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Electron Transfer Quenching of Fluorine Substituted Aryl Alkyl Ketones. ^{19}F Polarization via the Triplet Mechanism

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Abstract: The interaction of photoexcited α.α,α-trifluoroacetophenone (**1**) and several of its derivatives with dimethoxybenzene (**3**) results in concentration and acidity dependent ^{19}F polarization. The effects observed at low concentrations and in acidic solutions are compatible with the radical pair theory whereas the results obtained at high reactant concentrations in neutral solutions can be explained by a mechanism involving preferential intersystem crossing to one triplet sublevel, fast electron transfer quenching of the polarized triplet. and electron–nuclear cross relaxation in the resulting radical ions. The signal direction observed for the CF_3 group (enhanced absorption) can be explained by predominantly scalar cross relaxation. whereas the emission observed for meta and para fluorines requires a predominantly dipolar cross relaxation mechanisms. The kinetic requirements for this polarization mechanism are delineated and the probability of quenching an electron spin polarized triplet is formulated.

Ten years ago, the first reported cases of chemically induced nuclear spin polarization[1,2] were explained by invoking a mechanism featuring electron–nuclear cross relaxation in free radicals[3,4] in a way similar to the Overhauser effect. However, this mechanism was soon found to be unsatisfactory because it fails to explain or is in conflict with experimental results such as the multiplet effect[2,4] and the dependence on the mechanism of product formation[5] or the spin multiplicity of the precursor.[6] An alternative polarization mechanism, proposed by Closs and co-workers[7] and by Kaptein,[8] is based on hyperfine induced singlet–triplet mixing in radical pairs. This so-called radical pair theory, in the initially proposed form or in later, refined versions,[9,10] has been remarkably successful and can account satisfactorily for the overwhelming majority of nuclear spin polarization effects reported during the last 10 years.[11-14]

Nevertheless, the nuclear spin polarization phenomena observed in a limited number of reactions are not compatible with the radical pair theory. Among these are the effects observed in the following reactions: the irradiation of anthraquinone[15] and several derivatives of benzoquinone[16] as well as phenazine[17] and several diazanaphthalenes[18] in the apparent absence of a reaction partner; the photolysis of pyruvic acid;[19] and the illumination of benzoquinone or tetrafluorobenzoquinone in the presence of suitable reactants.[20,21] The effects observed in these reactions have been explained by mechanistic schemes involving a cross relaxation step.

In continuing our studies of potential electron transfer reactions by the CIDNP technique[22-25] we have recently reported CIDNP effects observed during the irradiation of α,α,α-trifluoroacetophenone (**1**, TFA) in the presence of 1,4-diazabicylo[2.2.2]octane (**2**, Dabco) or 1,4-dimethoxybenzene (**3, DMB**). These results were independently observed by Thomas and Wagner.[26] The intensity, signal direction, and mode of these effects depend on the concentration of both quencher and ketone, an observation which led us to conclude that two different polarization mechanisms are operative in this system. The polarization observed at low concentrations of quencher and ketone is compatible with the radical pair theory whereas the polarization observed at higher concentrations of the reactants is compatible with the so-called triplet mechanism.[20,21]

In this publication, we present a more detailed discussion of the system TFA–DMB, including the kinetic formulation of the probability of quenching an electron spin polarized triplet state. In addition, we discuss the acidity dependence of the polarization at high quencher concentrations and we report CIDNP effects observed during the electron transfer quenching of the *m*- and *p*-fluoro derivatives of TFA and of two homologues, pentafluoropropiophenone and heptafluo-

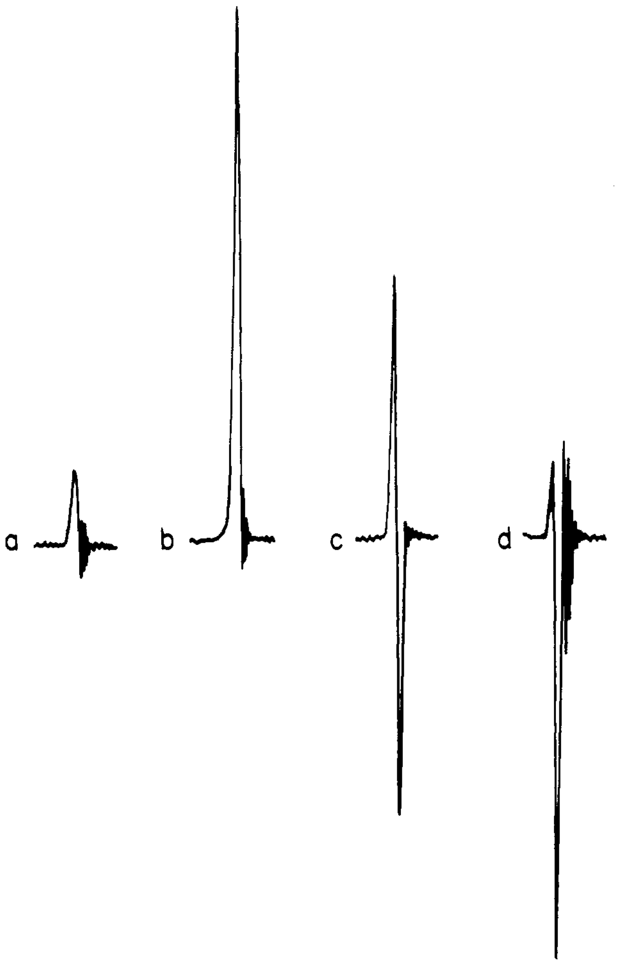


Figure 1. ^{19}F NMR spectrum (56.4 MHz) of a 0.03 M solution of TFA in the dark (a) and during irradiation in the presence of 0.2 M DMB in neutral acetonitrile (b) and after addition of 2×10^{-2} M (c) and 9×10^{-2} M acetic acid (d), respectively.

