

compound 9-anthracene-(CH₂)₃-*p*-*N,N*-dimethylaniline. For exciplexes in general, the geometric effects on formation rates are greatly affected by the energy separation between the locally excited singlet state and the exciplex state. The geometric constraints become less stringent as the energy difference increases.

(2) We have established that the dynamics of exciplex formation are influenced by the starting ground-state conformations. For the model compound studied, it was found that exciplexes with different emission energies were formed independently from two distinct groups of ground-state conformers at different rates. The structures of these conformers are not known but possibly differ in the relative orientation of the anthracene and the dimethylaniline chromophores.

(3) The observed viscosity dependence we find, combined with literature values for other three-chain systems, points to the

methylene chain motions as the key factor in determining the viscosity dependence of the rates. The attached end groups alter the formation rates but not the viscosity dependence of the rates for most of the cases considered.

(4) The experimentally observed exponential rise for intramolecular exciplex formation suggests that a single chain relaxation mode, perhaps the large-scale end-to-end relaxation mode, is dominant, at least in the picosecond to nanosecond time regime we have examined.

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Magnetic Field Dependence of ¹⁹F Nuclear Spin Polarization. The System Tetrafluorobenzoquinone–Tetrafluorohydroquinone

Richard S. Hutton,[†] Heinz D. Roth,^{*†} Marcia L. Manion Schilling,[†] Anthony M. Trozzolo,[†] and Thomas M. Leslie^{‡,§}

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974, and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. Received December 4, 1981

Abstract: The magnetic field dependence of the ¹⁹F polarization observed in the reaction of tetrafluorobenzoquinone with tetrafluorohydroquinone in benzene has been studied. The results can be interpreted in terms of three different polarization mechanisms. The effects observed at fields below 100 G can be ascribed to a radical-pair mechanism involving S–T_± mixing. At fields of 1–20 kG two different contributions have been identified which can be observed separately under appropriate experimental conditions. One contribution showing a maximum near 4 kG is assigned to a biradical adduct between the triplet quinone and the solvent, benzene. The other contribution shows a monotonical increase with magnetic field strength. This effect is assigned to the triplet-Overhauser mechanism in the reaction of the triplet quinone with the hydroquinone.

Introduction

Recently, we reported the magnetic field dependence of the ¹⁹F polarization generated in the photoreaction of trifluoroacetophenone with dimethoxybenzene.¹ We concluded that these effects, when evaluated in the light of supplementary experimental results, provided strong evidence for the triplet-Overhauser mechanism, a relatively rare spin polarization mechanism with electron-nuclear cross relaxation as a key step.² In the paper presented here, we report the magnetic field dependence of ¹⁹F polarization effects observed during the irradiation of tetrafluorobenzoquinone (1) in the presence of tetrafluorohydroquinone (2) in benzene solution. This reaction was first studied by Vyas and Wan³ who suggested tetrafluorosemiquinone (3) as an intermediate and ascribed the strong ¹⁹F emission observed for the quinone to the triplet-Overhauser mechanism. Several experimental results were adduced in support of this assignment including the magnetic field dependence of this enhancement between 1 and 7 and at 14 kG. This dependence was compared with a theoretical prediction and appeared to match it reasonably well.^{2a}

The theory underlying the triplet-Overhauser mechanism has been discussed in detail elsewhere^{1,2} and only a brief recapitulation of its principal features will be given here. The intensity of the nuclear spin polarization (*P_n*) induced via this mechanism can

be expressed as a function of two magnetic field dependent factors, the initial electron polarization (*P_e*) of a radical and the efficiency (*ξ*) of electron nuclear cross relaxation,

$$P_n \propto P_e \xi \quad (1)$$

The initial electron polarization is determined by

$$P_e \propto \frac{\omega_z \tau_1}{\omega_{2fs}} {}^3T_{1e}^{-1} T^\dagger \quad (2)$$

Of these factors, ω_{zfs} , the zero-field splitting of the triplet species, and τ_1 , the "rotational" correlation time, are independent of the magnetic field, whereas ω_z , the Zeeman splitting, ${}^3T_{1e}$, the electron relaxation time of the triplet, and T^\dagger , the probability that the triplet is quenched, are magnetic field dependent.^{1,2}

The efficiency of cross relaxation is a complex function of various relaxation rates. It can be evaluated by solving the different rate equations governing the populations of the spin levels of the substrates and the intermediate radicals. Adrian has solved these equations for the case of a radical whose unpaired electron

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[†] Bell Laboratories.

