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Relevant

Magnetic field effects

Peter Atkins

The study of the effect of magnetic fields on chemical reactions has long been a romping ground for charlatans.[1] Contributions to the literature of the subject range over the span of scientific competence, from the benignly insane to whatever lies at the other extreme removed by a hair's breadth from the first. Disentanglement of the science from the deceit is hardly the task of an article of this nature, for it requires further careful experiments rather than arm-chair journalism. There is, however, a body of modern literature which seems reliable, and this will be our domain.[1]

Restriction to the reliable rules out a consideration of most of the more entertaining effects of magnetic fields. Rheumatic old ladies cannot expect this article to account for their relief in the presence of a nocturnal magnet, nor can copulating couples learn the appropriate arrangement of field strength and direction to guarantee a female offspring. Effects of varying degrees of indelicacy have been claimed for magnetic fields, and whatever evidence there is for the physiological effects of magnetism has been summarised by Barnothy.[2] These effects range from the orientation of mud snails, re-tardation of growth, rejection of tumours, pathological changes in the liver, drop in body temperature, disappearance of the oestrus cycle, to what can be the only relief after such varied torment, namely death. Amusement can be had with cray-fish, which, after moulting in a bed of iron-containing sand, can be induced to swim on their backs in the presence of a magnet. In this case the effect seems to be well documented, and can be understood quite simply on the basis of the function of the organs that sense orientation, and the competition of gravitational and magnetic forces. The effect has been proposed (appa-rently seriously; but in this subject it is sometimes hard to tell) as a method of orientating space travel-lers, but unfortunately man's otoliths are only weakly paramagnetic.

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Even when we turn to purely chemical effects of magnetic fields the difficulty remains of knowing what to believe. The best of the sane, moderately recent surveys of the effects which have been claimed is by Figueras Roca[3] whose emphasis is on catalysis. The difficulty then (analogous to the physiological situ-ation, where a mouse might simply be frightened into stunted growth by the sight or sound of a magnet) is that direct effects are difficult to distinguish from secondary heating or stirring brought about by the presence of a field (or just the bulky magnet).

One of the reasons for scepticism about the role of magnetic fields is rooted in a facile thermodynamic argument. A brief calculation of the change in the Gibbs function for a system when a magnetic field is applied shows that a substance with magnetic susceptibility of magnitude 10^{-4} (typical of diamagnetic mater-ials) changes energy by 5×10^{-4} J mol^{-1} in a magnetic field of 1 T (10 kG). Since this is wholly negligible, the argument runs, a magnetic field cannot be expected to influence chemical reactions. Even a paramagnetic sample will contri-bute only a couple of orders of magnitude to this ΔG and so it would appear that only unattain-ably high magnetic fields can be expected to give significant results. As always in arguments of this kind, we have to be careful to distinguish kinetic from equilibrium behaviour and to consider whether the overall dynamical scheme can be influenced by the presence of a field. In some systems, which are apparently at equilibrium (as in the attainment of photostationary states) an entirely

peculiar situation may develop where the magnetic field has a profound influence. The modern work on magnetic field effects makes use of these kinetic and pseudostationary situations and concentrates on sys-tems in which the magnetic field opens, enhances, or inhibits channels of reaction. Effects such as these have been observed which change yields and rates by up to 30 per cent, and sometimes even more. Far from being wholly insignificant, mag-netic fields of a few Tesla can in-fluence reactions dramatically.

The type of mechanisms to be described here, have developed from the early work of Farkas[4] on the interconversion of *ortho* and *para* hydrogen by paramagnetic ions and magnetised surfaces. The argu-ments used to explain that effect lie at the heart of the explanations of chemically induced nuclear and elec-tronic polarisation[5] and the pro-cesses that occur within radical pairs. The modern era of magnetic field effects arose as an extension of the study of chemically induced magnetic polarisation processes and as an extension to fluids of the study of triplet excitons in solids. The chemical consequences of these two effects are summarised in a book by Buchachenko.[6] (Although the book is in Russian a substantial amount, with variations, is available in English.[7,8,9])

The basic mechanism

The basic mechanism can be illus-trated by the processes that occur when a molecule undergoes homo-lysis into a pair of doublet radicals. Variations on this mechanism also account for other processes, as we shall see. The initial spin-state of the molecule is as a singlet (spin-paired) and the homolysis step is generally supposed to leave the spin vectors in the same relative, paired orientation when they are centred on two different radicals (*Fig. 1*). In the absence of a mag-netic field the two separated spins are at some indefinite overall orien-tation but at a well-defined relative orientation. In the presence of a magnetic field the spins precess[10]

about the direction of the field with a rate determined by its strength. If the field is identical at the two separated spins the precession rates are identical and the relative singlet phase is preserved: the pair of radicals remains an overall singlet. If the fields differ at the two spins their precession frequencies differ (*Fig. 2*) and they lose their initial singlet phasing. Losing singlet phasing implies the acquisition of triplet phasing and so the radical pair alternates between singlet and triplet.