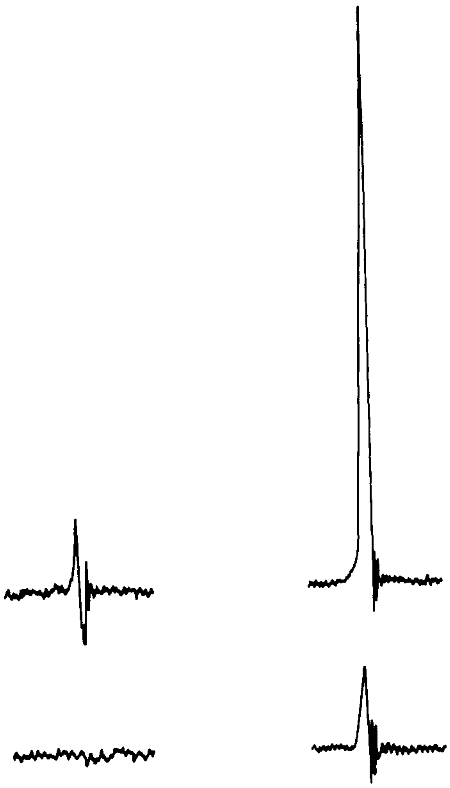


Figure 2. ^{19}F NMR spectra (56.4 MHz) of acetonitrile solutions containing 0.2 M DMB and either 10^{-4} M (left) or 10^{-1} M TFA (right) in the dark (bottom) and during irradiation (top) with UV light.

robutyrophenone. These results can be interpreted as additional evidence for an Overhauser type mechanism making the system TFA–DMB a well-documented example of nuclear spin polarization via the triplet mechanism, perhaps the most convincing case as yet.

Experimental Section

Materials. Trifluoroacetophenone (Aldrich), its *m*- and *p*-fluoro derivatives (Columbia Organic), and pentafluoropropiophenone and heptafluorobutyrophenone (Aldrich) were purified by gas chromatography (10-ft column of 20% Carbowax on Chromosorb, 100 °C). The quenchers, 1,4-dimethoxybenzene and 1,4-diazabicyclo[2.2.2]-octane (Aldrich), were purified by vacuum sublimation. For the ^{19}F NMR experiments acetonitrile (MCB, spectroquality) was used as solvent; it was purified by passing through a column of neutral aluminum oxide, Woelm. For the ^1H NMR experiments acetonitrile-d_3 (Merck Sharp and Dohme) was used after similar purification. To achieve reproducible results we found it essential to purify the acetophenones and the solvent immediately before preparing the samples and to deaerate the samples by purging thoroughly with argon immediately before irradiation.

Apparatus. The NMR spectra were recorded on a Jeolco JNM-C-60HL spectrometer (56.4 MHz for ^{19}F, 60 MHz for ^1H) or on a Bruker WH90 Fourier transform spectrometer (84.6 MHz for ^{19}F, 90 MHz for ^1H). The probe of the Jeolco instrument was modified by the manufacturer to permit UV irradiation of the samples in the area of the receiver coil. The light source is mounted on an optical bench positioned on top of the instrument. A collimated beam is reflected first by a front-side aluminum mirror to enter the probe in a direction parallel to the sample tube and then by a second mirror onto the receiver coil. The rear wall of the all-quartz insert is covered with an aluminum film. The probe of the Bruker instrument has a quartz insert and a receiver coil with spaced turns and is constructed to permit irradiation of the sample in the receiver coil area from the rear of the instrument without requiring mirrors. An Osram 200-W high-pressure mercury lamp or an Oriel 1000-W high-pressure mercury lamp, filtered through a 9-cm water filter, was used as the light source.

Results

α,α,α-Trifluoroacetophenone (**1**), its *m*- (**4**) and *p*-fluoro (**5**) derivatives, and pentafluoropropiophenone (**6**, PFP) and heptafluorobutyrophenone (**7**, HFB) were irradiated in acetonitrile solutions containing DMB and Dabco as quenchers. As the concentrations of ketones and quenchers were varied systematically, the following results were observed. At TFA concentrations, [**1**] = 0.03 M, the CF_3 signal showed enhanced absorption (A) for Dabco concentrations [**2**] $> 10^{-2}$ M, emission (E) for [**2**] $< 10^{-3}$ M, whereas with DMB as quencher A was observed for [**3**] $> 10^{-2}$ M (Figure 1b) and an A/E multiplet effect for [**3**] $> 10^{-2}$ M (Figure 1b) and an A/E multiplet effect for [**3**] $< 10^{-3}$ M. At constant DMB concentration, [**3**] = 0.2 M, the observed effects showed a dependence on the concentration of TFA: A was observed for [**1**] $> 10^{-3}$ M whereas an A/E multiplet effect is found for [**1**] $\leqslant 10^{-3}$ M (Figure 2).

The acidity of the solutions has a pronounced effect on the experimental results. The enhanced absorption observed at high concentrations of TFA and DMB (Figure 1b) can be changed to a strong A/E effect by acidifying the solutions with 2×10^{-2} M acetic acid or 8×10^{-5} M hydrochloric acid (Figure 1c). Increasing the acidity to 9×10^{-2} M acetic acid or 10^{-3} M hydrochloric acid leads to the observation of strong emission (Figure 1d).

The results observed for the CF_3 signals of *m*-F-TFA (**4**) and *p*-F-TFA (**5**) are similar to those found for TFA; strongly enhanced absorption was observed at ketone concentrations, [**4**], [**5**] $\geqslant 0.02$ M, and at DMB concentrations, [**2**] $\geqslant 10^{-3}$ M.

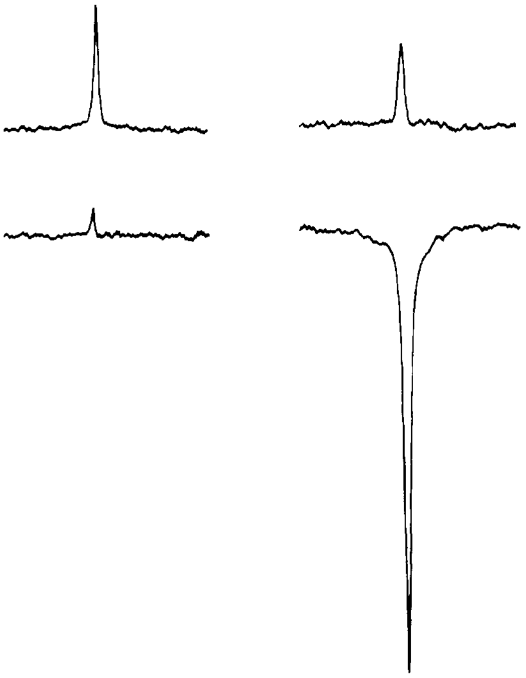


Figure 3. ^{19}F signals of *m*-fluorotrifluoroacetophenone (left) and of the para isomer (right), 0.03 M in CD_3CN solutions containing 0.2 M dimethoxybenzene. The top spectra were recorded in the dark, the bottom ones during UV irradiation.

