{^{13}C}\varphi}{k+\varphi}(1-\theta)t}. \quad (48)$$

The extent of conversion χ is defined as

$$\chi(t) = 1 - \frac{[XY]+[XY^*]}{[XY]_0+[XY^*]_0}.$$

The degree of enrichment will then be related to the extent of conversion by the formula

$$\delta(t) = \frac{\delta_{^{13}C}[XY]_0 - \frac{n_\nu \delta_{^{13}C}\varphi}{k+\varphi}(1-\theta^*)t}{[XY]_0(1+\delta_{^{13}C})[1-\chi(t)]}. \quad (49)$$

Clearly, the greater the extent of conversion $\chi(t)$ the higher the isotope content $\delta(t)$, in agreement with qualitative predictions.

Equation (49) holds only when the extent of conversion is not too large, since it takes no account of enrichment in the second, third, etc. stages: i.e. it disregards variation in the initial content of the isotope. For this reason Eqn. (49) gives an incorrect asymptotic approximation as $\chi(t) \to 1$. In principle, however, exact kinetic equations can be deduced for isotope enrichment. The corresponding kinetic parameters n_ν, φ, and k or their combinations can be determined from the kinetics of the consumption of the substance, quantum yields, etc., i.e. from the usual kinetic measurements.

The enrichment of magnetic isotopes in chemical reactions, predicted here and given a theoretical basis, has been detected experimentally[27] in the photolysis of an aliphatic ketone, which becomes enriched with carbon-13. The degree of enrichment increases with the extent of conversion (in conformity with theoretical predictions). This novel principle of isotopic enrichment differs significantly from all other known principles: in none of the latter are magnetic effects in chemical reactions used for enrichment.

The principle of the enrichment of magnetic isotopes in chemical reactions formulated here is quite general and applicable to the sorting of nuclei not only in the carbon-13–12 system but also in other systems (oxygen-17–16, uranium-235–238, boron-10–11, etc.). The efficiency of enrichment is determined mainly by three factors—firstly the convenience of the chemical system (it is extremely desirable that the system should generate triplet radical-pairs), secondly the magnitude of the hyperfine electron–nuclear interaction (it is desirable that the chemical system system should generate radicals having large hyperfine interaction constants), and thirdly the electronic and nuclear relaxation times in the radicals, which should be sufficiently long. If such relaxation is rapid (occurring in times less than or comparable with the duration of triplet–singlet evolution of the pair), spin correlation in the pair is lost rapidly, and the pair remains all the time in an uncorrelated state. In other words, rapid relaxation leads to phase randomisation of the electrons, and prevents the triplet–singlet evolution of the pair from being controlled by hyperfine interaction. As a result, the efficiency of the reaction in selecting magnetic isotopes diminishes. Rapid relaxation in radicals may be caused by strong spin–orbital or spin–rotational interaction (for electrons) and also by quadrupole interaction (for the nuclei).

VI. EFFECT OF A MAGNETIC FIELD ON CHEMICAL REACTIONS

A fourth remarkable consequence of non-conservation of the angular momentum of electrons is that the probability (and the rate) of a chemical reaction depend on the strength of a steady magnetic field. This relation is predicted for radical reactions by Eqns. (3) and (7), according to which a magnetic field changes the probabilities of triplet–singlet transitions in radical-pairs. The effect of a field can be estimated by means of the equations deduced for calculating the chemical polarisation of nuclei.

The probabilities of the generation of molecules from triplet, singlet, and uncorrelated pairs are given by the equations

$$P^T = \sum_{ab} \pi^{1/2} \varepsilon m \,|\, \mathcal{H}_{ab} \,|^{1/2} \qquad (50)$$

$$P^S = \alpha + (1-\alpha) \int_0^\infty \varepsilon f(t)\, dt - (1-\alpha) \sum_{ab} \pi^{1/2} \varepsilon m \,|\, \mathcal{H}_{ab} \,|^{1/2} \qquad (51)$$

$$P^U = \tfrac{1}{2}\alpha + \tfrac{1}{2}(1-\alpha) \int_0^\infty \varepsilon f(t)\, dt + \tfrac{1}{2}\alpha \sum_{ab} \pi^{1/2} \varepsilon m \,|\, \mathcal{H}_{ab} \,|^{1/2}. \qquad (52)$$

Equations (50) and (51) have been obtained by generalising (25) and (26). Since we are now interested not in nuclear polarisation but in the aggregate probability of the generation of molecules in all nuclear spin states, the summations in (50) and (51) have been made over all such states. The deduction of (52) will be found in Ref. 3.

