Magnetic field dependence of nuclear spin polarization as a criterion for the triplet-Overhauser mechanism

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Magnetic field dependence of nuclear spin polarization as a criterion for the triplet-Overhauser mechanism

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The magnetic field dependence of nuclear spin polarization effects is evaluated as a mechanistic criterion for the triplet-Overhauser mechanism. The relation between CIDNP intensity and magnetic field strength is generally complex since at least three of the four steps of this mechanism are magnetic field dependent. The effects observed during the photoreaction of trifluoroacetophenone with dimethoxybenzene in acetonitrile show a high field maximum, which is compatible with the triplet-Overhauser mechanism, and two low field maxima, which can be assigned to $S-T_+$ mixing in a radical ion pair. These assignments were confirmed by the quencher concentration dependence at the fields that give rise to maximum effects.

INTRODUCTION

The earliest examples of chemically induced nuclear spin polarization[1,2] were explained via electron–nuclear cross relaxation in *free radicals*.[3,4] However, this mechanism was soon found to be inadequate[2,4–7] and was replaced by an alternative polarization mechanism involving hyperfine induced singlet–triplet mixing in *radical pairs*.[8–11] The radical pair mechanism (RPM) has been generally accepted since it can account satisfactorily for the overwhelming majority of the nuclear spin polarization effects reported during the last twelve years.[12–15] Among the rare exceptions are several photoreactions of quinones[16–18] and ketones[19,20] for which Adrian, Vyas, and Wan have invoked the so-called triplet-Overhauser mechanism (TOM).[21,22] This mechanism requires the precise timing of four consecutive steps:

(1). Preferential intersystem crossing from a photoexcited singlet state to one of the triplet sublevels;

(2). Fast quenching of the resulting polarized triplet to generate a pair of radicals or radical ions;

(3). Electron–nuclear cross relaxation in the resulting radical (ions); and

(4). Fast degenerate exchange between nuclear spin polarized radical (ions) and their precursors to transfer the nuclear spin polarization to a diamagnetic product.

In previous publications we have evaluated potential experimental criteria, such as the dependence of the observed CIDNP intensity upon quencher concentration (which affects the rate of quenching, step (2)),[19,20,23] upon acid concentration (which affects the rate of degenerate exchange, step (4)),[20,23,24] and upon the relative orientation of the plane of polarization of linearly polarized light (which had been suggested as a criterion for step (1)).[25] In the paper presented here we evaluate the magnetic field dependence of the CIDNP intensity, which Adrian, Vyas, and Wan had suggested as a criterion for the triplet-Overhauser mechanism. The photoinduced interaction of α, α, α-trifluoroacetophenone (TFA) with 1,4-dimethoxybenzene (DMB), which had allowed us to demonstrate several other features of the triplet-Overhauser mechanism, appeared to be the system of choice. Our results show that the magnetic field dependence is complex; nevertheless when used in conjunction with other criteria, specifically with the quencher concentra-

tion dependence, it may provide useful insights as well as a strong argument for the triplet-Overhauser mechanism.

EXPERIMENTAL

The magnetic field dependence of a photoinduced CIDNP effect is determined by irradiating the sample for a specified time in a magnet with adjustable field strength and transferring it to a high resolution NMR spectrometer for measurement. It is essential that the duration of the irradiation and the interval between irradiation and measurement are reproduced as exactly as possible. An irradiation time several times the magnitude of T_1 is chosen to ensure that the polarization has reached a steady state. The delay between irradiation and measurement is dictated by the time required for sample transfer. Transfer methods that have been employed include transfer by flow as well as mechanical or manual transfer.

For the experiments reported here we used an Osram 200W high pressure mercury lamp in a Schoeffel housing and a Varian 4004 electromagnet with 2 in. pole faces and an adjustable gap, whose field can be varied between 0 G and 20 kG. The duration of irradiation was controlled by a mechanical shutter. Samples were purged with argon for 120 sec, irradiated, while spinning, for 60 sec, and transferred manually to a Jeol C60HL continuous wave NMR spectrometer. The signal intensities were measured 5 ± 0.5 sec after the irradiation had been discontinued. This instrumental setup is not universally applicable but it is sufficient to measure relatively strong CIDNP effects for nuclei with reasonably long spin lattice relaxation times and a simple absorption pattern, preferably a singlet. The system discussed here meets these conditions. Trifluoroacetophenone has a single ^{19}F signal which shows strongly enhanced absorption during the photoreaction with dimethoxybenzene and which has a reasonably long relaxation time (6 sec, in acetonitrile-d_3). Accordingly, the observed signal intensities are sufficiently reproducible to allow meaningful conclusions.

MATERIALS

Trifluoroacetophenone (Aldrich) was purified by gas chromatography (10′×3/8″ column, carbowax on Chro-

mosorb W, 100 °C). 1,4-dimethoxybenzene, and 1,4-diazabicyclooctane (Aldrich) were purified by vacuum sublimation whereas N, N, N', N'-tetramethyl-1,4-phenylenediamine (Aldrich) was used without further purification. For experiments in "neutral" solution, acetonitrile (Spectrograde, Eastman) was passed through a column of neutral alumina (Woelm); for experiments in acidic solution, the acetonitrile was acidified with known quantities of glacial acetic acid (Target).