Table I. Triplet Energies and Reduction Potentials of Fluorine-Substituted Ketones

			$E_{ox} - E_{red}$, V	
Ketone	E_T, eV[a]	E_{red}, V[b]	DMB	Dabco
$C_6H_5COCF_3$	3.06	−1.40	2.74	2.08
m-$FC_6H_4COCF_3$	3.05	−1.21	2.55	1.89
p-$FC_6H_4COCF_3$	3.08	−1.39	2.73	2.07
$C_6H_5COC_2F_5$	3.03	*c*		
$C_6H_5COC_3F_7$	3.00	*c*		

[a] From the position of the 0-0 phosphorescence band measured in methylcyclohexane at 77 K. [b] Measured in *N,N*-dimethylformamide solutions vs. SCE. [c] The reduction of these compounds was not reversible. Their reduction wave occurred at a slightly less negative potential than that of TFA.

Under the same conditions, the signals representing the fluorine atoms of the aromatic ring showed emission in the case of the para isomer and decreased absorption (i.e., net emission) in the case of the meta isomer (Figure 3). Since the aromatic ^{19}F nuclei, particularly that of the meta isomer, are represented by complex multiplets, it was advantageous to study the fully proton-decoupled spectra. At high quencher concentrations, the CIDNP effects observed for the CF_3 groups of **4** and **5** showed an acidity dependence analogous to that of **1**. The higher homologues of TFA, pentafluoropropiophenone and heptafluorobutyrophenone, when irradiated in neutral solutions containing DMB or Dabco, showed enhanced absorption for the α fluorine atoms but no significant effects for the signals representing the β and γ fluorine atoms.

Discussion

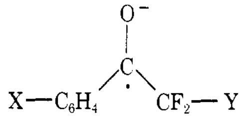
Energetics. The key reaction underlying the effects at both high and low quencher concentrations is the electron transfer from quencher to photoexcited ketone resulting in the formation of radical ion pairs. The generation of nuclear spin polarization by either radical pair or triplet mechanism requires that some of these pairs are separated by diffusion. The change in free energy (ΔG) for this reaction can be calculated from the equation[27]

$$\Delta G = E_{ox} - E_{red} - E_T - e^2/\epsilon a - T\Delta S$$

where E_{ox} and E_{red} are the one-electron oxidation potential of the quencher and the one-electron reduction potential of the ketone, respectively; E_T is the triplet excitation energy (0-0 transition) of the ketone; $e^2/\epsilon a$ is a Coulomb term which accounts for ion pairing; and $T\Delta S$ is an entropy term.

For the systems discussed here, these terms have the following values: the triplet energy of TFA is 3.06 eV,[28] the other ketones have similar triplet energies (Table I); the one-electron reduction potential of TFA has been reported as −1.42 V vs. SCE,[28] the other ketones have similar reduction potentials (Table I); the one-electron oxidation potentials of DMB and Dabco are +1.34[29] and +0.68 V,[30] respectively, vs. SCE. The entropy of formation of a radical ion pair should be somewhat smaller than that of an exciplex (−18 eu)[31] so that the entropy term is not likely to be larger than 0.2 eV. These data suggest that the electron transfer from Dabco or DMB to TFA and its derivatives to form radical ion pairs is energetically feasible.

Polarization via the Radical Pair Mechanism. An examination of the spin polarization effects in terms of the formalism suggested by Kaptein[32] reveals that the effects observed at low reactant concentration are compatible with the radical pair mechanism. The polarization determining parameters can be assigned as follows: the intermediate ion pairs, **8-9** or **8-10**,



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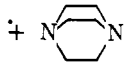
a, X = H; Y = F
b, X = *m*-F; Y = F
c, X = *p*-F; Y = F
d, X = H; Y = CF_3
e, X = H; Y = C_2F_5



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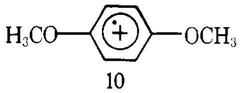

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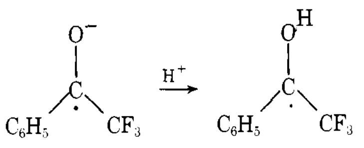
are generated from triplet precursors ($\mu > 0$); these pairs regenerate the diamagnetic precursors by in-cage electron return ($\epsilon > 0$); the sign of the ^{19}F hyperfine coupling constant of $TFA^{-}\cdot$ (**8a**) is assigned in analogy to known β fluorine coupling constants[33-35] and on the basis of CIDNP experiments involving hydrogen abstraction by ^3TFA from phenol[36] ($a_F > 0$); for the reaction of TFA with Dabco, the *g* factor of the ketyl anion ($TFA^{-}\cdot$, $g = 2.0037$)[37] is smaller than that of the radical cation (**9**, $g = 2.0040$).[37] Consequently, this reaction is expected to produce a net effect ($\Gamma < 0$, emission) in agreement with the experimental result.

In the case of quenching by DMB, the *g* factor of the radical cation (**10**, $g = 2.0037$)[38] is nearly equal to that of $TFA^{-}\cdot$ so that a multiplet effect is expected. The multiplet phase is determined by μ, ϵ, and a_F, as discussed above, and by three additional parameters. The CF_3 group of TFA is weakly coupled to the ortho protons of the phenyl ring ($^5J_{H,F} \approx +1$ Hz); in analogy to the ortho protons of the benzyl radical ($a_H < 0$),[39] a negative hyperfine coupling constant is assumed for these protons in $TFA^{-}\cdot$. The parameter σ, accounting for the relative position of the coupled nuclei, is positive by definition.[32] These parameters lead one to expect an A/E multiplet effect in agreement with the experimental result (Figure 2).

The net emission observed during the quenching of photoexcited TFA by DMB in acidic solutions (e.g., Figure 1d) was first reported by Thomas and Wagner[40] and can be explained by assuming a protonated ketyl, **11a**, paired with the DMB radical cation, **10**, as intermediates. The *g* factor of **11a** is expected to be somewhat smaller than that of **8a**. In analogy to the difference between the dimethyl ketyl anion and the dimethylhydroxymethyl radical[41] the difference is estimated



8a **11a**

at 2 × 10^{-4}, placing the g factor of **11a** near 2.0035. Consequently, the g factor difference, $g_{11a} - g_{10}$, appears marginally sufficient for a net effect ($\Delta g < 0$; μ, ϵ, $a > 0$; therefore $\Gamma < 0$).