A magnetic field obviously accelerates triplet–singlet evolution and increases the probability of recombination in a triplet pair (provided, of course, that $\Delta g \neq 0$). However, the field accelerates equally the reverse, singlet–triplet evolution, so that the probability of recombination in a singlet pair is diminished. Equation (51) shows that this decrease is greater for smaller α, i.e. the smaller the proportion of primary recombination and the greater the proportion of pairs undergoing secondary recombination, in which singlet–triplet conversion takes place. It follows from Eqn. (52) that recombination in uncorrelated pairs is accelerated by a magnetic field.

In estimating the dependence on a magnetic field of the probability of formation of a molecule we can for simplicity neglect hyperfine interaction and assume that

$$\mathcal{H}_{ab} = \frac{1}{2} \Delta g \beta H .$$

Since we have thus postulated that radicals do not contain nuclear spins, the summation in Eqns. (50)–(52) no longer makes sense in this approximation. For a numerical estimate of the effect we consider only uncorrelated pairs, the most general case in chemistry. With $\alpha = \epsilon = 0.8$ and $m = 10^{-6}$ s$^{\frac{1}{2}}$ we find from Eqn. (52) that

$$(P - P_0)/P_0 \simeq 10^{-3} \,|\, \Delta g H \,|^{1/2}, \qquad (53)$$

where P_0 and P are the probabilities of recombination in the absence and in the presence of a field respectively. Equation (53) defines the relative effect of a magnetic field. Values of $H = 10^4$ and $\Delta g = 10^{-2}$ (the latter is typical of pairs of organic radicals) lead to $(P - P_0)/P_0 = 10^{-2}$, about 1%, which is, of course, small. An appreciable effect of a field can be expected only in the recombination of radicals having markedly different g-factors, i.e. in exceptional cases.

It would appear at first glance that weak magnetic fields should have no effect, for $\Delta g \beta H$ is small. However, in such fields a significant contribution to the triplet–singlet conversion of a pair is made by transitions from T_+ and T_- substates induced by hyperfine interaction with a probability proportional to a^2. With increase in field strength the T_+ and T_- levels diverge, with an accompanying decrease in the contribution to triplet–singlet conversion made by transitions from them. Therefore the effect of a weak magnetic field on reactions is due to elimination of degeneracy from the triplet levels. This mechanism is significant only when the hyperfine interaction and the contribution of T_+ and T_- states to recombination are large.

The influence of a magnetic field exerted by this mechanism was first observed by Sagdeev et al. in the reaction between perfluorobenzyl chloride and n-butyl-lithium[28–30]. This reaction involves $\cdot CF_2C_6F_5$ radicals, in which the energy of hyperfine interaction with fluorine-19 nuclei is large and the contribution by T_+ and T_- states to triplet–singlet conversion of radical pairs is considerable. No effect of the field has been detected in the corresponding reaction of benzyl chloride, since hyperfine interaction with the protons in the $\cdot CH_2C_6H_5$ radical is weak, and therefore the contribution of T_+ and T_- states to recombination small. For the same reason no effect of a magnetic field has been detected on the photosensitised decomposition of benzoyl peroxide[31].

Thus the influence of a magnetic field on the probability of the recombination of radicals can operate by two mechanisms. Firstly, the relative contributions by S–T_0 and S–$T_\pm$ transitions to triplet–singlet conversion of a pair changes on passing from weak (or zero) to strong fields. If the precursor of the recombination product is a singlet

radical-pair, the probability of recombination increases as the field becomes stronger. If the precursor is a triplet or an uncorrelated pair, the probability of recombination diminishes with increase in the field. This mechanism operates only when considerable electron–nuclear hyperfine interaction is present in the radicals. Secondly, if Δg is large in the radical-pairs, the probability of recombination increases in proportion to $|\Delta g\beta H|^{\frac{1}{2}}$ for triplet and uncorrelated pairs, but decreases in proportion to $|\Delta g\beta H|^{\frac{1}{2}}$ for singlet pairs. This mechanism is far more important and will be extended to other reactions.