THEORETICAL CONSIDERATIONS

The nuclear spin polarization effects P_n induced via the triplet-Overhauser mechanism can be formulated in terms of four factors:

(1). The rate ρ of generating the substrate triplet state;

(2). The initial electron polarization of the radical ions P_e;

(3). The efficiency ξ with which the electron polarization is converted to nuclear polarization and then transferred to diamagentic products; and

(4). The rate k_l of polarization loss in the diamagnetic products.

$$P_n = \rho P_e \xi / k_l \qquad (1)$$

The electron polarization of a radical (ion) generated by a bimolecular quenching reaction of an electron spin polarized triplet state has been studied in detail[11,21] and can be expressed as

$$P_e = \frac{\omega_s T_t}{\omega_{sfs}} \, {}^3T_{1e}^{-1}T^\# (2p_z - p_x - p_y) . \qquad (2)$$

In this equation, ω_s is the Zeeman splitting, ω_{sfs} is the zero-field splitting of the triplet species, p_x, p_y, p_z are the sublevel populations of the triplet immediately after it is generated, ${}^3T_{1e}$ is its electron relaxation time and $T^\#$ is the probability of quenching the electron spin polarized triplet at a quencher concentration $[Q]$ before it undergoes electron relaxation; finally, τ_t is the "rotational" correlation time of the radical ion and the triplet.

$$T^\# \propto \frac{{}^3k_q[Q]}{{}^3k_q[Q] + {}^3T_{1e}^{-1}} \qquad (3)$$

$${}^3T_{1e}^{-1} = \frac{2}{15}\omega_{sfs}^2\tau_t \left(\frac{1}{1 + \omega_s^2\tau_t^2} + \frac{4}{1 + 4\omega_s^2\tau_t^2} \right) \qquad (4)$$

Of these factors, ω_s is directly proportional to the magnetic field whereas $T^\#$ and ${}^3T_{1e}$ show a complex dependence upon the magnetic field strength.

The efficiency of the predominant cross relaxation process can be evaluated by solving the differential rate equations governing the populations of the various radical and substrate spin levels. The solutions can differ substantially, depending on the type of reaction under investigation, on the number of different nuclei in the radical intermediate and on the model chosen to represent the system. Adrian et al. have solved the equations for the simplest model, that of one nucleus of spin 1/2 interacting with one free electron spin for several reaction types.[21] For a bimolecular electron transfer reaction which ultimately regenerates the reactants, the efficiency ξ may be formulated as[21-23]

$$\xi = \frac{k_e[S](W_2 - W_0)}{4W_nW_e + 4W_2W_0 + 2(W_2 + W_0)(W_e + W_n) + \kappa k_e[S](2W_e + W_2 + W_0)} \qquad (5)$$

In this equation the rate $k_e[S]$ accounts for the transfer of nuclear spin polarization from the radical ions to the diamagnetic product by degenerate electron exchange, W_0 and W_2 are the rates of scalar and dipolar cross relaxation, respectively, and W_e and W_n are the electron and nuclear spin lattice relaxation rates of the radical ions (cf. Fig. 1). Of these, W_n is independent of the magnetic field whereas the others are magnetic field dependent (vide infra),

$$W_e, W_0, W_2 \propto \frac{1}{(1 + \omega_s^2\tau_t^2)} \qquad (6)$$

The parameter κ accounts for the fraction of substrate which is not converted to either triplets or radicals,

$$\kappa = \frac{2W_s}{\rho + k_e[S^\pm] + 2W_s} . \qquad (7)$$

Three processes contribute to the loss of polarization in the product, re-excitation (ρ), degenerate exchange ($k_e[S^\pm]$) and spin lattice relaxation (W_s). All of these terms are independent of the magnetic field strength.

$$k_l = 2(\rho + k_e[S^\pm] + 2W_s) \qquad (8)$$

In summary, the complex relation between the relaxation rates, ${}^3T_{1e}^{-1}$, W_0, W_2, and W_e, and the magnetic field strength is expected to result in a complex magnetic field dependence of Overhauser induced nuclear spin polarization effects. These considerations are borne out by the results presented and discussed below.
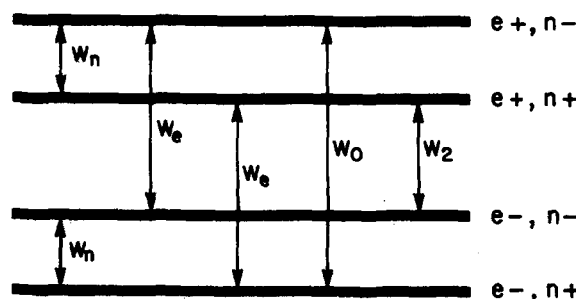

FIG. 1. Schematic representation of the relaxation processes in a system with one unpaired electron and one nucleus of spin $I = 1/2$.