^{*} University of Notre Dame.

[‡] Present address: Bell Laboratories.

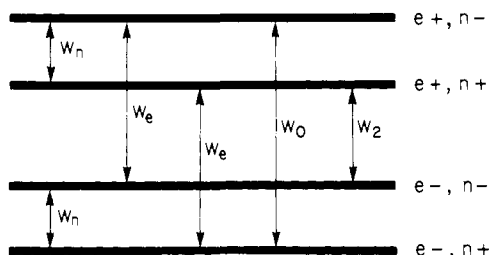


Figure 1. Schematic representation of the relaxation processes in a system with one unpaired electron and one nucleus of spin $I = 1/2$.

is coupled to one nucleus of spin $1/2$; this species was assumed to be generated by a bimolecular hydrogen abstraction reaction and to ultimately regenerate its parent. This approach yielded an efficiency,

$$\xi = [k_c[S](W_2 - W_0)]/[4W_nW_e + 4W_2W_0 + 2(W_2 + W_0) \times (W_e + W_n) + \kappa k_c[S](2W_e + W_2 + W_0)] \quad (3)$$

In this equation, W_0 and W_2 are the rates of scalar and dipolar cross relaxation of the radicals, respectively; W_e and W_n are the rates of electron and nuclear spin lattice relaxation (cf. Figure 1); and $k_c[S]$ accounts for the transfer of nuclear spin polarization from the radical to its diamagnetic parent (S) by degenerate electron exchange. Of these rates, W_0 , W_2 , and W_e are magnetic field dependent. With the exception of $k_c[S]$ these rates are proportional to the squares of the hyperfine couplings of the individual nuclei,

$$W \propto B_{zz}^2 \quad (4)$$

Adrian's solution^{2a,b} of ξ proved to reproduce the nuclear spin polarization induced in the reaction of trifluoroacetophenone with dimethoxybenzene over a wide range of magnetic field and quencher concentration remarkably well.¹ However, the system 1–2 is more complicated because the proposed intermediate, the semiquinone radical 3, has two different types of ¹⁹F nuclei; those in the ortho positions have strong positive hyperfine interactions ($a_{ortho}^F = 13.2$ G) whereas those in the meta positions have weaker negative hyperfine coupling constants ($a_{meta}^F = -3.7$ G).^{2a} The effects induced in these different nuclei cannot be separated experimentally; both contributions are observed in the single ¹⁹F transition of the quinone. Adrian et al. assumed that the overall efficiency of cross relaxation is the sum of two independent contributions due to the different types of nuclei. With a rotational correlation time, $\tau_1 = 3 \times 10^{-11}$ s, calculated from the Stokes–Einstein equation and with values of B_{zz} approximately one-half as large as those derived from the known isotropic hyperfine coupling constants according to the empirical relation,⁴ $B_{zz}^F = 2.4a^F$, this approach results in the field dependence curves shown in Figure 2 which appear to agree reasonably well with the experimental data points.^{2a} There are, however, several points which deserve comment. (a) According to this simulation, the ¹⁹F nuclei in the meta position, despite their relatively weak hyperfine coupling constant, dominate the overall polarization. (b) The experimentally observed intensities increase monotonically up to a field strength of 7 kG whereas the theoretical curve has a maximum below 5 kG. (c) The CIDNP intensity at 14 kG, which is largely responsible for the apparent overall agreement between experiment and theory, was measured in a different experimental setup, by irradiation in the probe of the NMR spectrometer; the comparison of this intensity with those obtained by manual transfer at lower fields is not trivial.