The results observed at higher Dabco concentrations, [**2**] $> 10^{-2}$ M, could be explained if the pair, **8a–9**, were generated from a singlet precursor, i.e., if excited-singlet TFA were quenched preferentially. However, the crossover from E to A occurs at a quencher concentration where no more than a few percent of singlet quenching is plausible[26] (vide infra). Alternatively, the results could be explained if the higher Dabco concentrations would favor a different reaction, such as hydrogen abstraction. This process would produce a different pair of radical intermediates, **11a–12,** with $\Delta g > 0$. However, such a change in mechanism as a function of quencher concentration is not very plausible and is without precedent. Similarly, the change from net to multiplet effect at low concentrations of DMB to net effect at high DMB concentrations could be explained by a change in mechanism from electron transfer to hydrogen abstraction. The radical pair, **11a–13,** that would

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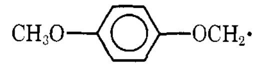

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result from this reaction has a g factor difference ($\Delta g > 0$) which could account for the observed enhanced absorption. However, the failure to observe products of ketone reduction even after prolonged irradiation does not appear to be compatible with a mechanism involving hydrogen abstraction and a sudden change in mechanism again is without precedent. Hence, the radical pair theory fails to explain the CIDNP effects observed at high concentrations of Dabco or DMB. Because of this failure, we examine the feasibility of nuclear spin polarization via the triplet mechanism.[20,21]

The Triplet Mechanism. In addition to singlet-triplet mixing in a radical pair followed by an electron spin dependent radical pair reaction, nuclear spin polarization can be induced by electron-nuclear cross relaxation in an electron spin polarized intermediate. This mechanism depends crucially on the appropriate timing of a sequence of key steps. In a strong magnetic field, the intersystem crossing of an excited-singlet state can preferentially populate one triplet sublevel, resulting in an electron spin polarized triplet (eq 1). Electron nuclear cross relaxation within the triplet (eq 2) has been considered[15-18] but is not very probable because the electron spin relaxation of triplets (eq 3) is assumed to be exceedingly fast,[42] probably orders of magnitude faster than the cross relaxation step. However, the electron polarization can be transferred to radicals or radical ions if the triplet undergoes a chemical reaction (eq 4) at a rate, ${}^3k_r$ [Q], which is competitive with that of electron spin relaxation. An efficient polarization transfer requires reactions at close to diffusion-controlled rates.

Since the electron spin relaxation of doublets (eq 5) is considerably slower than is that of triplets, electron–nuclear cross relaxation (eq 6) may compete with the relaxation process, thus leading to nuclear spin polarized radicals or radical ions. A subsequent degenerate exchange process (eq 7) will transfer the nuclear spin polarization to a diamagnetic molecule, where it may be observed if the exchange reaction is sufficiently fast to prevent excessive nuclear spin lattice relaxation (eq 8). These steps and their first-order rate constants are summarized below for the reaction of a ketone, K, with a quencher, Q. In this scheme, * denotes an excited state, and ‡ and † denote electron polarization and nuclear polarization, respectively.

$$
\begin{array}{lll}
{}^1\mathrm{K}^* \rightarrow {}^3\mathrm{K}^{\ddagger} & & (1) \\
{}^3\mathrm{K}^{\ddagger} \rightarrow {}^3\mathrm{K}^{\dagger} & {}^3k_{\mathrm{cr}} & (2) \\
{}^3\mathrm{K}^{\ddagger} \rightarrow {}^3\mathrm{K} & T_{1,\mathrm{t}}^{-1} & (3) \\
{}^3\mathrm{K}^{\ddagger} + \mathrm{Q} \rightarrow {}^{\ddagger}\mathrm{K}^{-}\cdot + \mathrm{Q}^{+}\cdot & {}^3k_{\mathrm{r}}[\mathrm{Q}] & (4) \\
{}^{\ddagger}\mathrm{K}^{-}\cdot \rightarrow \mathrm{K}^{-}\cdot & T_{1,\mathrm{e}}^{-1} & (5) \\
{}^{\ddagger}\mathrm{K}^{-}\cdot \rightarrow {}^{\dagger}\mathrm{K}^{-}\cdot & k_{\mathrm{cr}} & (6) \\
{}^{\dagger}\mathrm{K}^{-}\cdot + \mathrm{K} \rightarrow {}^{\dagger}\mathrm{K} + \mathrm{K}^{-}\cdot & k_{\mathrm{e}}[\mathrm{K}] & (7) \\
{}^{\dagger}\mathrm{K}^{-}\cdot \rightarrow \mathrm{K}^{-}\cdot & T_{1,\mathrm{n}}^{-1} & (8)
\end{array}
$$

The principal elements of this scheme had been considered by Closs and Closs for the photoreactions of benzophenone and diphenylmethylene with benzylic hydrogen donors.[43] However, the rates of hydrogen abstraction in these systems are too slow to compete with the electron spin relaxation of the triplet intermediates. Several years later, Wan and co-workers revived this mechanism to explain several cases of electron and of nuclear spin polarization. As a result of their work, reactions of the type represented by eq 1 and 4 are generally accepted as the key steps in generating the electron spin polarization effects in several photoreactions of quinones and ketones.[44-47] The additional cross relaxation step, eq 6, is considered to be the key to the nuclear spin polarization observed for several quinones.[20,21]

For the aryl fluoroalkyl ketone reactions discussed here, the key steps for nuclear spin polarization via the triplet mechanism appear kinetically feasible. At quencher concentrations, $[\mathrm{Q}] > 10^{-2}$ M, the rate of triplet quenching (${}^3k_q > 10^{10}$ M^{-1} s^{-1})[26] should be sufficiently fast to compete with the electron spin relaxation of the triplets, provided that their relaxation rates are not substantially faster than known relaxation rates of triplet states (e.g. duroquinone, $T_{1,\mathrm{t}} = 2.7 \times 10^{-9}$ s).[45] Because of their large ^{19}F hyperfine coupling constants ($a \sim 27$ G)[37,48] the radical ions, **8,** appear well suited for the cross relaxation step considering that $k_{\mathrm{cr}} \propto a^2$.[49] The third requirement, $k_{\mathrm{e}}[\mathrm{K}] > T_{1,\mathrm{n}}^{-1}$, appears to be met as well. Nuclear spin lattice relaxation times of radicals are equal to or larger than 10^{-6} s.[50,51] The degenerate exchange reaction (eq 7) can compete favorably with this process at ketone concentrations $> 10^{-3}$ M, if k_{e} is as large as that reported for the benzophenone ketyl anion ($k_{\mathrm{e}} = 10^8$ M^{-1} s^{-1}).[52]