RESULTS AND DISCUSSION

The irradiation of trifluoroacetophenone (TFA, 1) in the presence of electron donor quenchers such as, 1,4-dimethoxybenzene (DMB, 2), 1,4-diazabicyclo[2.2.2] octane (DABCO, 3) or tetramethylphenylene diamine (TMPD, 4) results in the formation of radical ion pairs and in the generation of strong ^{19}F polarization effects independently discovered by Thomas and Wagner[19] and in our laboratory.[19,20] These effects lend themselves readily to mechanistic investigation. In contrast to the reactions of tetrafluorobenzoquinone which allow the study of only one signal,[18,21] TFA and its derivatives allowed the investigation of no fewer than five signals representing five different types of nuclei: the ^{19}F and ^{13}C signals of the CF_3 group, the ^{13}C quartet of the carbonyl group, and the signals of ^{19}F substituents in the meta and para positions. This system has several other advantages over tetrafluorobenzoquinone: the electron donor quenchers 2–4 are readily soluble so that a wide range of quencher concentrations can be studied; and the difference between its triplet lifetime ($^3\tau \sim 1\ \mu$ sec) and its triplet spin lattice relaxation time ($^3T_{1e} \sim 1$ nsec) is substantial so that the quencher concentration dependence provides an unambiguous criterion for the nature of the precursor.[19,20] Because of the greater variety of experimental results available in this system, the polarization mechanism(s) can be identified with a high degree of confidence.

Some of the effects observed for TFA are fully compatible with the radical pair theory whereas others suggest the involvement of the triplet-Overhauser mechanism. For example, at low quencher concentrations in slightly acidic acetonitrile solutions, emission is observed for the reaction with DABCO but an A/E multiplet effect is observed for the reaction with DMB; these results reflect the different g factors of the radical cations, 6($g_6 = 2.0037$; $g_5 \approx g_6$) and 7($g_7 = 2.0040$; $g_5 < g_7$), relative to that of the radical anion 5 in full agreement with the radical pair theory.[19,20,24]

2.0035   2.0035   2.0040

   6   5   7
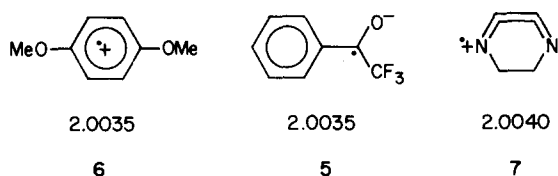
On the other hand, at high quencher concentrations in neutral solutions, strongly enhanced absorption is observed regardless of the quencher, a result which is obviously incompatible with the radical pair mechanism so that one is persuaded to consider the triplet-Overhauser mechanism. However, the TFA polarization discussed here is opposite to that of tetrafluorobenzoquinone in its reaction with tetrafluorohydroquinone.[18,21] In order for both results to be compatible with the triplet-Overhauser mechanism one of the factors determining the polarization must be different for the two reactions.

The direction of triplet-Overhauser induced polarization is determined by factors such as the initial electron polarization, the predominant mechanism of cross relaxation, and the sign of the gyromagnetic ratio γ of the type of nucleus which is polarized. The sign of γ can be eliminated as the source of the different polarizations since the same type of nucleus (^{19}F) is studied in the two systems. Similarly, the initial electron polarization can be eliminated as the source of the difference. This is suggested by the study of simple benzoquinones and phenyl ketones with optically detected magnetic resonance, which showed that the triplet sublevels of both types of compounds are populated at rates of the same ordering, $p_z > p_x$, p_y.[26,27] In addition, radicals or radical ions generated in quenching reactions of quinone triplet states showed the same electron polarization, emission, as those derived from ketone triplet states.[28–32] This leaves the mechanism of cross relaxation as a possible source of the different spin polarization effects.

The polarization observed for tetrafluorobenzoquinone can be ascribed to a very common relaxation mechanism. Rotational tumbling contributes to the relaxation of radicals or radical ions in solution. This motion modulates the anisotropic component of the hyperfine interactions and gives rise chiefly to dipolar transitions (W_2). The contributions to the relaxation rates are proportional to the square of the anisotropic component B_{zz} of the hyperfine tensor along the symmetry axis and can be formulated as[33,34]

$$W_2 = 12W; \quad W_e = 3W; \quad {}^aW_0 = 2W, \tag{9}$$

where

$$W = \frac{1}{80} \frac{B_{zz}^2 \tau_t}{\hbar^2 (1 + \omega_z^2 \tau_t^2)}, \tag{10}$$

and as

$$W_n = \frac{3}{80} \frac{B_{zz}^2 \tau_t}{\hbar^2}. \tag{11}$$

For nuclei with a positive gyromagnetic ratio (^{1}H, ^{13}C, ^{19}F) a predominantly dipolar cross relaxation mechanism will convert an electron spin level population corresponding to CIDEP emission to nuclear spin level populations corresponding to CIDNP emission. Accordingly, the ^{19}F emission observed for tetrafluorobenzoquinone is compatible with such a mechanism.