In order to eliminate possible ambiguities, to determine the exact position of the polarization maximum and to bridge the gap between the data at lower fields and at 14 kG, we determined the CIDNP signal intensities under identical conditions for all field strengths. In addition, we have explored new dimensions of these

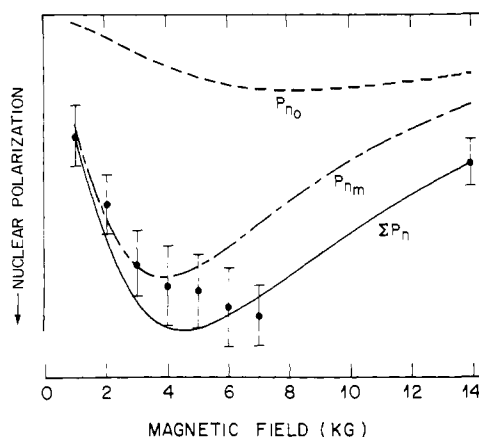


Figure 2. Theoretical prediction of ¹⁹F polarization induced in tetrafluorosemiquinone (contributions due to ortho and meta nuclei and their sum) as a function of magnetic field and experimental results (full circles) of ref 2a. The calculated curve is based on the values $B_{zz}^o = 3.2 \times 10^8$ rad s⁻¹, $B_{zz}^m = -0.84 \times 10^8$ rad s⁻¹, and $\tau_1 = 3 \times 10^{-11}$ s.

effects and have introduced new elements in their analysis. We determined the dependence of the ¹⁹F polarization upon the hydroquinone concentration at several magnetic field strengths, and we measured the field dependence of these effects in the absence of hydroquinone. Finally, the UV spectra of appropriate solutions were studied to determine which species absorb(s) the incident light, and time-resolved absorption spectroscopy was applied to determine the lifetimes of key intermediates as well as the rates of their reactions.

Experimental Section

Nuclear Spin Polarization Experiments. Samples were purged with argon for 2 min and irradiated, while spinning, with the light of an Osram 200-W high-pressure mercury lamp in the (adjustable) gap of a Varian 4004 electromagnet with 2-in. pole faces. The irradiation was discontinued by a mechanical shutter, the samples were transferred manually to a JEOL C60HL continuous-wave NMR spectrometer, and their ¹⁹F intensities were recorded after 5 ± 0.5 s. This experimental setup is adequate to measure the relatively strong ¹⁹F signals of the quinone ($T_1 = 11$ s), whereas the hydroquinone intensities, because of its shorter relaxation time ($T_1 = 4$ s), may have to be interpreted with somewhat greater caution.

Laser Flash Photolysis Experiments. The laser flash photolysis equipment and monitoring systems have been described in detail elsewhere.⁵ Light pulses (~ 9 ns, 337.1 nm) were obtained from a Molectron UV-400 nitrogen laser and were used to irradiate the samples. Transient intermediates were detected by a monitoring system capable of micro- to nanosecond resolution. All of the laser flash photolysis experiments were carried out using deoxygenated solutions.

Materials. Tetrafluoro-1,4-benzoquinone (Aldrich) was purified by vacuum sublimation whereas tetrafluoro-1,4-hydroquinone (Aldrich) was used without purification. Of the solvents, carbon tetrachloride (Fisher) and chloroform (Eastman Organic Chemicals, Spectrograde) were used without purification, whereas benzene (Mallinckrodt) was used both unpurified and after purification (photooxidation by chloranil, distillation from P₂O₅).⁶

Results and Discussion

The ¹⁹F CIDNP enhancements observed for tetrafluoro-1,4-benzoquinone (TFBQ) after its UV irradiation in benzene solutions containing tetrafluorohydroquinone (TFHQ) are shown in Figure 3 as a function of magnetic field. It is obvious that the intensity increases monotonically up to the highest field strength studied. Up to fields of 7 kG these results are quite compatible with those reported earlier,^{2a} but at higher fields the data are substantially different. An obvious explanation for this discrepancy lies in the difficulty of comparing results obtained in substantially different experimental setups.

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 (6) R. Steinmetz, quoted by W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

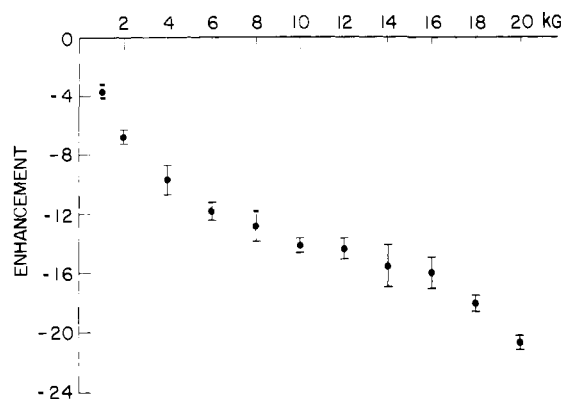


Figure 3. Magnetic field dependence of tetrafluorobenzoquinone polarization observed during irradiation of a 0.1 M benzene solution in the presence of tetrafluorohydroquinone (0.01 M). The data are corrected for relaxation during transfer from the external magnet to the spectrometer.