Both these effects can be calculated theoretically in each case, and the dependence of the probability of recombination on the intensity of the magnetic field can be predicted. In the reactions of organic radicals, however, considerable effects can be expected (cf. the above numerical estimates), because values of Δg are usually small in pairs of organic radicals. Considerably greater effects may be expected in reactions involving transition-metal ions and organic molecules or radicals, when Δg may be considerable. Thus in the pair (Fe^{2+}, O_2), which probably precedes the electron-transfer reaction

$$Fe^{2+} + O_2 \rightleftarrows Fe^{3+} + O_2^-$$

for example, $\Delta g \simeq 2$, and with $H = 10^4$ oersteds the effect of the magnetic field may reach ~10%.

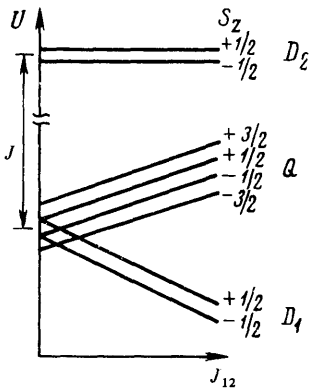


Figure 5. Energy levels and spin states of a triplet–doublet pair (T, D).

In more complicated reactions involving species in higher spin states (triplets, quartets, etc.) a magnetic field induces transitions between states differing in spin multiplicity. For example, a "triplet + doublet" reaction (an example is the interaction of oxygen in a triplet state with a radical in a doublet state) is preceded by a (T, D) pair containing three unpaired electrons. Such a pair may exist in states of total spin $\frac{3}{2}$ and $\frac{1}{2}$, corresponding to a quartet and two doublet states (Fig. 5). One of the doublet states (D_2) corresponds to singlet oxygen and is situated at a great height, so that it will be of no interest to us. A magnetic effect arises from the mixing of quartet and doublet states Q and D_1, of substates of Q having $S_Z = \pm\frac{1}{2}$ with the corresponding substates of D_1, i.e. of states having the same z-components of the total electron spin. The physical meaning of quartet–doublet mixing is the same as for triplet–singlet mixing in radical-pairs.

A calculation has been made of the effect of a magnetic field in such a system [32]. Since reaction occurs only in the doublet state D_1, it should be accelerated by a magnetic field which induces additional quartet–doublet transitions. Fig. 5 shows that the exchange interaction J_{12} between the electrons of the components of the pair removes the degeneracy of the miscible levels D_1 and Q and slows down the quartet–doublet evolution (just as exchange interaction retarded triplet–singlet evolution in a radical-pair). However, if it is accepted that the molecular dynamics of the pair (T, D) is the same as for a radical-pair, the exchange interaction J_{12} can be neglected, and the effect of the field is then proportional to $|\Delta g\beta H|^{\frac{1}{2}}$.

The influence of a magnetic field on other, more complicated reactions has been discussed in Ref. 3, where numerical estimates are given of the effects to be expected.

The influence of a magnetic field on biological systems and processes, reported in many papers on magnetobiology, may be due to molecular mechanisms of the above type. Such mechanisms should operate in biochemical reactions involving species having unpaired electrons (e.g. processes involving the transfer of electrons along the chain of cytochromes and the associated reactions of oxidative phosphorylation, many enzymic reactions, the oxidation of non-haemin iron by oxygen, certain stages of photosynthesis, etc.). Experimental results summarised in several monographs of magnetobiology [33–36] show that the effect of a field is most significant in these particular biochemical systems (or in those organelles, e.g. in mitochondria, where these processes take place).

Thus there are clear and soundly based physical reasons for the influence of a magnetic field on the rates of chemical reactions. They are due to the influence of the field on the probabilities of intersystem transitions between states of different spin multiplicities in the reactant-pairs. Even within the framework of this general mechanism, however, the effects of a magnetic field may be extremely diverse, for several reasons.

Firstly, a magnetic field should have no effect if $\Delta g = 0$ in the reactant-pair.

Secondly, the magnitude of the effect is strongly dependent on the molecular dynamics of the reacting pair. Thus in a radical-pair in a liquid the dynamics is described by the function $f(t) = mt^{-\frac{3}{2}}$, so that the field effect is proportional to $|\Delta g\beta H|^{\frac{1}{2}}$. If the dynamics of the pair is described by an exponential function, the effect is proportional to $(\Delta g\beta H)^2$. [3] With reaction between charged species diffusion in the pair takes place in a Coulombic field, and the function $f(t)$ has a completely different form [3]. Magnetic effects may be expected in principle even if the reactant centres are fixed in certain structural units (e.g. in mitochrondrial membranes), and reaction between them (electron transfer) occurs by a tunnel mechanism. Such a mechanism is often assumed in biochemical systems.