In contrast, the enhanced absorption observed for the CF_3 signal of TFA requires a different mechansim of cross relaxation for the radical anion 5. Scalar cross relaxation may be induced by the rotation of the CF_3 group relative to the unpaired electron spin.[22,33] This motion modulates the isotropic hyperfine tensor causing a scalar cross relaxation ${}^iW_{0,r}$

$$^iW_{0,r} = \frac{(\delta A)^2 \tau_r}{2\hbar(1 + \omega_z^2 \tau_r^2)} \tag{12(a)}$$

Here, δA is the mean square variation in the isotropic hyperfine coupling constant and τ_r is the rotational correlation time of the CF_3 group, which is equal to the inverse of the rotational frequency, $\tau_r = v_r^{-1}$.

An additional contribution to scalar cross relaxation ${}^iW_{0,e}$ may be caused by the fast degenerate exchange reaction between the radical anions and their diamagnetic precursors. This term is described by Eq. (12), when τ_r is the inverse of the frequency of exchange, $\tau_r = (k_e[S])^{-1}$.
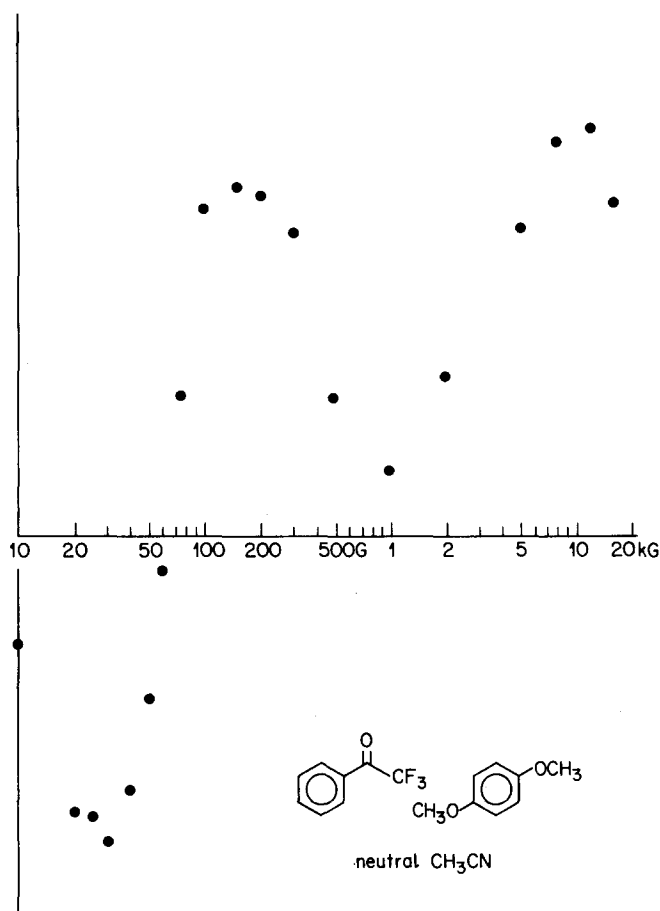
FIG. 2. Magnetic field dependence of the nuclear spin polarization effects observed in the system TFA–DMB in neutral acetonitrile (0.03 M TFA; 0.4M DMB).

$$^{i}W_{0,e} = \frac{(\delta A)^2 (k_e[S])^{-1}}{2\hbar\{1 + \omega^2(k_e[S])^{-2}\}} \qquad [12(b)]$$

Considering the large isotropic hyperfine coupling constant of TFA^{-}(4.5×10^8 rad sec^{-1}), this term may well be important. A quantitative consideration of all contributions suggests that the cross relaxation of TFA^{-}is dominated by the scalar terms.[35]

In the following we discuss the magnetic field dependence of the CF$_3$ polarization observed during the reaction of TFA with DMB in neutral acetonitrile. Under these conditions the triplet-Overhauser mechanism is likely to be involved; at least it accounts for the polarization observed at 14 kG.[20] The magnetic field dependence of this effect is shown in Fig. 2. Below ~60 G this reaction results in emission with a maximum intensity near 30 G whereas above ~60 G, up to the highest field strength investigated (20 kG), enhanced absorption is observed with maxima near 150 G and 12 kG and a minimum near 1 kG where the polarization is close to zero. The effects between 1 and 20 kG are compatible with the triplet-Overhauser mechanism and show the general trends predicted by the theory of Adrian *et al.*; in fact, they are reproduced quite well by this theory (*vide infra*).

Although such agreement between an experimental re-

sult and a theoretical model might be considered satisfactory support for the model, we considered a more rigorous comparison of experiment and theory desirable. An examination of the factors determing P_e [Eq. (2)] suggests an interrelation between field dependence and quencher concentration dependence. Because of the field dependence of the electron spin relaxation of the triplet state [Eq. (4)] the efficiency of quenching the polarized triplet [Eq. (3)] should also be field dependent. Conversely, the field dependence of this effect must be expected to depend on the quencher concentration. Accordingly, we studied the CIDNP intensity as a function of DMB concentration at several values of magnetic field strength. Obviously, the simultaneous variation of two reaction parameters is a much more rigorous test for the theory than the variation of only one parameter.