Concentration Dependence. Two of the essential steps of the triplet mechanism, the quenching reaction (eq 4) and the exchange process (eq 7), are bimolecular reactions competing with unimolecular relaxation processes (eq 3, 5). Therefore, the efficiency of nuclear spin polarization via the triplet mechanism can be expected to show a pronounced dependence on the concentration of both reactants. The potential significance of the triplet mechanism for the observed polarization can be evaluated by comparing the concentration dependence of the observed effects with the probability, $T^{\ddagger}$, of quenching an electron polarized triplet and with the probabilities, S and T^*, of quenching a singlet and a relaxed triplet, respectively. In general, the probability of quenching a photoexcited state depends on the rate of quenching relative to the rate of decay in the absence of quenching (τ^{-1}):

$$P = \frac{k_q[\mathrm{Q}]}{k_q[\mathrm{Q}] + \tau^{-1}} = \frac{1}{1 + \dfrac{\tau^{-1}}{k_q[\mathrm{Q}]}}$$

The probability of quenching a state which is formed by decay of a photoexcited precursor depends, in addition, on the unquenched fraction of the precursor state and on the quantum

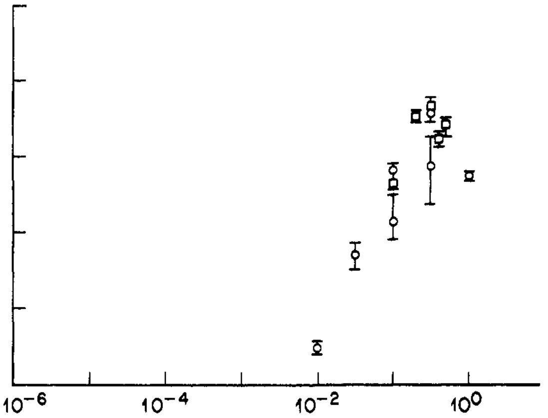

Figure 4. ^{19}F signal intensities of polarized TFA during the electron transfer quenching of ^{3}TFA by DMB as a function of DMB concentration.

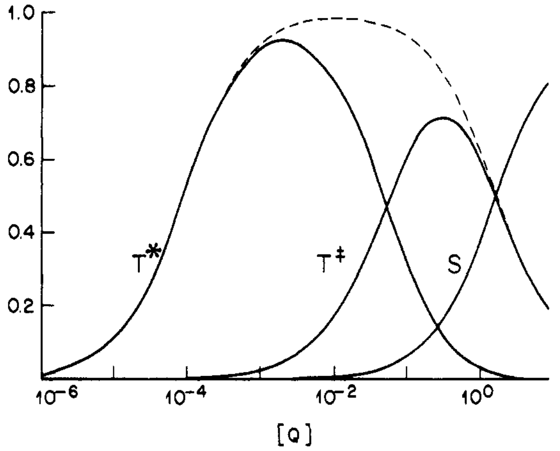

Figure 5. Quenching probabilities of singlet TFA (S), nonrelaxed triplet TFA ($T^{\ddagger}$), and relaxed triplet TFA (T^*) by DMB as a function of DMB concentration. The dashed curve indicates the total triplet quenching probability (T).

yield of formation in the absence of quenching:

$$P_s = \frac{{}^s k_q[\mathrm{Q}]}{{}^s k_q[\mathrm{Q}] + \tau_s^{-1}}(1 - P)\Phi$$

$$= \frac{{}^s k_q[\mathrm{Q}]}{{}^s k_q[\mathrm{Q}] + \tau_s^{-1}} \frac{\tau^{-1}}{k_q[\mathrm{Q}] + \tau^{-1}} \Phi$$

Assuming that intersystem crossing is the only route of decay of ^{1}TFA*, i.e., $\Phi_{isc} = 1$, and that the rate of decay to the ground state is considerably slower than the relaxation of ‡TFA, i.e., $T_{1,t}^{-1}/(T_{1,t}^{-1} + {}^3\tau^{-1}) \approx 1$, the probabilities of quenching the consecutively arising states, singlet, polarized triplet, and relaxed triplet, become

$$S = \frac{{}^1k_q[\mathrm{Q}]}{{}^1k_q[\mathrm{Q}] + {}^1\tau^{-1}}$$

$$T^{\ddagger} = \frac{{}^3k_q[\mathrm{Q}]}{{}^3k_q[\mathrm{Q}] + T_{1,t}^{-1}} \frac{{}^1\tau^{-1}}{{}^1k_q[\mathrm{Q}] + {}^1\tau^{-1}}$$

$$T^* = \frac{{}^3k_q[\mathrm{Q}]}{{}^3k_q[\mathrm{Q}] + {}^3\tau^{-1}} \frac{T_{1,t}^{-1}}{{}^3k_q[\mathrm{Q}] + T_{1,t}^{-1}} \frac{{}^1\tau^{-1}}{{}^1k_q[\mathrm{Q}] + {}^1\tau^{-1}}$$

The concentration dependence of the CIDNP intensities observed during the quenching of TFA by DMB is shown in Figure 4. Similar results were observed for the other ketones studied, e.g., for the CF_2 groups of **6** and for both the CF_3 groups (enhanced absorption) and the p-F signal (emission) of **5**. For comparison, the concentration dependence of the probabilities, S, $T^{\ddagger}$, and T^*, is shown in Figure 5. These curves are calculated using the following rate parameters: a triplet lifetime, ${}^3\tau = 6 \times 10^{-7}$ s, as measured by Wagner and Lam; a rate constant of triplet quenching, ${}^3k_q = 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, as derived by the same authors; a rate constant of singlet quenching, ${}^1k_q$, assumed to be equal to ${}^3k_q$; and a singlet lifetime, ${}^1\tau \approx 3 \times 10^{-11}$ s.

The experimental results (Figure 4) are incompatible with quenching either the relaxed triplet (Figure 5, curve T^*; ${}^3\tau = 6 \times 10^{-7}$ s) or the singlet state of TFA (Figure 5, curve S; ${}^1\tau \approx 3 \times 10^{-11}$ s). Instead, they indicate an intermediate with a "lifetime" near 2×10^{-9} s. The curve $T^{\ddagger}$, calculated from the above parameters and using a relaxation time, $T_{1,t} = 2 \times 10^{-9}$, parallels the increase in signal intensity and has a maximum near the concentration (0.3 M) for which the experimental maximum is observed. The obvious agreement between the observed CIDNP intensity and a quenching probability calculated with an electron spin relaxation time which is quite reasonable for a triplet state is a strong argument for the involvement of the triplet mechanism.