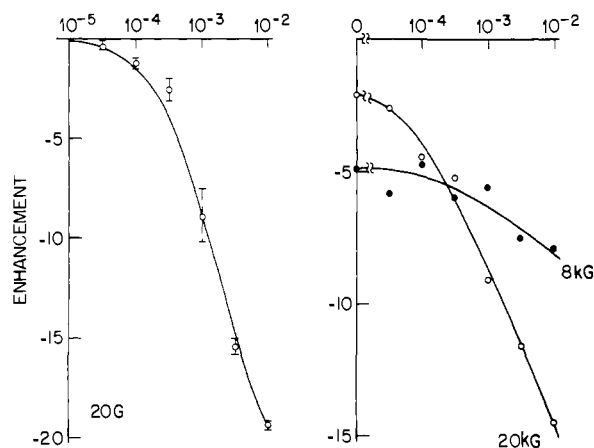


Figure 4. Tetrafluorobenzoquinone polarization as a function of tetrafluorohydroquinone concentration in benzene at magnetic fields of 20 G (left), 8 kG (right, full circles), and 20 kG (right, open circles). The line shown for 20 G is calculated using eq 5 with $(^3\tau \times ^3k_q)^{-1} = 1.5 \times 10^{-3} \text{ mol L}^{-1}$.

More disconcerting is the discrepancy between our experimental results (Figure 3) and the magnetic field dependence predicted by Adrian's theory (Figure 2, solid curve). A possible explanation for this discrepancy lies in the assumption that the observed effects have more than one independent contribution. In order to evaluate this possibility, we studied the quencher concentration dependence of the ^{19}F polarization at several magnetic fields. In the system trifluoroacetophenone-dimethoxybenzene this approach had resulted in the most convincing argument for the triplet-Overhauser mechanism.^{1,7}

The efficiency of intermolecular quenching reaction can be expected to show a quencher concentration dependence of the type

$$I \propto \frac{k_q[Q]}{k_q[Q] + t^{-1}} \quad (5)$$

dictated by the competition of decay or relaxation processes with the quenching reaction. In this expression, t is either a lifetime or a relaxation time. The quencher concentration dependence of the ^{19}F polarization of the quinone was studied at three values of magnetic field strength: at 20 G where Adrian, Vyas, and Wan had observed a low field maximum;^{2a} at an intermediate field of 8 kG; and at 20 kG, the highest field strength we could reach with the maximum voltage of the power supply and the minimum gap

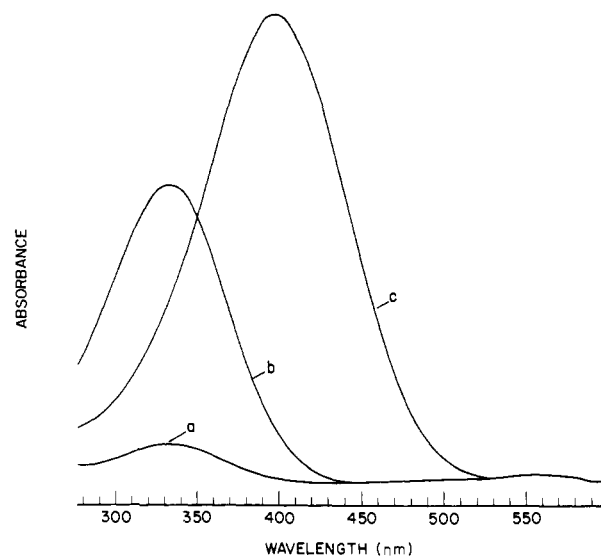


Figure 5. UV spectra of solutions of tetrafluorobenzoquinone ($\sim 3.5 \times 10^{-3} \text{ M}$) in (a) acetonitrile, (b) benzene, and (c) mesitylene.

that permitted spinning of the sample. The results document at least two different contributions to the overall polarization.