The experimental results of this double dependence are shown in Fig. 3, whereas the predictions of the theory are presented in Fig. 4. The theoretical intensities were calculated with the following parameters. Two of the rate parameters, the triplet lifetime ($^3\tau$ =6×10^{-7} sec) and the rate constant of triplet quenching (^3k_q=10^{10} l mol^{-1} sec^{-1}) were determined in the laboratory of P. J. Wagner.[36] The corresponding parameters for the singlet excited state can be derived from the CIDNP intensities at high quencher concentrations. The decline of polarization intensity at [DMB]> 2×10^{-1} M is compatible with any combination of values for ^1k_q and $^1\tau$ satisfying the relation, $^1k_q \times ^1\tau$ =0.8. The range of reasonable rate constants is limited since ^1k_q cannot be expected to be smaller than ^3k_q; the range of possible lifetimes is limited by the absence of ^{1}TFA* fluorescence. Accordingly, a value of 10^{10} l mol^{-1} sec^{-1} was used for ^1k_q and a value of 8×10^{-11} sec for $^1\tau$. For the remaining rate constants typical values for free radical recombination
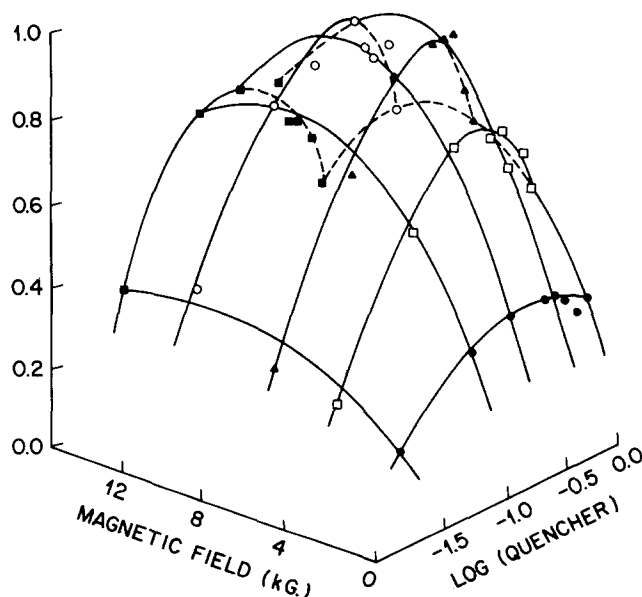

FIG. 3. ^{19}F CIDNP effects observed during the irradiation of TFA in neutral acetonitrile in the presence of DMB as a function of DMB concentration at magnetic fields of 16 kG (filled squares), 12 kG (open circles), 8 kG (filled triangles), 5 kG (open squares), and 2 kG (filled circles).
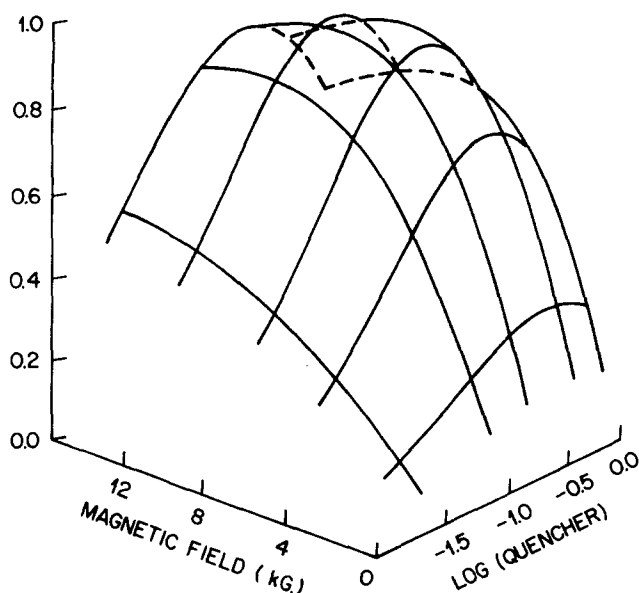
FIG. 4. Relative ^{19}F CIDNP effects predicted for the system TFA−DMB on the basis of the triplet-Overhauser mechanism as a function of DMB concentration and magnetic field.

$(k_{rec} = 10^{10}$ l mol^{-1} sec$^{-1})$ and for the degenerate electron exchange between a ketyl radical ion and its parent ketone were assumed $(k_e = 10^8$ l mol^{-1} sec$^{-1})$. [37]

The magnetic parameters needed for the simulation were assigned as follows. The values $\delta A = 31$ G and $B_{ss} = 13$ G were assigned on the basis of the isotropic hyperfine coupling, $A = 25.8$ G, [38,39] in analogy to the results observed for the radical $CF_3CFCONH_2$. [40,41] The zero-field parameter of ^{3}TFA, $D^* = 0.13$ cm^{-1}, was determined from the $\Delta m = 2$ transition of the triplet EPR spectrum of photoexcited TFA at 5 °K. The last two parameters, the correlation times for the tumbling motion (τ_t) and for the rotation of the CF_3 group (τ_r) are assigned on the basis of the following considerations. The tumbling motions of large molecules in solution are described satisfactorily by hydrodynamic theory with the conventional sticking boundary condition which yields the well-known Stokes−Einstein equation for the correlation time.