Because of the importance of this kinetic analysis as an argument for the triplet mechanism, we consider the effects of errors in the rate parameters on the quenching probability $T^{\ddagger}$ or on the derived relaxation time, $T_{1,t}$. The rise of each curve with increasing quencher concentration is determined by the rate of quenching relative to the rate of decay or, in the case of $T^{\ddagger}$, the rate of relaxation. Shorter relaxation or lifetimes (i.e., greater decay rates) or lower quenching rate constants would shift the curves toward higher quencher concentrations; longer relaxation or lifetimes and higher quenching rate constants would shift them toward lower concentrations. Of the parameters determining the rise of curve $T^{\ddagger}$, the rate constant of triplet quenching by DMB has been measured and should be accurate to within 10%. A change of this magnitude, even an error of 20%, does not have a substantial effect on either the relaxation time $T_{1,t}$ or on the curve $T^{\ddagger}$. An error in the assumed quantum yield of intersystem crossing would affect the maximum of $T^{\ddagger}$ but would not affect the quencher concentration where it occurs. The position of the maximum can be affected by a change in the singlet quenching probability, i.e., by an error in the assumed singlet lifetime or in the assumed rate of singlet quenching. We consider it unlikely that ${}^1k_q$ differs significantly from the diffusion controlled value of ${}^3k_q$; the value of the singlet lifetime is less certain. We have considered lifetimes within the range $10^{-10}\ \mathrm{s} > {}^1\tau > 10^{-11}$ s. Over this range, the concentration for which the maximum is expected varies between 0.18 M and 0.56 M; the experimental maximum near 0.3 M fits best a singlet lifetime near 3×10^{-11} s.

In summary, the experimentally observed increase of CIDNP intensity with quencher concentration can be reproduced by a kinetic model with $T_{1,t} \approx 2 \times 10^{-9}$ s and ${}^1\tau \approx 3 \times 10^{-11}$ s. We consider this agreement a strong argument in favor of the triplet mechanism.

Competition of Radical Pair and Triplet Mechanism. An appropriate ketone concentration is crucial for the observation of nuclear spin polarization via the triplet mechanism because it provides a mechanism to eliminate any polarization due to the radical pair mechanism. In most systems, the radical pair polarization predominates because it is developed on a much faster time scale[7-10] and because the expected enhancement factors are larger.[21] In addition, since the radical ions are generated in pairs (cf. eq 4), the radical pair mechanism should be operative over the entire concentration range where triplet quenching is observed. The probability of generating CIDNP via the radical pair mechanism should, therefore, be proportional to the sum, T, of curves T^* and $T^{\ddagger}$ (Figure 5).

However, the radical pair mechanism can be rendered inefficient in systems where no net reaction occurs and where the lifetime of the free radicals (ions) with respect to a degenerate exchange reaction (e.g., electron exchange, eq 7) is sufficiently short to prevent appreciable spin-lattice relaxation (eq 8). Under these conditions, the in-cage polarization (eq 9) and the escape polarization (eq 11), identical in magnitude but opposite in sign, may cancel each other. (In these equations, a *dagger* denotes in-cage polarization; an *inverted dagger* denotes the escape polarization.)

$$^{1}\overline{{}^{\dagger}K^{-}\cdot + Q^{+}\cdot} \rightarrow {}^{\dagger}K + Q \qquad (9)$$

$$^{3}\overline{{}^{\rotatebox[origin=c]{180}{$\dagger$}}K^{-}\cdot + Q^{+}\cdot} \rightarrow {}^{\rotatebox[origin=c]{180}{$\dagger$}}K^{-}\cdot + Q^{+}\cdot \qquad (10)$$

$${}^{\rotatebox[origin=c]{180}{$\dagger$}}K^{-}\cdot + K \rightarrow {}^{\rotatebox[origin=c]{180}{$\dagger$}}K + K^{-}\cdot \qquad (11)$$

The cancellation of in-cage and escape polarization is fortuitous and may be avoided by increasing the lifetime of the radical or radical ion intermediate, which is inversely proportional to the rate constant of exchange and to the ketone concentration, $\tau_r \propto (k_e \times [K])^{-1}$. We studied the TFA concentration dependence at a quencher concentration where the quenching probability, $T^{\ddagger}$, is high ([DMB] = 0.2 M). For TFA concentrations between 1 M and 3×10^{-3} M, enhanced absorption was observed, the effect ascribed to the triplet mechanism. However, at lower TFA concentrations, between 10^{-3} and 10^{-4} M, an A/E multiplet effect was observed (Figure 2), which can only be explained on the basis of the radical pair theory (vide supra). Apparently, the fortuitous cancellation of in-cage and escape polarization is no longer effective at these ketone concentrations. Assuming an electron exchange rate constant similar to that for the exchange between diphenylketyl and benzophenone (10^{8} M^{-1} s^{-1}) our results suggest that the spin-lattice relaxation of **8a** becomes significant for lifetimes of 10^{-5} s. A similar concentration-dependent change from triplet mechanism to radical pair polarization was postulated to account for the effects observed during the photolysis of benzoquinone in trichloromethane (net emission at high quinone concentrations, enhanced absorption at low quinone concentrations).[21]

The prevailing polarization mechanism should also depend on the rate constant of degenerate exchange. We attempted to affect this parameter by varying the acidity of the solutions and the reaction temperature. Protonation of a fraction of the radical ions creates a dynamic equilibrium between **8a** and **11a** and, therefore, is expected to lower the effective rate constant of exchange since hydrogen atom transfer is slower than electron transfer.[53] At appropriate acidities, the spin-lattice relaxation may become significant causing a change from triplet mechanism to radical pair polarization. However, the average radical ion pair may not yet be affected during the relatively short lifetime required for the generation of radical pair polarization. The effects observed at intermediate acid concentrations (Figure 1c) can be ascribed to the pair **8a–10** and, thus, are in agreement with this model. At higher acidities, the protonation can occur during the polarization inducing encounter; in this case, the observed polarization (Figure 1d) has to be ascribed to the pair **11a–10** (vide supra). Wagner and Thomas, who originally observed the CIDNP effects at high acid concentration, considered protonation of the free ions unlikely.[40] We suggest that the acid concentration determines which intermediate is being protonated. Our model of dynamic protonation/deprotonation can explain the effects at all acid concentrations and, at high acid concentrations, may even accommodate an exciplex as an intermediate. The reaction temperature should also influence the rate constant of exchange. Therefore, we studied the temperature dependence of the CIDNP effects. No significant temperature dependence was observed in neutral solutions, but in weakly acidic solutions (6×10^{-3} M acetic acid) the change from 10 °C to −9 °C was sufficient to change a pure multiplet effect to a nearly pure net effect (Figure 6). However, the interpretation of these findings is not straightforward. The reaction temperature should affect a variety of parameters that may influence the polarization mechanism, inter alia the rate constant of exchange, the viscosity of the medium, and, in acidic solutions, the acid–base equilibria of the added acid and of the radical intermediates. Because of the complexity of these parameters it is not obvious to which factor the observed change has to be ascribed.

