

Figure 2. Correlation of theoretical f^+ (eq 4) with experimental ρ^+ for carbonium ions in Table I.

lated and experimental ρ^+ 's are numerous.⁹ Use of ab initio rather than MINDO/3 results could lead to even better accord.¹⁰ In addition, the assumption of equal β (eq 1) for the different ions is suspect since variations in the carbonium carbon to aryl ring bond length are expected as well as variations in the planarity of the carbonium carbon. Ground state effects on the ionizations are also important. For example, the experimental ρ^+ 's for cyclopentyl and 3-cyclopentenyl seem anomalously high compared to the calculated values and isopropyl. This may be attributed to steric acceleration that relieves eclipsing interactions in the solvolyses leading to the five-membered ring cations. The strain relief decreases the electron demand on the substituents in the transition state for solvolysis and raises ρ^+ .³¹ Similarly, the calculated ρ^+ for cyclohexyl is too high probably due to steric deceleration which increases the substituent sensitivity of the transition state and lowers ρ^+ . The steric effects can be compensated somewhat by using Peters' values for ρ^+ which correlate the solvolysis rates of the tertiary, aryl species with their secondary parents.¹² As shown in Table I, Peters' values (in parentheses) are in significantly better agreement with the calculated ρ^+ 's than the experimental results for the tertiary species only. A new fit of eq 4 to the experimental ρ^+ 's including Peters' data reduces the mean deviation between theory and experiment to 0.20 ρ^+ units. The decision on which experimental values to use is complicated by the lack of linearity observed by Peters in some of his Hammett-Brown plots, e.g., for cyclohexyl and Coates' cation.¹² We have chosen to use the consistent data base involving only the solvolyses of the tertiary, aryl *p*-nitrobenzoates and emphasize that the theoretical method ignores conformational effects on this reaction. It is not clear that the benefits gained by attempting to take such factors into account would offset the loss of simplicity. One element that does not appear to be affecting the results is differences in solvation for the various carbocations.²¹ This is reasonable, however, since the ρ^+ 's correspond to the generation of highly delocalized, π -conjugated and/or homoaromatic carbocations. The solvation of such ions should be uniformly weak.^{2,11}

Predictions of ρ^+ for some systems that have not yet been studied experimentally are recorded in Table II. The total accumulation of data permits some general observations. (1) The low f^+ 's (high ρ^+ 's) for the homoaromatic species result from a combination of both extensive delocalization (low Q_L) and high LUMO energy (ϵ_1). (2) The low f^+ 's for π -conjugated cations are due primarily to delocalization. (3) The ρ^+ 's and the ϵ_1 's and Q_L 's for the cyclopropylcarbinyl cations are intermediate between those of the homoaromatic and simple, classical ions. (4) It must be emphasized that the key factor for delocalization is the delocalization of the LUMO, not the actual charge delocalization which is determined by the occupied orbitals.

Table II. Calculated Sensitivity Factors and ρ^+ 's for Additional Cations

R ⁺	Q_L ^{a,b}	$-\epsilon_1$ ^{a,c}	f^+ ^d	$-\rho^+$ ^{calcd} ^e
Bridged 2-norbornyl	0.351	4.98	0.067	2.09
Trishomocyclopropenyl ^g	0.526	3.87	0.083	2.31
3-Bishomocyclopropenyl ^{f,h}	0.575	4.41	0.099	2.53
2-Cyclobutenyl	0.496	5.45	0.104	2.60
7-Norbornadienyl ^f	0.423	3.65	0.065	2.07
Bicyclo[3.1.0]hex-3-yl	0.776	6.76	0.226	4.25
Bicyclo[3.1.0]hex-2-yl	0.507	5.83	0.116	2.76
α -Methylbenzyl	0.427	6.17	0.106	2.62
1,3-Dimethylallyl	0.443	6.49	0.119	2.80

^a MINDO/3 results with complete geometry optimization. ^b Single electron population for the carbonium carbon in the LUMO. ^c LUMO energy in eV. ^d Sensitivity factor defined in eq 4 with $\epsilon_H = -10.2$ eV. ^e Calculated from eq 5. ^f The NLUMO is the appropriate orbital with *S* symmetry in this case. ^g From bicyclo[3.1.0]hex-3-yl. ^h From 3-cyclopentenyl.