$$\tau_t = 4\pi a^3 \eta / 3kT \tag{13}$$

where a is the molecular radius and η is the viscosity of the solvent. For TFA in acetonitrile a value of 4×10^{-11} sec is calculated for τ_t using Eq. (13). However TFA is not a large molecule in the sense of this equation. It has been shown that as the molecular size decreases, Eq. (13) becomes less accurate and for small molecules correlation times calculated from it may be as much as a factor of ten too large. [42,43] Other hydrodynamic models having different boundary conditions have been formulated to predict τ_t for small molecules. [44,45] From the theory which uses a slipping boundary condition we obtain $\tau_t = 2 \times 10^{-12}$ sec. [43,44] The tumbling correlation time may also be determined from the ^{13}C nuclear spin−lattice relaxation times, [42,46,47] using

$$\tau_t = r^6 / (n\hbar^2 \gamma_H^2 \gamma_C^2 T_1) \tag{14}$$

where r is the effective carbon−hydrogen separation, n is the number of protons attached to the carbon atom and T_1 is the relaxation time due to the dipole−dipole interaction. Using the ^{13}C relaxation times determined for molecules comparable in size to TFA[47] we estimate that $\tau_t = 3 \times 10^{-12}$ sec. The assignment of the rotational correlation time τ_r for the trifluoromethyl group is based on the observation that the fluorine hyperfine coupling constants of several fluoroalkyl ketyl anions were found to be virtually temperature independent. [48] Knolle and Bolton interpreted this finding as indicating free rotation of the fluoroaklyl groups. A maximum value for the correlation time may be estimated from the linewidth (Γ) of the EPR spectrum (~ 0.5 G) using the relation[49]

$$\Gamma = \Gamma_0 + \gamma_e \tau_r (\delta A)^2 / 4 \tag{15}$$

where the limiting width (Γ_0) is set equal to zero. Using this equation, we obtain a value of 10^{-10} sec for τ_r. Since this is a maximum value, we have assumed a somewhat smaller value, $\tau_r = 3 \times 10^{-11}$ sec.

A comparison between Fig. 3 and 4 shows that the experimental results are reproduced quite well by the theory, with the possible exception of minor differences at high quencher concentrations. These differences may be related to the formation of aggregates or adducts such as the zwitterionic species 8 formed between TFA and DABCO. [50] Otherwise, however, the agreement between experiment and theory is excellent, specifically the observation that the CIDNP intensities at low quencher concentrations show maxima at higher fields than the intensities at higher quencher concentrations. This result may be ascribed to the effect of the magnetic field dependence of $^3T_{1e}$ on the quenching probability, T^* Eq. (3). Electron relaxation times of triplet states have been determined from the quencher concentration dependence of chemically induced electron[30] or nuclear polarization. [19,20] However, while previous studies were limited to one value of magnetic field strength (3 or 14 kG), the results reported here represent the first determination of these relaxation times as a function of magnetic field. The values of $^3T_{1e}$ determined from the quencher concentration dependence of the polarization at each field and those calculated from Eq. (4) (Table I) show excellent agreement. We consider this agreement strong evidence that the theory describes the triplet-Overhauser mechanism adequately and, at the same time, that this

TABLE I. Magnetic field dependence of the electron relaxation time of triplet trifluoroacetophenone.

| Field (kG)	T_{1e} (nsec)	
	calc	expt
2	0.8	1.1
5	1.0	0.9
8	1.3	0.8
12	1.8	1.2
16	2.6	2.0

mechanism is indeed the source of these spin polarization effects.
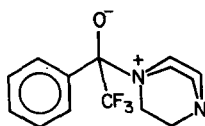
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RADICAL PAIR INDUCED POLARIZATION IN THE SYSTEM TFA-DMB

In contrast to the CIDNP absorption observed at high fields (> 1 kG), the effects at intermediate and low fields and the effects observed in acidic solutions over the entire range of magnetic field strength (Fig. 5) are incompatible with the triplet-Overhauser mechanism. All these diverse effects are likely to be generated during the interaction of radical pairs. Among these effects, the emission observed in acidic solution above 2 kG can be attributed to singlet–triplet mixing in a pair consisting of a protonated ketyl radical and a DMB radical cation. While this effect is an unexceptional example of radical pair polarization, the effects at intermediate and low fields deserve more comment. At these fields, the effects in neutral and in acidic solutions are very similar yet characteristically different: between 50 G and 1 kG enhanced absorption is observed in both solutions but the effects in acidic solution are stronger; below 50 G emission is observed in both solutions but at these low fields the effects in the neutral solution are stronger; indeed the acidic solutions show yet another crossover, to enhanced absorption below 15 G. Low-field CIDNP effects in radical pair reactions were observed as early as ten years ago.[51–53] Several theoretical models have been advanced to account for these effects.[54–62] However, even a cursory discussion of these models surpasses the scope of this paper. Moreover, the radical pair, 5–6, poses a challenge to any theoretical treatment because it contains no fewer than eighteen nuclei with significant hyperfine coupling constants,[20,38,63] even though the three ^{19}F nuclei, the six ^{1}H nuclei of the methyl groups and the two pairs of aromatic ^{1}H nuclei of 6 are magnetically equivalent both in the paramagnetic intermediates and in the diamagnetic products.