Figure 6. Temperature dependence of ^{19}F CIDNP spectra observed during irradiation of CH_3CN solutions containing 0.03 M TFA, 0.2 M DMB, and 1×10^{-2} M acetic acid.

The kinetic considerations discussed above should be generally applicable to systems in which an Overhauser-induced CIDNP effect depends crucially on a fast electron exchange reaction. These systems should exhibit an acidity dependent change of polarization mechanism. Results observed in the system benzoquinone–chloroform-d[21] confirm this assumption. The following steps are important for the generation of nuclear spin polarization via the triplet mechanism:

$${}^{3}BQ^{\ddagger} + CDCl_3 \rightarrow {}^{\ddagger}BQD\cdot + \cdot CCl_3 \qquad (12a)$$

$$\text{or} \left\{ \begin{array}{c} {}^{3}BQ^{\ddagger} + CDCl_3 \rightarrow {}^{\ddagger}BQ^{-}\cdot + CDCl_3{}^{+}\cdot \\ CDCl_3{}^{+}\cdot \rightarrow \cdot CCl_3 + D^{+} \end{array} \right\} \qquad (12b)$$

$$BQ^{-}\cdot + H^{+} \rightleftarrows BQH\cdot \qquad (13)$$

$${}^{\ddagger}BQ^{-}\cdot \rightarrow {}^{\dagger}BQ^{-}\cdot \qquad (14)$$

$$BQ + {}^{\dagger}BQ^{-}\cdot \rightarrow {}^{\dagger}BQ + BQ^{-}\cdot \qquad (15)$$

Protonation of the semiquinone radical ions should favor the radical pair mechanism whereas deprotonation of the semiquinone radicals is expected to favor the triplet mechanism. We studied this system at a quinone concentration ([BQ] = 10^{-2} M) for which *decreased absorption* had been reported.[21] Using commercially available $CDCl_3$ as solvent, we observed the previously reported result (Figure 7b). Under otherwise identical conditions, a *strong emission* signal (Figure 7d) was observed, when the solvent was purified by passing it through basic alumina. In contrast, an *enhanced absorption* signal was observed (Figure 7c) upon addition of 10^{-2} M acetic acid to the solutions. These results confirm the importance of fast electron transfer for the generation of CIDNP via the triplet mechanism and the role of protonation in interfering with this mechanism.

Signal Direction of CIDNP Due to the Triplet Mechanism. So far we have limited the discussion to kinetic arguments for the involvement of the triplet mechanism. We have yet to

Table II. Sign of ^{19}F Hyperfine Coupling Constants and Direction of CIDNP Effects

			Signal direction			
Radical ion	Position	Sign of a^{36}	Expt[a]	Predicted[b]	Expt[c]	Predicted[d]
TFA$^{-}\cdot$	α	+	E	E	A	A
m-F-TFA$^{-}\cdot$	m	−	A	A	E	E
	α	+	E	E	A	A
p-F-TFA$^{-}\cdot$	p	+	E	E	E	E
	α	+	E	E	A	A
PFP$^{-}\cdot$	α	+	E	E	A	A

[a] Observed in benzene solution of ketones with phenol as quencher.[36] [b] Radical pair mechanism. $\Delta g < 0$. [c] Observed in neutral solutions of ketones with DMB as quencher (this paper). [d] Triplet mechanism.

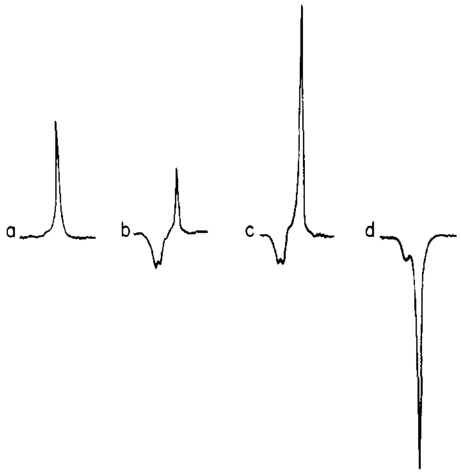

Figure 7. ^{1}H NMR spectra (90 MHz) of benzoquinone solutions (10^{-2} M) in CDCl$_3$: (a) dark spectrum; (b) during irradiation in unpurified solvent; (c) during irradiation in unpurified CDCl$_3$ containing 10^{-2} M acetic acid; (d) during irradiation in purified solvent.

comment on the observed signal directions. The sign of nuclear spin polarization induced via the triplet mechanism is determined by two factors: the initial electron polarization of the radical ions and the predominant mechanism of electron-nuclear cross relaxation.

A radical or radical ion with electron spin levels in nonequilibrium populations has a variety of relaxation mechanisms available, including two electron-nuclear cross relaxation processes. Transitions between the levels (e^+, n^+) and (e^-, n^-) with a net change in spin quantum number of 2 (W_2) are dipolar in nature whereas the transitions between levels (e^+, n^-) and (e^-, n^+) without a net change in spin quantum number (W_0) are scalar.[54] The rate of these cross relaxation processes can be affected substantially by a modulation of the hyperfine interactions, which may be caused by the rapid reorientation of the radicals in solution.[46] Rotational tumbling of the radicals, which changes the orientation of the unpaired spin and the nucleus relative to the magnetic field, modulates the anisotropic component of the hyperfine interactions and gives rise chiefly to dipolar transitions (type W_2). The relaxation rate for this case is given by

$$W_d \approx \frac{B_{zz}{}^2\tau_r}{8\hbar^2(1 + w_z{}^2\tau_r{}^2)}$$

where B_{zz} is the component of the anisotropic hyperfine tensor along the symmetry axis and τ_r is the rotational correlation time.[21,46]

Internal motions of radicals or radical ions may change the orientation of nuclei relative to the unpaired spin to which they are coupled. The rotation of groups such as CH$_3$ or CF$_3$ may modulate the isotropic component of the hyperfine interaction (A). As a result, the scalar cross relaxation process (type W_0) will be facilitated. In this case, the rate of relaxation is given by

$$W_s = \frac{(\delta A)^2\tau_A}{2\hbar^2(1 + w_z{}^2\tau_A{}^2)}$$

where δA is the mean-square variation in the isotropic hyperfine coupling constant and τ_A is the correlation time for the molecular motion which causes A to vary with time.[21,46] It is noteworthy that, in contrast to the radical pair mechanism, the cross relaxation mechanism gives rise to signal directions which are independent of the *sign* of the hyperfine coupling constants.