Tetrafluoroquinone Polarization at Low Fields. At a field strength of 20 G (Figure 4, left), tetrafluorobenzoquinone shows a pronounced increase of CIDNP intensity with increasing quencher concentration suggesting a first-order dependence. The maximum enhancement, $I/I_{\text{dark}}^{4kG} = -20$, is observed at the highest quencher concentration employed. The slope of the observed curve is compatible with any combination of values for $^3\tau$ and 3k_q satisfying the relation $(^3\tau \times ^3k_q)^{-1} = 1.5 \times 10^{-3} \text{ mol L}^{-1}$. Given a transient lifetime in benzene as determined by laser flash spectroscopy, $2 \times 10^{-7} \text{ s}$, the quencher concentration dependence of the CIDNP intensities suggests a quenching rate constant, $^3k_q = 3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. The fact that this value is very close to that determined by laser flash spectroscopy, $2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, gives us confidence that these different techniques indeed monitor the same process.

Nuclear spin polarization effects at very low fields are documented in a wide range of reactions.⁸ It is quite clear that the triplet-Overhauser mechanism is not involved here because the initial electron polarization (P_e) is linearly proportional to the Zeeman splitting and, therefore, becomes negligible at fields substantially below 1 kG. On the other hand, a radical-pair mechanism involving $S-T_{\pm 1}$ mixing can explain these effects readily⁸ and was indeed invoked by Adrian, Vyas, and Wan.^{2a} However, the exact nature of the intermediate pair and the detailed mechanism of its formation are open to question. The assumption of a pair of tetrafluorosemiquinone radicals generated by the triplet quinone in a hydrogen abstraction reaction appears oversimplified because the quinone absorbs only a small fraction of the incident light.

The existence of a donor-acceptor complex between TFBQ and benzene has been noted.⁹ The π, π^* transition of this complex coincides with the n, π^* transition of the carbonyl compound and its absorbance is more than six times as high as that of the quinone in acetonitrile (Figure 5). On the other hand, the interaction between the quinone and hydroquinone is less pronounced. Even in polar solvents such as acetonitrile, the quinone spectrum is not significantly affected when the hydroquinone is admixed. Accordingly, the quinone-benzene complex has by far the highest

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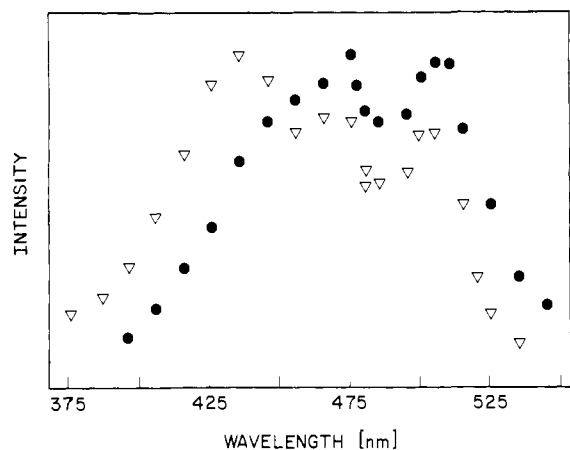


Figure 6. Transient UV spectra observed in acetonitrile (open triangles) and benzene solutions (full circles) containing tetrafluorobenzoquinone after excitation with a nitrogen laser pulse.

optical density in the reactant solution and most of the incident light is adsorbed by the charge-transfer complex and not by the quinone.

The nature of the excited-state species intercepted by the hydroquinone cannot be delineated unambiguously. The transient spectra observed in benzene and acetonitrile (Figure 6) show several similar features but also characteristic differences. This observation is not incompatible with the involvement of an excited-state complex between the quinone and the solvent.

Tetrafluoroquinone Polarization in the Absence of a Quencher.

In contrast to the polarization observed at low fields, the results obtained at higher fields cannot be explained by a single bimolecular reaction. The intensity at 8 kG (Figure 4, right, filled circles) is largely independent of quencher concentration whereas the effect at 20 kG (Figure 4, right, open circles), though strongly dependent upon quencher concentration, also has a component which is independent of TFHQ. We assign this additional effect to an interaction of the photoexcited quinone with benzene.