3F	25.8G	1H	5.1G
1H	4.1G	1H	3.5G
1H	1.2G	1H	1.1G

	cis	trans
2H	2.7G	3.0G
2H	1.8G	1.5G
6H	3.3G	3.5G
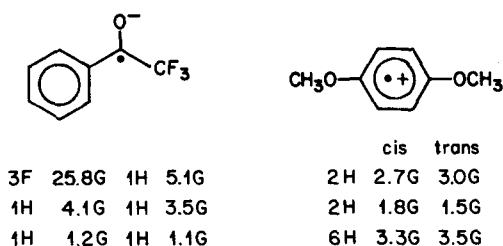
Accordingly, we limit our comments to a comparison of the low field polarization of TFA with the polarization of trichloromethane observed during the photolysis of diisopropyl ketone in tetrachloromethane[56] and with the polarization of ethane and ethane-d_3 observed during the thermolysis of acetyl peroxide and acetyl peroxide-d_3, respectively.[59,64] We note that the "oscillation" of the TFA polarization with varying magnetic field is quite
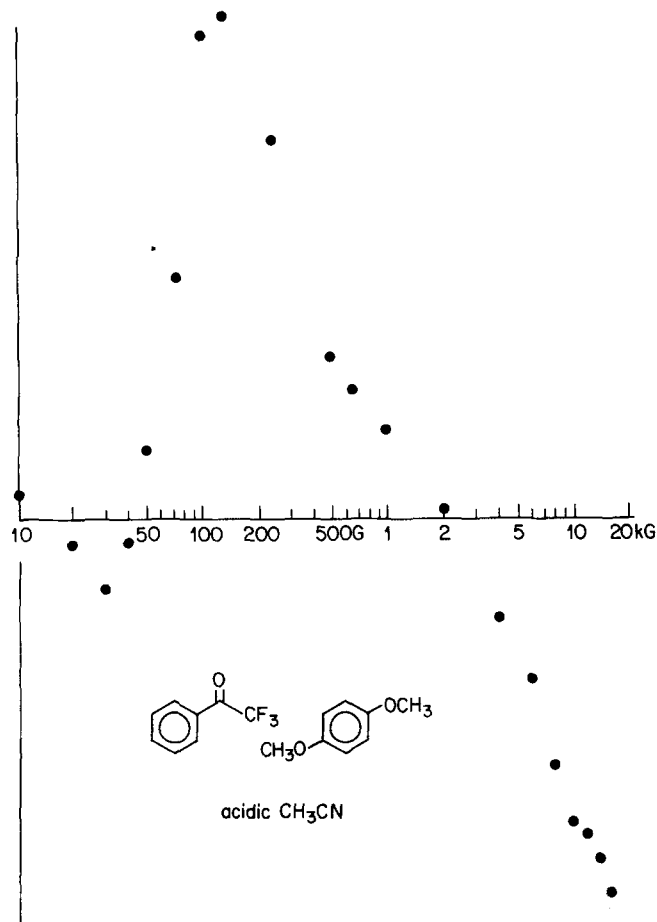
FIG. 5. Magnetic field dependence of ^{19}F CIDNP effects observed in the system TFA–DMB in acidic acetonitrile solution (3×10^{-2} M TFA; 3×10^{-3} M DMB; 2×10^{-2} M acetic acid.)

similar, though opposite in phase, to the trichloromethane polarization mentioned above, which was explained as resulting from a perturbation of the $S-T$ mixing process by the $T_\pm$ levels at intermediate fields and by $S-T_\pm$ mixing at low fields. The different phase observed for the two systems is the result of different precursor spin multiplicities: the singlet is the reactive state in the case of diisopropyl ketone whereas the triplet state of TFA is involved in the reaction with DMB. The effects observed in both reactions follow the rules derived by den Hollander for intermediate fields.[59]