Radicals produced in homolysis diffuse apart but their probability of re-encounter before they finally escape is high. Geminate recombination may occur on a re-encounter but the re-encounter is productive only if the spins are singlet-phased, for only then may a bond be formed. If the spins are triplet-phased by the time the encounter takes place the radical pair does not recombine but its components separate and ultimately react with new partners. This is the crux of the magnetic field effects: the rate of singlet–triplet rephasing may depend on the strength of some applied field; if it does, the proportion of cage and escape products will be affected because the extent of triplet character of the radical pair will be modified by the action of the field.

As a first step in the analysis of this approach, we can assess the time-scale of the steps involved. If the precession frequencies of the two spins differ by $\Delta\omega$ the time for singlet–triplet rephasing is of the order of $\pi/\Delta\omega$. The difference $\Delta\omega$ reflects the presence of different *local* fields, and their source may be either the nuclear magnetic moments or the g-factors of the radicals.

In the first case the local field is of the form $B + am_I$, where B is the applied field, a the hyperfine coupling constant, and m_I the spin projection of the relevant nuclei. In this case $\Delta\omega \sim a_1 m_{I1} - a_2 m_{I2}$ and the extent of the cage reaction is determined by the nuclear hyperfine constants and the spins of the nuclei present. This might be developed as a technique for isotope separation but is in any case a reminder that nuclei may play a far from passive role in chemical reactions.

In the case of radicals with different g-values the difference of the precession frequencies is $\Delta\omega \sim (g_1 \mu_B B - g_2 \mu_B B)/\hbar$ where μ_B is the Bohr magneton and g_1 and g_2 are the two g-values. In a field of 1 T (10 kG) the value of $\pi/\Delta\omega$ is approximately $(3/\Delta g) \times 10^{-11}$ s,
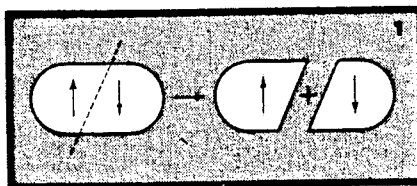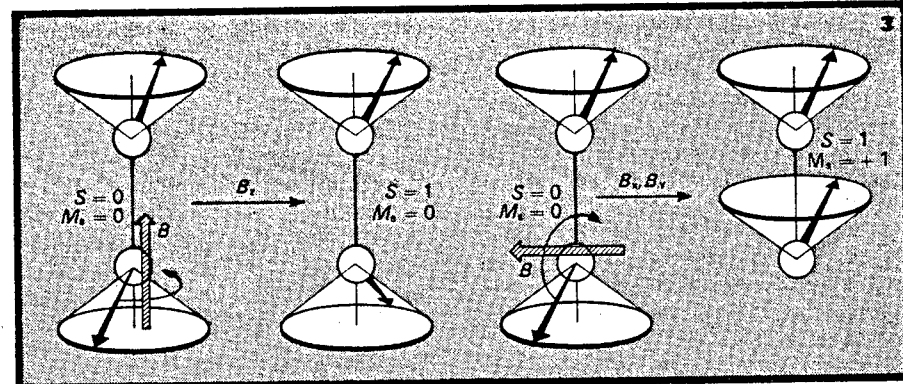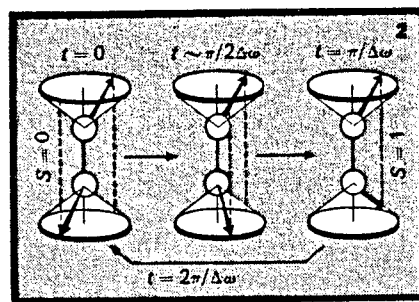

Fig. 1. **Homolysis breaks a bond but leaves the overall spin angular momentum unchanged at zero.**