In view of the frequent occurrence of CIDNP effects in electron-transfer reactions,¹⁰ we have considered the possibility of an electron transfer from benzene to the triplet quinone. This reaction should be rather inefficient since benzene is a poor electron donor ($E_{D/D^+} = 2.43$ V)¹¹ and the rate constant of quenching by benzene in acetonitrile, $k_q = 1.6 \times 10^6$ M⁻¹ s⁻¹, is in keeping with this expectation. However, the irradiation of TFHQ in benzene does not produce any significant polarization between 0 and 1 kG whereas radical-pair reactions involving the tetrafluoroquinone radical show characteristic effects at low fields (vide supra, infra). Because of the absence of any low-field polarization, we eliminate the electron-transfer process as a cause of the observed polarization.

Some evidence for the nature of the intermediate in question can be derived from the magnetic field dependence of this effect which can be studied in the absence of the quencher. The result (Figure 7) resembles the field dependence curves observed, for example, during the photolysis of cyclic ketones, which have been assigned to the intermediacy of biradicals.¹² The maximum enhancement, $I/I_{\text{dark}}^{4kG} = -6$ is observed near 4 kG, close to the magnetic field strength where 1,8-biradicals give rise to maximum effects. Because of the similarity of the field dependence of the

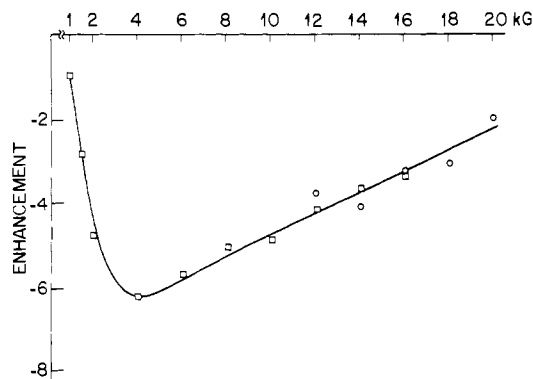
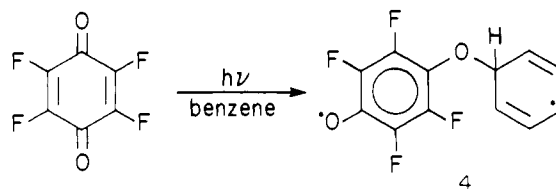


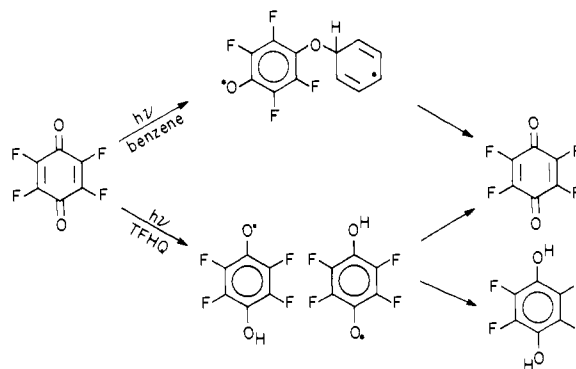
Figure 7. Magnetic field dependence of tetrafluorobenzoquinone polarization observed in benzene solution in the absence of tetrafluorohydroquinone.

quinone polarization in benzene with that of cyclic ketones, we ascribe these effects to a biradical adduct, 4, between the triplet



state of the quinone and the solvent, benzene. An adduct of this type is not without precedent. Similar adducts have been invoked to explain the relatively low lifetimes of n,π^* triplet states in benzene,¹³ and in at least one case, that of benzophenone, spectroscopic evidence has been adduced for the intermediacy of such a biradical.¹⁴ Similarly, the formation of oxetanes from triplet benzoquinone and various olefins is considered to proceed via biradical adducts; intermediates of this structure type have been intercepted by molecular oxygen or sulfur dioxide.¹⁵

Tetrafluoroquinone Polarization in the Presence of Tetrafluorohydroquinone. The quinone–benzene adduct cannot be the sole source of the polarization between 1 and 20 kG. The polarization shown in Figure 3 has at least one additional component associated with the presence of tetrafluorohydroquinone. We have used several approaches to determine the field dependence of this contribution without interference from the polarization induced in the biradical or its mechanistic equivalent. This dependence



can be measured directly either by carrying out the reaction in a solvent to which the quinone cannot add (tetrachloromethane)