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William L. Jorgensen

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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Competing Triplet and Radical Pair ¹⁹F Polarizations in the Electron Transfer Quenching of Triplet α,α,α -Trifluoroacetophenone

Sir:

We have applied the CIDNP technique¹ to study the interaction of photoexcited α,α,α -trifluoroacetophenone (TFA, **1**) with strong electron donors such as 1,4-diazabicyclo[2.2.2]-

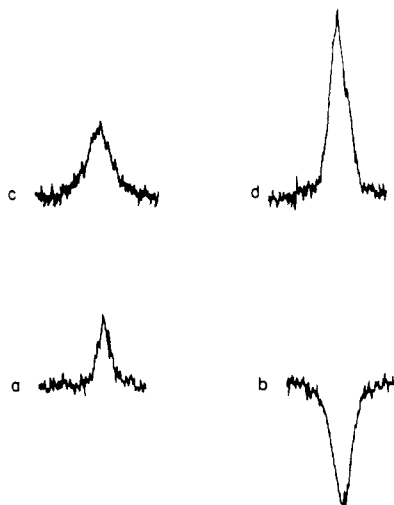
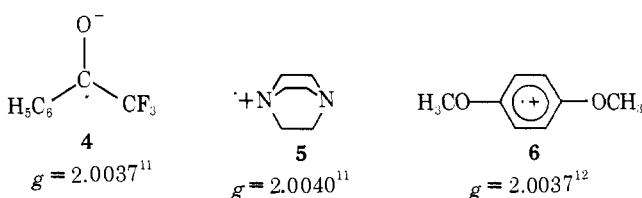


Figure 1. ^{19}F NMR signal at δ 90.2 (CFCl_3) in acetonitrile solutions containing 0.08 M TFA and various concentrations of DABCO: (a) in dark; (b–d) during irradiation; (b) 10^{-3} to 10^{-2} M; (c) 0.05 M, (d) 0.11 M DABCO.

octane (DABCO, **2**) or 1,4-dimethoxybenzene (DMB, **3**). When carefully deaerated acetonitrile solutions containing TFA and a quencher are irradiated in the probe of an NMR spectrometer,² ^{19}F nuclear spin polarization is observed; its intensity, signal direction, and type depend on the concentration of both quencher and ketone. The results can be summarized as follows: (1) with DABCO as quencher, the ^{19}F polarization changes from emission (E) to enhanced absorption (A) as the quencher concentration is increased (Figure 1); (2) with DMB ($>10^{-2}$ M) as quencher, A is observed at $[\text{TFA}] > 10^{-3}$ M, whereas a weak A/E multiplet effect is found at $[\text{TFA}] < 10^{-3}$ M (Figure 2).

These observations lead us to conclude that two different polarization mechanisms are involved: the effects observed at low quencher concentrations are compatible with the radical pair mechanism³ whereas those observed at high quencher concentration are best explained by the so-called triplet mechanism.⁴

Kaptein has summarized the radical pair theory in two simple rules which allow one to predict the direction or phase of a CIDNP effect on the basis of parameters such as the initial spin multiplicity of the pair (μ), the mode of product formation (ϵ), the sign of the hyperfine coupling constants (hfc, a), and the relative magnitude of the g factors of the radicals involved.⁵ For the systems discussed here the polarization determining parameters can be assigned as follows. It has been established that benzene derivatives quench the triplet state of TFA by a charge transfer process.⁶ In polar solvents complete electron transfer from **2** or **3** to photoexcited **1** is energetically feasible^{7,8} and generates the ketyl anion **4** paired with a radical cation **5** or **6**.



These radical ion pairs are generated from triplet TFA ($\mu > 0$) and they regenerate the ketone and the electron donor via in-cage electron return ($\epsilon > 0$). The sign of a_{F} for **4** is assumed to be positive in analogy to known β -fluorine coupling constants;¹³ such an assignment is uniquely consistent with other CIDNP experiments conducted in our laboratories. Finally, the g factor differences are $g_4 - g_5 < 0$ and $g_4 - g_6 \approx 0$, for



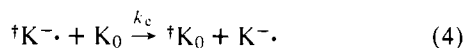
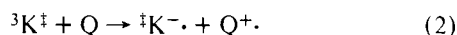
Figure 2. ^{19}F NMR spectra of acetonitrile solutions containing 0.2 M DMB and either 10^{-4} M (left) or 10^{-1} M TFA (right) in the dark (bottom) and during irradiation (top) with UV light. Splitting by the ortho-protons is not resolved in this dark spectrum but can be under higher resolution.

quenching by DABCO and DMB, respectively. Given these parameters, the radical pair theory can account for the ^{19}F emission observed at low concentrations of DABCO ($\Gamma_{\text{net}} = \mu \cdot \epsilon \cdot a \cdot \Delta g < 0$) and for the multiplet effect ($\Gamma_{\text{m}} = \mu \cdot \epsilon \cdot \sigma \cdot a_{\text{H}} \cdot a_{\text{F}} \cdot J_{\text{HF}} < 0$)¹⁴ observed at low TFA concentrations with DMB as quencher.