Fig. 2. **Different Larmor precession frequencies at the two spins of an overall singlet generates a triplet ($S = 1$).**
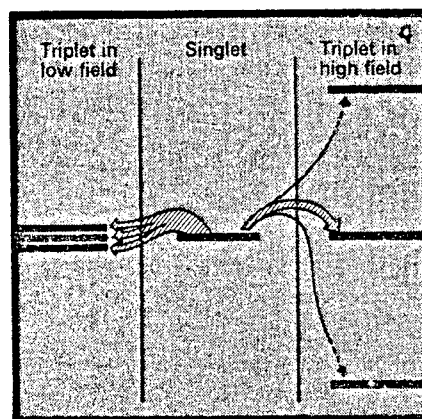

Fig. 4. **In a low field all three triplet states may take part in the rephasing but at high field rephasing to $M_s = \pm 1$ is blocked by the energy difference.**

Fig. 3. **Local field differences cause transitions to the $M_s = 0$ state of the triplet if they are in the z-direction but to $M_s = +1$ or $M_s = -1$ (not shown) if they lie in the x, y plane.**

and if $\Delta g \sim 10^{-3}$ the rephasing time ($\sim 3 \times 10^{-8}$ s) is comparable to the radical cage lifetime (even if it is significantly longer, an appreciable amount of triplet character might be introduced in the period between the initial separation and the re-encounter).

The roles of the magnetic field may now be discerned. In the first place it is the driving force for the Δg-induced rephasing. As the field is strengthened, so the rephasing time $\pi/\Delta\omega$ shortens. In the second place it is important to appreciate that a magnetic field can also influence the nuclear hyperfine induced rephasing process. This can be seen by the following argument. If a local magnetic field acts in the z-direction the relative rephasing occurs about the z-direction (*Fig. 3*) and the singlet switches into the $M_s = 0$ state of the triplet. If the local field lies in the x, y plane the rephasing occurs as one of the spins is twisted from α to β or β to α, leaving the other un-

affected (ignoring overall precessions and considering only relative effects). The states formed in this way are the $M_s = 1$ and $M_s = -1$ states of the triplet. If no external magnetic field is present the three triplet states ($M_s = 0, \pm 1$) are degenerate, and apart from minor factors arising from the details of the transition process, the rates of formation of the three states are identical. If, however, a magnetic field is applied the degeneracy is lifted, and the $M_s = +1$ orientation is shifted upwards in energy by $g \mu_B B$, the $M_s = 0$ energy is unaffected, and the $M_s = -1$ energy drops to $-g \mu_B B$ (*Fig. 4*). If the singlet–triplet separation J is small (which is often the case for the large average separations characteristic of a radical pair) the singlet state and the $M_s = 0$ state of the triplet are approximately degenerate whatever the field strength but the $M_s = \pm 1$ states are removed in energy from the singlet when the field is applied. The ability of the
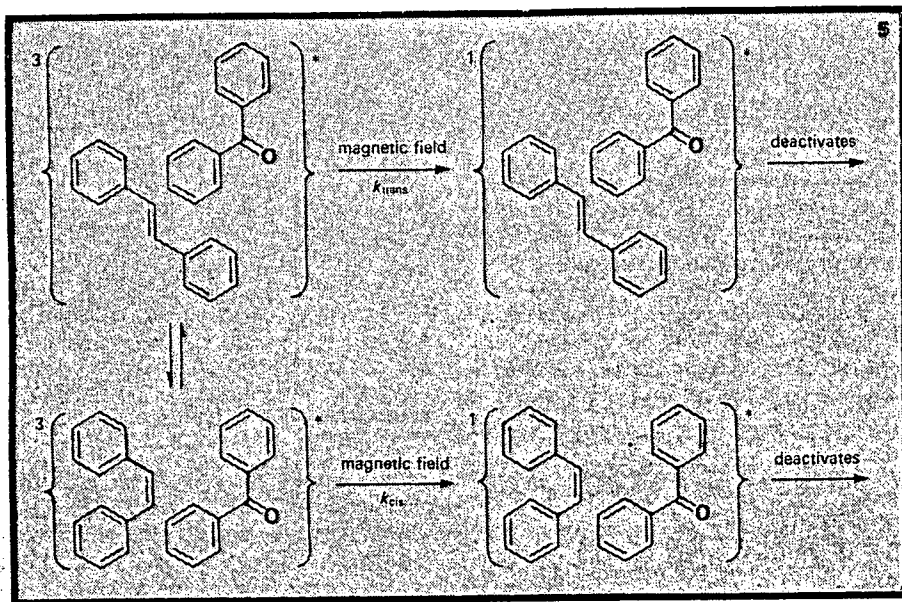
Fig. 5. Scheme for accounting for the effect of a magnetic field on a photosensitised reaction. If k_{cis} and k_{trans} differ the photostationary concentrations of the isomers differ.