Thirdly, exchange interaction between electrons in the reactants forming a pair has a significant influence on transitions between spin states in the pair: the greater this interaction the smaller the effects to be expected. Different situations may arise, of course, in different (especially biochemical) systems: in some cases exchange interaction may be negligible, and in others considerable (as e.g. in the reaction of oxygen with deoxyhaemoglobin to form diamagnetic oxyhaemoglobin). For this reason threshold phenomena are possible, or even a change in sign of the effect with change in intensity of the magnetic field.

Fourthly, the observation of magnetic field effects requires that intersystem transitions between states of different spin multiplicities in the reacting pairs should be induced by a difference in Zeeman energies $\Delta g\beta H$, and this requires that the electronic relaxation times of the components of the pair should be sufficiently long: otherwise, rapid electronic relaxation will lead to randomisation of the precession phases of the electrons and disrupt evolution of the pair from one spin state to another. Such loss of spin correlation in a pair because of rapid electronic relaxation would lead to a loss of magnetic effects. (As shown in Section V, the efficiency of selection of magnetic isotopes in chemical reactions decreases markedly for the same reason.)

The problem of the effect of a magnetic field on chemical and biochemical processes has a long and rich history; much and often contradictory information has been obtained on magnetobiology and magnetomedicine. Examination shows that much of it is naive and physically unsound, and often it is erroneous. However, there is also a considerable proportion of reliable results, showing convincingly that magnetic effects in chemical and biological processes are real and frequently significant. It would be interesting to consider such data from the viewpoint of the molecular mechanisms discussed here, test several predictions following from these mechanisms, and also set up experiments at a molecular level.

VII. CONCLUSION

The intrinsic angular momentum of both electrons and nuclei is conserved in elementary chemical reactions involving substitution, dissociation, recombination, electron transfer, addition, disproportionation, etc: i.e. these elementary processes take place without change in the spins of electrons and nuclei. This conclusion applies equally to homolytic and to heterolytic reactions, as is directly indicated by results for the chemically induced magnetic polarisation of electrons and nuclei.

The reason for the conservation of spin in elementary chemical processes is that their duration is extremely short, around 10^{-14}–10^{-13} s. This is considerably less than the reciprocal of the rates for all the interactions that are able to induce change in the spin of an electron or a nucleus during a chemical process.

If in a chemical reaction, however, long-lived states are established, in which transitions are possible between levels differing in spin multiplicity, the intrinsic angular momentum of electrons and nuclei is not conserved in such states. A clear example is provided by the radical-pairs that precede chemical acts of recombination or disproportionation. Their lifetime (10^{-11}–10^{-8} s) is sufficiently long for transitions between states differing in spin multiplicity (triplet and singlet), accompanied by changes in electron and nuclear spins. This time is already comparable with the reciprocal of the interaction that induces transitions between singlet and triplet. (Quite weak interaction, e.g. an external radio-frequency field H_1, is able to change the angular momentum of electrons and nuclei. The energy of interaction of the field with an electron or a nucleus is γH_1, where γ is the gyromagnetic ratio for the electron or the nucleus. However, a longer time, of the order of $(\gamma H_1)^{-1}$, is now required to change the spin. Thus with $H_1 = 1$ oersted the time necessary for reorientation of an electron or a proton is respectively $\sim 4 \times 10^{-7}$ and 3×10^{-4} s. Such a change in spins is the essence of the phenomena of electron spin resonance and nuclear magnetic resonance.)

A long period of existence of radical-pairs (or reactant-pairs in general, with a set of electron-spin states) is not the sole condition ensuring the non-conservation of spin. Another important condition is that the exchange interaction between the electrons of the components of the pair should be sufficiently weak. Strong exchange interaction stabilises the angular momentum, maintains the electron spin of the system, and suppresses the evolution of the pair from one spin state to another.

Finally, a third condition is an interaction that induces transitions between spin states and alters the angular momentum. As shown above, the most important of this type are Zeeman and hyperfine interactions. The latter is especially important in weak fields, where the bonding between electron and nucleus is stronger than that of electrons and nuclei with the external magnetic field. Electron and nucleus then behave as a single spin system, change in the electron spin being balanced by a simultaneous change in the nuclear spin.

If all three conditions are satisfied, the angular momentum of the electrons and nuclei in a chemical system may not be conserved. This leads to magnetic effects in chemical reactions, the most striking of which are the chemical polarisation of nuclei, the enrichment of magnetic isotopes in chemical reactions, and the effect of a magnetic field on the rates of chemical reactions.

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