In contrast, the radical pair theory fails to explain the effects observed at higher quencher concentration. In the case of DMB, the radical ion pair **4–6** cannot account for a net effect since $\Delta g \approx 0$; in the case of DABCO, the pair **4–5** can account for the enhanced ^{19}F absorption only if generated predominantly from excited singlet TFA. However, this possibility can be eliminated. The excited singlet states of phenyl ketones have very short lifetimes ($\approx 10^{-11}$ s);¹⁵ even at diffusion-controlled quenching rates 0.1 M quencher should intercept no more than 1% of excited-singlet TFA. In support of this premise, we observed that neither 0.1 M DABCO nor 0.1 M DMB lowers the efficiency with which TFA photosensitizes the cis–trans isomerization of 1,3-pentadiene;¹⁶ the quantum yield of intersystem crossing remains unity⁶ within experimental error.

Since a chemical mechanism of unprecedented complexity would be required to explain the high concentration enhanced absorbance by the radical pair theory, we examine the possibility that an alternative polarization mechanism is involved. The triplet mechanism has been proposed in order to explain several CIDEP and CIDNP phenomena.^{4,17} This mechanism involves the following steps: (1) generation of an electron spin polarized triplet state via preferential population of one triplet sublevel during intersystem crossing; (2) transfer of the electron polarization to a radical or radical ion by a fast chemical reaction; (3) electron–nuclear cross-relaxation; and (4) transfer of the resulting nuclear spin polarization to a diamagnetic species by degenerate electron exchange. Scheme 1 summarizes these steps for the reaction of a ketone K with a quencher Q: * denotes an excited state, † and ‡ denote nuclear and electron polarization, respectively.

Scheme I



The first two reactions of this scheme are the key steps in the generation of electron spin polarization effects that can be unequivocally assigned to the triplet mechanism;¹⁷ their feasibility appears to be generally accepted. For the observation of nuclear spin polarization two additional steps are essential; the Overhauser process (eq 3) and the electron exchange reaction (eq 4). The efficient generation of nuclear spin polarization requires that cross relaxation ($k_3 \propto a^2$) competes favorably with electron spin lattice relaxation.^{4a,d} This requirement is likely to be met for TFA⁻ because of its large ¹⁹F hfc ($a \approx 27$ g).^{11,18} If the nuclear polarization is to be observed, the rate of exchange has to be sufficiently fast to prevent excessive nuclear spin lattice relaxation ($T_{1n} > 10^{-6}$ s).¹⁹ This requirement is met at [TFA] > 10⁻³ M if k_c is as large as that reported²⁰ for benzophenone ketyl, 10⁸ M⁻¹ s⁻¹.

The direction of polarization due to the triplet mechanism is determined by two factors: the electron polarization transferred to the radical ions by their triplet precursor; and the predominant mechanism of electron nuclear cross relaxation. The rotational tumbling of a radical modulates the anisotropic component of its hfc which facilitates dipolar cross relaxation;^{4a,d} this mechanism has been assumed for tetrafluoro-semiquinone radicals.^{4d} In the case of [†]TFA⁻, rotation of the CF₃ group can modulate the isotropic hyperfine component which causes scalar cross relaxation.^{4d} The latter mechanism may well predominate, since the isotropic ¹⁹F hfc of **4** is large and the rotational correlation time of the CF₃ group could be significantly longer than the molecular tumbling lifetime.²¹ Given a scalar relaxation mechanism, a ³TFA[‡] sublevel population analogous to that of other carbonyl triplets (e.g., benzoquinones^{4d} or phenyl ketones,²² where the upper triplet sublevels are preferentially populated) and a resulting [†]TFA⁻ electron polarization analogous to semiquinone radicals^{4d} or ketyl anions,^{17a,23} the TFA signal direction is expected to be opposite to that of tetrafluorobenzoquinone (E). The experimental result (A) is in agreement with these considerations and therefore compatible with the triplet mechanism.