perturbation (*eg* the nuclear fields) to induce rephasing is approximately proportional to the ratio of its strength to the energy it has to overcome, so whereas in a low magnetic field the perturbation can induce rephasing into all three triplet states, in a high field two of the rephasings are quenched and only the $M_s = 0$ state is accessible.

It follows that the proportion of cage products relative to escape products should be *increased* by the presence of the field, because two of the rephasing channels are then blocked and the radical pair is effectively frozen into its initial singlet state. Once in the high field region the proportions should begin to *decrease* again because the field can more effectively induce the transition into $M_s = 0$ by virtue of the Δg effect. The explicit analysis of these situations can be found elsewhere[7,8,11] If the initial radical pair is a triplet, the analysis presented is reversed.

Sagdeev *et al*[8] have examined the reaction of various substituted benzyl chlorides with butyl lithium; the cage recombination product is phenyl-pentane and the escape product is diphenylethane. If the preceding analysis is correct one should expect the diphenylethane yield to decrease relative to the phenylpentane. The ratio of cage to escape products was found to vary both as magnetic field and solvent were changed. For example, in hexane at 70 °C the ratio was 4.5 ± 0.5 in zero-field (actually 5×10^{-5} T) but changed to 6.2 ± 0.3 in 2.5 T, a change of about 37 per cent. In cyclo-

hexane at that temperature, the ratio changed by as much as 54 per cent (from 4.0 ± 0.3 to 6.1 ± 0.5), and in cyclohexane at 80 °C the change was 43 per cent (from 3.7 ± 0.3 to 5.3 ± 0.5). These huge changes are in the correct direction (increase of cage re-combination products) for singlet precursors, and of the correct order of magnitude on the basis of the analysis given above.
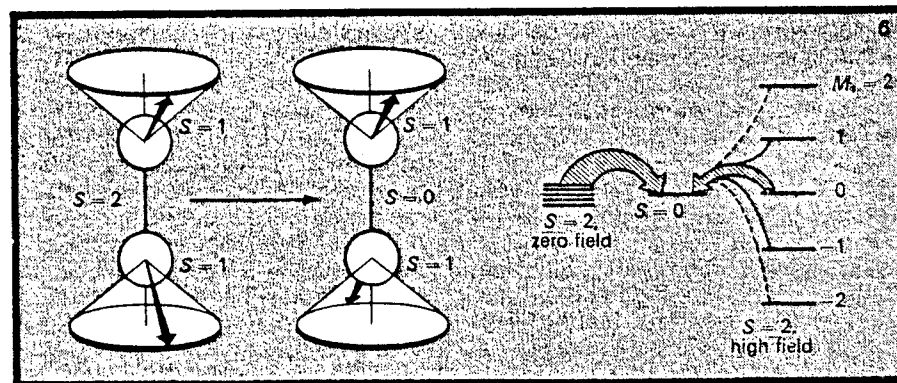
The quantitative analysis of the field-dependence depends on the nature of the motion of the caged pair. Chemically induced magnetic polarisation experiments give general support to a diffusive motion[12] and this has been incorporated into the structure of the magnetic-field effect model.[7,8,11] On this basis one would expect the dependence on the perturbation strength F to vary from $0.15 (F\tau)^{\frac{1}{2}}$ at high fields to
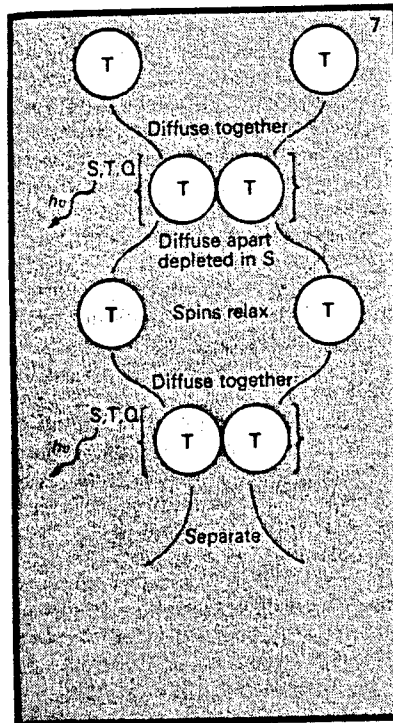
$0.30 (F\tau)^{\frac{1}{2}}$ in weak fields, where τ is a translation diffusion time which we may identify with the lifetime of the cage. If the system is in the high-field region F can be identified with $\Delta g \mu_B B / \hbar$ and the cage recombination probability is expected to fall as $0.30 (F\tau)^{\frac{1}{2}}$: this region has been discussed by Buchachenko[6] and Evans and Lawler.[11]