The initial electron polarization of the radical ions is determined by the triplet sublevel which is preferentially populated by intersystem crossing from the photoexcited singlet. For several carbonyl compounds, e.g., benzoquinone[21] or phenyl ketones,[55] the sublevel population rates have been shown to be $P_z > P_x, P_y$. Such a triplet would produce radical ions with electron spin populations resulting in CIDEP emission as observed in several cases.[44-47] Subsequently, dipolar cross relaxation would lead to nuclear spin level populations giving rise to CIDNP emission, as observed for benzoquinone and tetrafluorobenzoquinone.[21]

In contrast to the nuclei of these benzoquinones, the CF$_3$ groups of TFA and of its m- and p-fluoro derivatives appear in enhanced absorption. Assuming an initial ^{3}TFA‡ sublevel population analogous to that of other triplet carbonyls[21,55] and a resulting ‡TFA$^{-}\cdot$ electron polarization analogous to that of benzosemiquinones[19-21] and ketyl anions,[41,56] a scalar cross relaxation mechanism can account for the enhanced absorption of the trifluoromethyl groups of TFA and of its m- and p-fluoro derivatives.

The triplet mechanism and a scalar cross relaxation step can also account for the results observed during the electron transfer quenching of pentafluoropropiophenone and heptafluorobutyrophenone by DMB. Although we did not observe ESR spectra upon electrolysis of PFP or HFB under conditions where we observed the spectra of **8a–c**, we assume that the g factors of **8d,e** are very close to those of **8a–c** (2.0037).[37] Therefore the radical pair mechanism is expected to result in a multiplet effect. The signal direction (enhanced absorption) and the DMB concentration dependent of the effects observed for the α CF$_2$ groups of PFP and HFB are similar to those for the CF$_3$ groups of TFA and its ring-substituted derivatives. Therefore, it appears justifiable to assume that a similar mechanism is involved in all these systems.

We have tentatively ascribed the scalar cross relaxation of the TFA radical anion to the rotation of the CF$_3$ group.[26] Any significant contribution due to this mechanism would require rotational correlation times, τ_A, shorter than 10^{-9} s. The rotational frequencies corresponding to this correlation time are not inconceivable for a CF$_3$ group but they appear out of reach for bulkier groups of lower symmetry, such as C$_2$F$_5$ and C$_3$F$_7$. As a consequence, the mechanistic details of the scalar cross relaxation in TFA$^{-}\cdot$, PFP$^{-}\cdot$, and HFB$^{-}\cdot$ are uncertain.

The scalar cross relaxation mechanism postulated for the

CF_3 and the α CF_2 groups of the intermediate radical ions is, of course, limited to nuclei capable of reorientation relative to the unpaired spin. This mechanism cannot be applicable to the nuclei of the aryl groups because the EPR spectra of the radical ions, **8a–c**, do not show any evidence for rotation of the aryl groups. The spectra of **8a** and **8c** show quartets indicating the presence of three identical (fluorine) nuclei (**8a**, a = 25.79 G; **8c**, a = 27.06 G). They are further split by coupling to five different nuclei. Both spectra are complicated by large second-order splittings. The EPR spectrum of **8b** has even more lines than those of **8a** and **8c**, possibly owing to the presence of two rotamers.[37]

Since rotation can be eliminated, the cross relaxation of the aryl nuclei should be dominated by the anisotropic contribution and, therefore, should result in CIDNP emission. No significant polarization was found for the aromatic ^1H signals of TFA or any of its derivatives. However, we found the expected emission in the electron transfer quenching of both m- and p-fluoro-α,α,α-trifluoroacetophenone (**4**, **5**). Decreased absorption (i.e., net emission) was found for the meta fluorine; strong emission was observed for the para fluorine (Figure 3). The failure to observe ^1H polarization for TFA and its derivatives is understandable considering that the magnitude of the polarization is expected to be proportional to $B_{zz}{}^2$ and that the ^1H hyperfine couplings of **8a**, $a_H{}^o = -5.1$ G and $a_H{}^p = -4.05$ or -3.54 G, are considerably smaller than $a_F{}^\alpha$ (+25.8 G).[37,48] In addition, the ^1H hyperfine anisotropies of π radicals usually are substantially smaller than the ^{19}F anisotropies.[57]

Among the systems for which nuclear spin polarization via the triplet mechanism has been postulated, the case of TFA and its derivatives is unique because it is the only system for which the signal directions predicted by the radical pair and the triplet mechanism can be compared with experimental results for several different nuclei. Results obtained during the photoreaction of TFA and derivatives with phenol have established that the coupling constants of CF_3 and para fluorine are positive whereas that of the meta fluorine is negative.[36] Nuclear spin polarization induced via the radical pair mechanism should reflect these signs whereas polarization induced via the triplet mechanism should reflect the mechanism of cross relaxation. Our results show identical signal directions for the meta and para fluorine atoms, which have opposite hyperfine signs but should relax via identical mechanisms, and opposite signal directions for CF_3 and p-F, which have hyperfine coupling constants of identical signs[36] but should have different mechanisms of cross relaxation. The signal directions expected for radical pair and triplet mechanism are listed in Table II and compared with the signs of the hyperfine coupling constants and the experimental results. Clearly, the results are incompatible with the radical pair mechanism but fully consistent with the triplet mechanism.

Conclusion

The CIDNP effects observed during the irradiation of fluorine-substituted aryl alkyl ketones at high quencher concentrations are excellent examples of nuclear spin polarization via the triplet mechanism. Trifluoroacetophenone and its derivatives are more versatile substrates for the investigation of this mechanism than are the previously investigated benzoquinone and tetrafluorobenzoquinone. The fluorine-substituted ketones discussed in this paper enabled us to evaluate the polarization of several nuclei in different molecular environments, with different hyperfine constants, and with different cross relaxation mechanisms. In addition, these systems have allowed us to demonstrate the kinetic limitations of the triplet mechanism relative to the concentration of light-absorbing species and quencher, as well as the role of acidity. We expect that the concentration effects discussed in this paper will be found in other cases of nuclear spin polarization due to the triplet mechanism. A critical evaluation of previous claims of Overhauser-induced nuclear polarization is in preparation.

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