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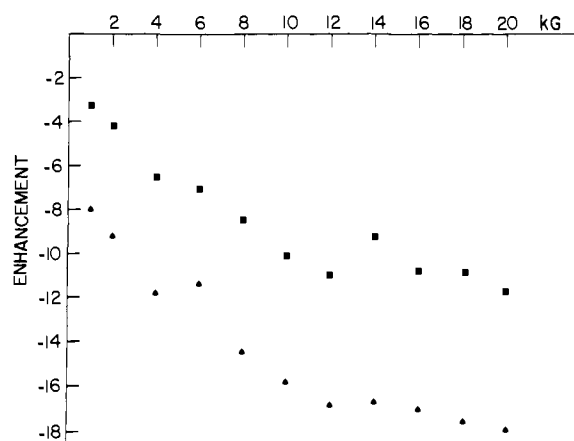


Figure 8. Magnetic field dependence of tetrafluorobenzoquinone polarization generated in CCl_4 in the presence of tetrafluorohydroquinone (triangles) and of tetrafluorohydroquinone polarization during irradiation of tetrafluorobenzoquinone in benzene (squares).

or by studying the polarization of the hydroquinone, whose only source of polarization is the semiquinone radical. Alternatively, the TFBQ enhancements measured in benzene can be corrected for the polarization induced in the biradical adduct.

The purely experimental approaches to the field dependence discussed here met with problems. The TFBQ polarization in tetrachloromethane increased monotonically with increasing field (Figure 8, triangles). However, the enhancements showed rather large variations with different batches of solvent. The polarization observed for TFHQ in benzene also showed a monotonic increase with magnetic field (Figure 8, squares). These effects also showed variations in intensity, and the short relaxation time of TFHQ renders the enhancements determined for this compound less certain.

Reliable and reproducible results were obtained by subtracting the contribution due to the biradical adduct from the TFBQ polarization observed in benzene. Since the triplet lifetime in this solvent (${}^3\tau_b$) and the rate constant of quenching by TFHQ in this solvent (3k_q) have been measured, the corrected enhancements can be calculated from the intensities, I and $I_{[Q=0]}$, observed in the presence and absence of TFHQ, respectively, as

$$I_{\text{cor}} = I - I_{[Q=0]} \left(\frac{{}^3\tau_b^{-1}}{{}^3k_q[Q] + {}^3\tau_b^{-1}} \right) \quad (6)$$

This polarization increases monotonically with increasing field (Figure 9, circles).

The field dependence of this contribution has to be compared with theoretical predictions in order to evaluate the potential involvement of the triplet-Overhauser mechanism. A comparison of the results shown in Figure 9 with the theoretical prediction^{2a} reproduced in Figure 2 (solid curve) shows that the agreement between experiment and theory is unsatisfactory. We have attempted to obtain a more satisfactory agreement by modifying the model used in the simulation and by varying the parameters employed in it.

The calculation of Adrian et al. treats the overall polarization as the sum of two independent contributions from the ortho and meta nuclei. However, these contributions take into account only the relaxation effects due to single ${}^{19}\text{F}$ hyperfine coupling. In the tetrafluorosemiquinone radical the electron is coupled to four fluorine nuclei, all of which affect the relaxation rates. The exact analytical expression for this radical requires the solution of a set of 23 rate equations, a task that was not attempted. Instead, we considered a "one-spin" model with a single "effective" anisotropic hyperfine coupling

$$B_{zz}^{\text{eff}} = [2(B_{zz}^{\text{o}})^2 + 2(B_{zz}^{\text{m}})^2]^{1/2} \quad (7)$$

In the framework of this modified model we varied principally two parameters, the hyperfine anisotropy, B_{zz} , and the rotational