Another example of the modification of a reaction by a field was provided by some experiments reported by Gupta and Hammond[13] in the course of their study of the photostationary concentrations of *cis* and *trans* isomers of various stilbenes and piperylenes in the presence of triplet sensitisers (such as benzophenone). They found that the ratio of isomers in the photostationary state was affected to the extent of about 5 per cent in fields of about 0.9 T, and a mechanism based on field-induced deactivation of a triplet intermediate state has been proposed.[14] In this case the field may work by driving a triplet–singlet rephasing: as soon as the intermediate state shifts into singlet it deactivates, *Fig. 5.* If the *cis* and *trans* isomers form different intermediate states their deactivation rates will differ, and the modification of the kinetic scheme is reflected in the modification of the *cis–trans* equilibrium constant. The *trans/cis* equilibrium ratio changes from 0.61 to 0.67 in a 0.9 T field, which would be equivalent to a change in the Gibbs function of 0.2 kJ mol^{-1} if equilibrium thermodynamics were applicable.
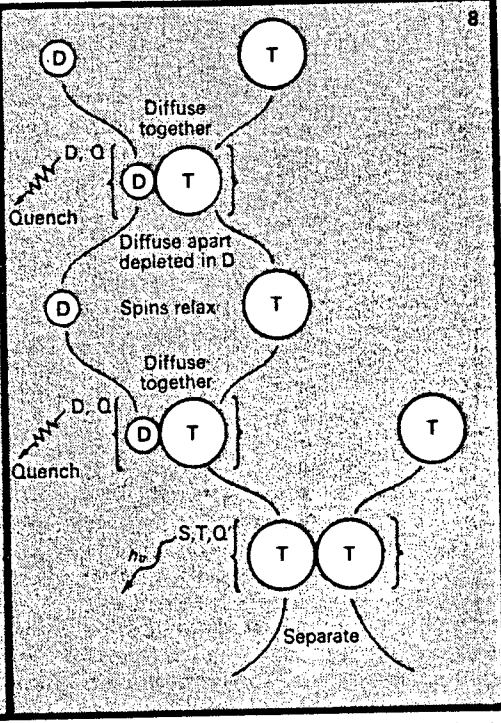
The final example in this section relates to the yield of excited states produced during the radiolysis of alkanes.[15,16] When solutions of alkanes are exposed to radiation the recombination of radical ions yields excited states through a reaction that may be expressed as $M^+ + M^-$

Fig. 6. Encounter of two triplet molecules may occur to give $S = 2$ (quintet). Different Larmor precession rates rephase this into $S = 0$ (singlet). If a strong field is present the $M_s = 0$ state of the quintet is the only one that contributes significantly to the rephasing.
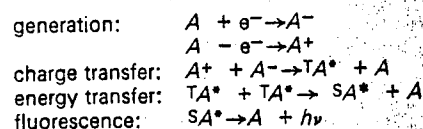
Fig. 7. Sequence of events in chemiluminescence (S: singlet; T: triplet; Q: quintet). The magnetic field inhibits the spin relaxation during the diffusive excursion.

Fig. 8. Sequence of events in doublet-quenched chemiluminescence (D: doublet; Q: quartet).