The dependence of the observed effects on both quencher and ketone concentration is fully consistent with the proposed scheme, in particular with the two bimolecular reactions of spin polarized intermediates (eq 2 and 4) which compete with spin relaxation processes. The intensity of the enhanced absorption increases markedly with increasing quencher concentration in the range 0.01–0.1 M. The rate constant for quenching of ³TFA by DMB has been determined to be 1.2 × 10¹⁰ M⁻¹ s⁻¹.²⁴ A Stern–Volmer plot of reciprocal CIDNP intensity vs. [DMB] indicates an intermediate with a lifetime of 1 ns, too long for ¹TFA*, too short for equilibrated ³TFA (1 μs),²⁴ but appropriate for an electron spin polarized triplet, ³TFA[‡]. A T_{11} value of 2.7 ns has been estimated for duroquinone on the basis of a similar quencher concentration effect on CIDEP intensity.^{17a}

The necessity for a rapid exchange reaction was noted above and has been pointed out in the literature; exchange of hydrogen atoms has been postulated to explain the concentration dependent CIDNP effects observed during the irradiation of benzoquinone in chloroform.^{4d} Degenerate electron exchange, which we invoke here, occurs in many photoinitiated electron transfer reactions as indicated by the line broadening observed upon irradiation of several donor–acceptor systems.^{25,26} Rapid

exchange prevents premature relaxation of the Overhauser induced ¹⁹F polarization and also minimizes competition from the more common radical pair mechanism. Radical pair polarization is developed on a faster time scale than is Overhauser polarization and therefore predominates in most systems. However, in a system such as TFA–DMB, where little or no net chemical reaction occurs, the “escape” polarization may cancel the “in-cage” polarization if the rate of exchange of the free ketyl radical is faster than the rate of nuclear spin relaxation (i.e., if $k_c[\text{TFA}] > T_{1n}^{-1}$). At sufficiently low ketone concentrations, relaxation becomes competitive with exchange; not only is the fortuitous cancellation of radical pair polarization now avoided, but the Overhauser-induced polarization is also weakened. As a result, the radical pair polarization predominates. The multiplet effect observed with DMB only at TFA concentrations < 10⁻³ M is fully consistent with these considerations and suggests that $T_{1n} \geq 10^{-5}$ s, in agreement with other estimates.¹⁹

We have obtained similar results with several ring-substituted derivatives of TFA and with several additional electron-rich benzene derivatives. These results will be discussed in forthcoming papers.

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 (27) NIH Postdoctoral Fellow, 1974–1975.

Michael J. Thomas,²⁷ Peter J. Wagner*

Chemistry Department, Michigan State University
 East Lansing, Michigan 48824

Marcia L. Manion Schilling, Heinz D. Roth*

Bell Laboratories
 Murray Hill, New Jersey 07974
 Received January 20, 1977

Acid Catalyzed CIDNP during Photoinduced Electron Transfer

Sir:

We report here an example of chemically induced dynamic nuclear polarization (CIDNP)¹ which occurs only upon acid catalysis.

Triplet α,α,α -trifluoroacetophenone, **1**, is quenched by substituted benzenes via a charge transfer mechanism which presumably involves an exciplex intermediate.² Degassed acetonitrile solutions 0.09 M in **1** or in *p*-Cl-**1** (**2**) and 0.0014 M in 1,4-dimethoxybenzene (DMB), upon being irradiated in the cavity of a Varian Model A56/60 NMR spectrometer,³ can display very weak ^{19}F emission, E, characteristic of the CF_3 group (for **1**, δ 90.2 (CCl_3F), t, J_{FH} (ortho) = 1.1 Hz). The signal intensity depends on the solvent's history; in extensively purified solvent there is no emission; when present, the polarization fades during irradiation, leaving the normal weak ^{19}F absorption of the ketone. This variable weak emission is apparently due to trace impurities which are consumed. In the presence of 0.005–0.1 M acetic acid or *p*-toluenesulfonic acid, strong steady-state ^{19}F , ^1H , and ^{13}C CIDNP⁵ signals are evident for **1** itself and also for several ring-substituted derivatives. Figures 1 and 2 display results for **1** and **2**; the acid-catalyzed CIDNP directions, which do not vary from 0.001 to 0.1 M DMB or with length of irradiation, are summarized in Table I. The ^1H absorption of the DMB is extensively broadened during irradiation.