The different polarization mechanisms prevailing at intermediate and low fields, respectively, and the special nature of the system TFA–DMB can account for the different intensity of the ^{19}F polarization in neutral solutions relative to that in acidic solutions at intermediate and at low fields, respectively. The polarization mechanism operative at intermediate fields is a spin sorting mechanism.[59] Such a mechanism can be rendered inefficient in a system where no net reaction occurs and where the starting material is regenerated by pair collapse as well as by a degenerate exchange reaction. In the system TFA–DMB the degenerate exchange reaction between the ketyl and the parent ketone is affected by the acidity of the solution. In neutral solution the exchange involves the ketyl anions and electron transfer; this ex-
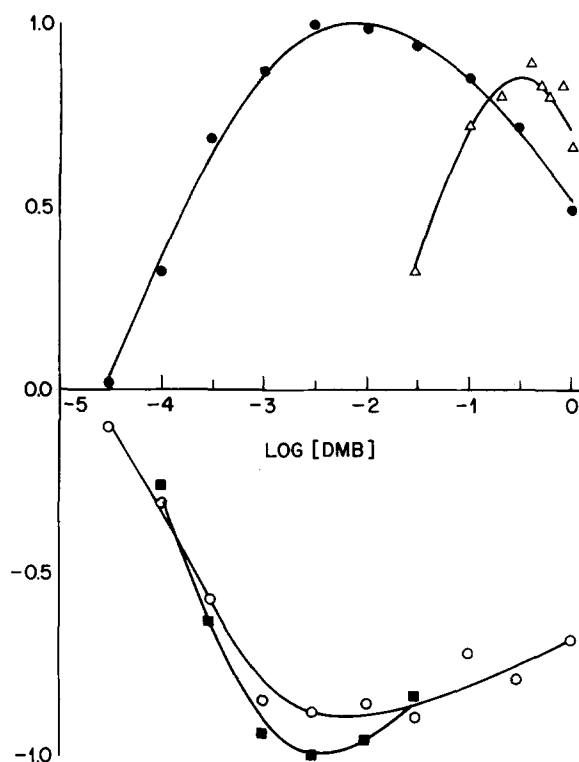
FIG. 6. Quencher concentration dependence of the nuclear spin polarization effects observed in the system TFA–DMB: (a) in neutral solution at 150 G (full circles), (b) in neutral solution at 12 kG (open triangles), (c) in neutral solution at 30 G (open circles), (d) in acidic solution at 12 kG (full squares).

change is fast and, therefore, transfers the "escape" polarization to the starting material without substantial relaxation, thus weakening the "pair collapse" polarization. In acidic solutions the exchange involves protonated ketyl radicals and hydrogen atom transfer. This exchange is slower and allows a higher degree of relaxation of the "escape" polarization. Accordingly, the polarization at intermediate fields should be stronger in acidic than in neutral solutions as observed.

At low fields, $S-T_\pm$ mixing prevails, a mechanism which generates net polarization of the same sign for products formed by pair-collapse or by a free-radical reaction.[59] Therefore, the conditions of fast exchange (neutral solutions) are expected to allow stronger effects than the conditions of slow exchange (acidic solutions), again in agreement with the experimental results.

By itself, the magnetic field dependence of the TFA polarization confirms the conclusion that the effects observed in neutral solutions at high field are due to the triplet-Overhauser mechanism whereas the results at lower fields confirm that the effects induced under these conditions are complex and that the delicate balance between different contributions is readily affected. A deeper insight into this system is gained when the magnetic field is varied in concert with the quencher concentration. We have discussed that at fields above 1 kG and quencher concentrations above 10^{-2} M this concerted variation provided a rigorous test for the theory of the triplet-Overhauser mechanism. A comparison of the

quencher concentration dependence of the maximum polarizations at low, medium, and high fields in neutral and in acidic solutions, respectively, yields an additional convincing argument for the involvement of two different triplet species and, indirectly, for the triplet-Overhauser mechanism.

Three of these quencher concentration curves, those representing the low- and medium- field polarization in neutral solutions and the high-field effects in acidic solutions, show a pronounced increase of CIDNP intensity as the quencher concentration is raised from 10^{-5} to 10^{-3} M (Fig. 6). The rise of these curves is compatible with an intermediate having a lifetime of 5×10^{-7} sec, i.e., with the involvement of triplet TFA. The fourth curve, showing the effects at high fields in neutral solutions is dramatically different. Under these conditions, CIDNP effects are only observed at quencher concentrations above 10^{-2} M suggesting an intermediate with a lifetime (or relaxation time) of 1.2×10^{-9} sec, almost three orders of magnitude shorter than that of ^{3}TFA. A relaxation time of this magnitude is typical for an electron spin polarized triplet state suggesting the involvement of the triplet-Overhauser mechanism.

The involvement of two different triplet intermediates with approximately the same difference in lifetimes was also suggested by effects observed during the reaction of m-fluoroTFA with DMB at 14 kG.[23] The line broadening effects observed during this reaction in neutral solutions and the CIDNP effects observed in acidic solutions show a quencher concentration dependence suggesting a triplet state as an intermediate whereas the CIDNP effects superimposed on the line broadening at high quencher concentrations in neutral solutions are compatible with an electron spin polarized triplet state.[23] We interpret the recurring implication of two different triplet intermediates by phenomena observed under a wide range of experimental conditions as a strong argument for the involvement of the photo triplet-Overhauser mechanism.

CONCLUSIONS

The studies reported in this paper demonstrate that the relation between nuclear spin polarization intensities and magnetic field strength is less than trivial, specifically, since the observed effects may be composed of several independent contributions. Accordingly, the magnetic field dependence of these effects cannot, by itself, be considered a satisfactory criterion for the triplet-Overhauser mechanism. However, when evaluated judiciously in the light of supplementary experimental tests, the magnetic field dependence may provide valuable mechanistic insights.

ACKNOWLEDGMENTS

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