$\rightarrow M^* + M$. If the encounters were random, the singlet and triplet states of M^* would be formed in the ratio $1:3$, but the ratios observed are of the order of $1:2$ (or less). The explanation[15] of this is that both the hole in M (to give M^+) and the electron on M^- came from the same solvent molecule as a result of the sequence

$$S \rightarrow S^+ + e^- \begin{cases} S^+ + M \rightarrow S + M^+ \\ e^- + M \rightarrow M^- \end{cases}$$

and so initially (M^+, M) constitute a radical-ion pair in an overall singlet spin state. If spin relaxation or spin rephasing is slow the product M^* will be largely singlet, as observed. The reason why the recombination is not purely singlet is that the many protons on the $M^{\pm}$ radical ions are a source of local field. The rate of rephasing is expected to be greater in low fields than in high because of the blocking of transitions to the $M_s = \pm 1$ states in the latter case, as already described. The fluorescence intensity (from singlet M^*) is in fact found to increase in accord with theory and the effect is pronounced even at 0.1 T.

The mechanisms lying beneath the observations described in this section involve *coherent* rephasing, in which, in principle, singlet and triplet states alternate indefinitely as the α and β spins come into and go

out of phase. In most cases the cage reaction has ensued before more than a fraction of a rephasing cycle has been completed. In the radiolysis experiment, the presence of a large number of protons generating a range of contributions to the local field give what appears to be a monotonic decay from singlet to triplet, but if the excursion were long enough the original singlet state would recur periodically. A set of magnetic field effects can be ascribed to relaxation phenomena in which spins relax to a true equilibrium and do not return to the original phasing. These are considered in the next section.

Magnetic fields have a pronounced effect on the fluorescence yield from the reactions involving charged ions[17] in fluid solutions. For example, when anthracene cations and anions A^+ and A^- are generated electrochemically in a fluid they diffuse together, and charge transfer leads to $^TA^* + A$, where $^TA^*$ is a triplet excited state. Two such triplet molecules, generated in different places, diffuse together, and when they collide energy exchange leads to an excited *singlet* anthracene molecule and a ground-state anthracene molecule. The excited singlet collapses to the ground state, and as it does so it fluoresces. The generation of light by this electrochemical redox sequence is called

electrogenerated chemiluminescence (ecl). The sequence may be written

generation: $\quad A + e^- \rightarrow A^-$
$\qquad\qquad\quad A - e^- \rightarrow A^+$
charge transfer: $\quad A^+ + A^- \rightarrow {}^TA^* + A$
energy transfer: $\quad {}^TA^* + {}^TA^* \rightarrow {}^SA^* + A$
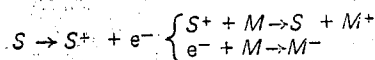fluorescence: $\qquad {}^SA^* \rightarrow A + h\nu$

The process as outlined is very similar to the sequence of triplet exciton annihilation in solids, the effect of magnetic fields on such solid state systems has been explained in detail by Johnson and Merrifield[18,19] and Frankevitch.[9] The effect of a magnetic field in solids can be understood in the same way as the inhibition of singlet–triplet rephasing already described. When two triplet excitons ($S = 1$) collide, their total overall spin may be singlet, triplet or quintet ($S = 0, 1, 2$) depending on the orientation of the spin vectors on the colliding molecules. If they happen to be in an overall singlet state, energy reorganisation to give singlet excited state plus singlet ground state may occur because it involves no change in the spin angular momentum. This energy exchange is blocked if the two triplets are triplet or quintet phased, because the reorganisation to two singlets would involve a loss of spin angular momentum. Overall quintet ($S = 2$) may, however, rephase into overall singlet under the influence of the different local magnetic fields within each triplet (these fields arising from the dipolar interactions of the electrons within each triplet) and as overall singlet is formed energy exchange and subsequent fluorescence is permitted (*Fig. 6*). In the presence of a magnetic field the five quintet orientations ($M_s = \pm 2, \pm 1, 0$) are no longer degenerate, and the only efficient rephasing channel is from the $M_s = 0$ level into the overall singlet. In this way the magnetic field inhibits singlet formation and decreases the fluorescence yield.

The Merrifield mechanism, as outlined, also accounts for the increase of fluorescence yield in the presence of doublet paramagnetic centres in solids. The magnetic field inhibits the quenching effect of the doublet centres. Inhibited quenching implies that fluorescence yield should increase with magnetic field, as is observed.

In fluid solution, the situation is complicated by the freedom of translation and rotation open to the triplet molecules and to any doublet species that may have been introduced as quencher. Nevertheless, abundant evidence confirms that the

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magnetic field effects are qualitatively the same as in solids.[17] A dynamical theory of the effect has been presented[20] which examines the overall process in the light of the steps shown in *Fig.* 7. We concentrate here on the processes that occur in the absence of any quenching agent.