GC analysis of extensively irradiated samples indicated no disappearance of ketone and no product formation. The 0.0014 M DMB used is sufficient to quench >90% of the ketone triplets formed.⁶ The combined redox potentials⁷ of the ketones and DMB indicate that dissociation of the exciplex to radical ions is some 6 kcal exothermic;⁹ radical ions are expected under such circumstances.¹⁰ Roth has described several examples of CIDNP from radical ions,^{11,12} and our observation of broadening of the DMB resonance strongly suggests degenerate electron exchange between $\text{DMB}^{\cdot+}$ and DMB.¹¹ The ketyl radicals can be protonated, as indicated by the acid-catalyzed photoreduction of **1** in benzene.¹³

Kaptein's rules¹⁴ for the direction of polarization resulting from net effects ($\Gamma_{\eta} = \Delta g \cdot a \cdot \mu \cdot \epsilon$) and multiplet effects ($\Gamma_m = a_i \cdot a_j \cdot J_{ij} \cdot \sigma \cdot \mu \cdot \epsilon$) predict A or emission/absorption (E/A) if Γ is positive. The strong polarization of the carbonyl carbons and of adjacent nuclei of both ketones indicates the involvement of ketyl radicals. The reaction is entirely triplet-derived ($\mu > 0$).^{2,6,15} The E/A multiplet for the carbonyl carbons requires an in-cage reaction ($\epsilon > 0$), since a_{C} ,¹² a_{F} ,¹⁷ $^2J_{\text{CF}}$,¹⁸ and σ (both nuclei on same radical) are all positive. Similar argu-

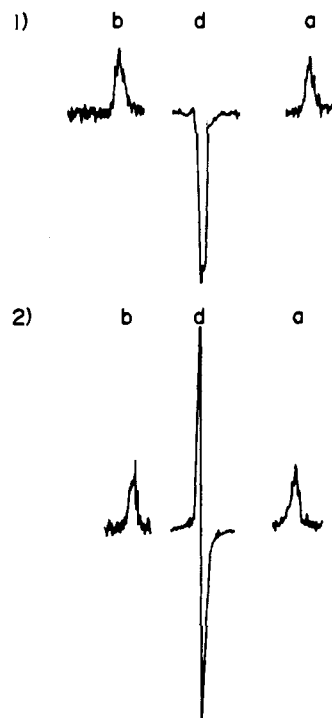
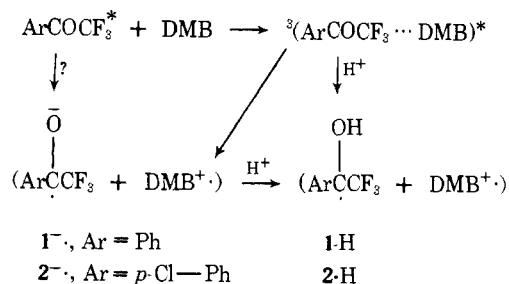


Figure 1. ^{19}F NMR signal at δ 90.2 (CCl_3F) of degassed acetonitrile solutions containing 10^{-3} M 1,4-dimethoxybenzene, 10^{-2} M *p*-toluenesulfonic acid, and (1) 0.1 M **1**; (2) 0.1 M **2**. b, d, and a denote before, during, and after irradiation. Note 2.5-fold decrease in spectrum amplitude during irradiation.

Table I. Summary of Polarizations Observed upon Irradiation of 0.09 M **1** and **2** in Acidic Acetonitrile Containing 0.001–0.1 M Dimethoxybenzene^a

Nucleus	1	2
^{19}F	A/E ^b + E	A/E
^1H (ortho)	A/E	A/E
C = 0	E/A	E/A
CF_3	E/A	E/A

^a A \equiv enhanced absorption; E \equiv emission. Low field portion of multiplet signals listed first. ^b Weak.



ments for the multiplet polarizations of the CF_3 carbon ($^1J_{\text{CF}} = -290$ Hz),¹⁹ the fluorines ($^5J_{\text{HF}} = 1.1$ Hz),²⁰ and the ortho-protons also require ϵ to be positive, since a_{H} (ortho)²¹ and a_{CF_3} ²² are negative. Moreover, it is not really possible for ϵ to be negative in such a totally reversible photoreaction.¹¹

Comparison of the ^{19}F spectra for **1** and **2** reveals that the acid catalyzed CIDNP results from protonated ketyls rather than from the ketyl radical anions. Since **1**^{·-} has a g value of 2.003 75²³ and $\text{DMB}^{\cdot+}$ one of 2.003 68,²⁴ only a multiplet effect, possibly accompanied by weak A, would be expected from the **1**^{·-}, $\text{DMB}^{\cdot+}$ radical pair. In the absence of acid,²⁵ no steady state CIDNP is seen at all at $[\text{AF}_3] > 10^{-3}$ M, but a weak A/E ^{19}F multiplet can be observed at $[\text{AF}_1] < 10^{-3}$ M.¹⁵