The triplet excited species diffuse from their points of generation by charge transfer from pairs of radical ions, and encounter as an overall singlet, triplet, or quintet (the possible overall spin states for two $S = 1$ species). The overall singlets may pass on to give fluorescence because the energy transfer step is permitted by the overall spin. The overall triplet and quintet pairs cannot distribute their energy to give an excited singlet plus a ground state singlet. Therefore they survive the encounter (disregarding the possibility of a Merrifield type of process during contact), diffuse apart but stand a high probability of re-encounter. During their diffusional excursion, the spins of the individual triplets can relax with high efficiency on account of their strong internal spin–spin dipolar interactions. Spin relaxation means that $M_s = \pm 1$ states drop down into $M_s = 0$ and $M_s = -1$ states and *vice versa*, and that random local fields alter the precession frequencies in a random

fashion. The chaotic rephasing and transitions between the spin states mean that overall quintet phased pairs of triplets may have relaxed into a singlet-phased pair of triplets, (*Fig.* 7). If it has it may undergo energy exchange and go on to give fluorescence (we call this 'entering the fluorescent channel') if it has not it departs and dies elsewhere. The magnetic field enters the process because the spin relaxation rate is dependent on the magnetic field. In low fields the M_s-separation in the triplets are small, the relaxation efficient, and the probability of entering the fluorescent channel on re-encounter is high. In high fields the M_s-separations are large, the rephasing brought about by the relaxation is inefficient, and the entry into the fluorescent singlet channel is inhibited. This accords with the inhibition of fluorescence by the magnetic field.

In the case of quenching by a stable doublet species the following sequence occurs. The doublet (spin $\frac{1}{2}$) and the triplet (spin 1) species collide and form an overall doublet (spin $\frac{1}{2}$) or quartet (spin $\frac{3}{2}$). The former collision complex may collapse non-radiatively into an overall doublet (spin $\frac{1}{2}$) formed from the doublet (spin $\frac{1}{2}$) species plus a ground state singlet (spin 0), *Fig. 8*), but

the overall quartet will break up and separate. After the separation the doublet and unquenched triplet re-encounter, but during the excursion relaxation rephases the spins so that they may re-encounter as overall doublet. Re-encountering as overall doublet means death to the triplet but as relaxation is inhibited by the presence of the field, the life of the triplets is extended and the fluorescence (when one surviving triplet encounters another) is enhanced.

Conclusion
It should be clear from this account that magnetic fields have a pronounced effect on a wide variety of reactions. Effects in the gas phase have not been treated but these, more details, and more literature references will be found in a longer review.[1] An effect can be anticipated when triplet or higher multiplicity states are involved, or when a reaction involved a radical pair in a cage. The effect on yields may be very significant, and it is conceivable that magnetic fields might in future be invoked in industrial processes to modify the yield of isomers, separate isotopes, and distort reaction pathways in the direction of particular products.

An elementary sense of safety

Alan Robertson

The limiting constraint on a man's safety performance is that he is human and possesses all the human frailties—forgetfulness, selfishness, vanity, stupidity—and we have to recognise that we are all members of the same club.

One of the puzzling aspects of safety, is that it is continuously necessary to remind and to discipline people about it. If put at risk by others, we all get fearfully uptight, but we can cheerfully ignore or fail to identify our own sins of omission and commission.

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The human element
We must all have had experience of accident investigations, when we come back to 'human failing' and ask, 'Why on earth did he do it?' Obviously, we cannot simply throw up our arms in despair, but it does create a very difficult situation in deciding how far we go in protecting people against their own actions or lack of action.

In some ways we are schizophrenic, if we compare attitudes on the plant and in the home. We operate, usually without instruction

or training, a wide range of equipment, both electrical and mechanical—washing machines, dishwashers, carpet cleaners, floor polishers, food mixers, waste disposers, central heating boilers, electric and gas ovens, and certain garden tools. All this equipment has to meet certain minimum requirements in a safety sense, but I suspect that if it was part of manufacturing plant it would be virtually unusable because of guards, trip outs, warning lights and the other paraphernalia of our technical age. I raise the point because it does concern a crucial and controversial problem, 'What is safe?' and 'How safe is safe?' Clearly a zero risk situation would be impracticable, but what is an acceptable measure of risk? There