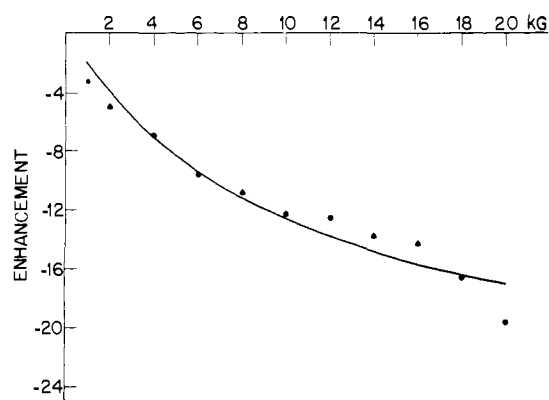


Figure 9. Magnetic field dependence of the enhancement (I/I_{dark}^{4kG}) observed for TFBQ (0.01 M) irradiated in the presence of TFHQ (0.01 M) in benzene (circles) corrected for the polarization due to the biradical adduct and for relaxation during transfer from the external magnet to the spectrometer. The line represents the enhancement calculated for the triplet-Overhauser mechanism with the following parameters: ${}^3k_q = 2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, $\tau_1(\text{radical}) = 1 \times 10^{-11} \text{ s}$, $\tau_1(\text{triplet}) = 1.7 \times 10^{-10} \text{ s}$, $D = 0.6 \text{ cm}^{-1}$, ${}^3\tau = 2 \times 10^{-7} \text{ s}$, $B_{zz}^{\text{eff}} = 50 \text{ G}$, $\delta g = 0.004$, light intensity $= 3 \times 10^{18} \text{ photons s}^{-1} \text{ cm}^{-2}$.

correlation time, τ_1 , of the intermediates.

The rotational correlation time, τ_1 , is important in two phases of the triplet-Overhauser mechanism. The tumbling of the triplet molecule causes the relaxation of its electron polarization, whereas the tumbling of the semiquinone radical causes the cross relaxation processes that convert electron polarization into nuclear polarization. The correlation times can be calculated from several models or they can be determined experimentally by a variety of methods. For TFBQ, the Stokes-Einstein model^{2a} yields a value of $3 \times 10^{-11} \text{ s}$, whereas the hydrodynamic model of Hu and Zwanzig¹⁶ gives a value of $1 \times 10^{-11} \text{ s}$. Light-scattering experiments¹⁷ suggest a correlation time, $\tau_1 = 8 \times 10^{-12} \text{ s}$, for hexafluorobenzene, a molecule quite similar to TFBQ in both shape and volume. These considerations suggest rotational correlation times near 10^{-11} s .

The parameter B_{zz} may be related empirically to the known isotropic hyperfine coupling; for different classes of radicals, B_{zz} falls within the range of 1.1 to 2.4 times the isotropic hyperfine coupling.¹⁸ The introduction of "effective" B_{zz} values allows us to use substantially higher values for this parameter. Nevertheless, values of B_{zz}^{eff} as high as 45 G and $\tau_1 = 1 \times 10^{-11} \text{ s}$ yield a reasonable agreement only for the shape of the field dependence curve, whereas the calculated enhancement factors are substantially smaller than the experimental values.

The agreement between calculated and observed enhancement factors can be improved when different correlation times are employed for the triplet and the doublet species. In the absence of specific interactions of either species with the solvent, the intermediates should have essentially identical correlation times. However, for TFBQ the possible interaction of the triplet state with the solvent (vide supra) could cause its correlation time to be longer than that of the radical. It is possible to use an indirect approach to the rotational correlation time of the triplet by determining its electron relaxation time, ${}^3T_{1e}$. This parameter is interrelated with τ_1 and with the zero-field splitting, ω_{zfs} , of the triplet by

$${}^3T_{1e}^{-1} = \frac{2}{15} \omega_{zfs}^2 \tau_1 \left(\frac{1}{1 + \omega_z^2 \tau_1^2} + \frac{4}{1 + 4\omega_z^2 \tau_1^2} \right) \quad (8)$$

Electron relaxation times of triplet states have been determined from the quencher concentration dependence of chemically induced electron¹⁹ or nuclear polarization effects.^{1,7a,b} For the reaction

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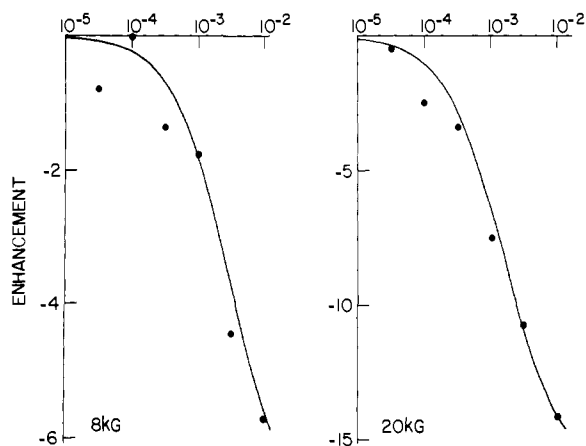


Figure 10. TFBQ polarizations as a function of TFHQ concentration in benzene at 8 kG (left) and 20 kG (right) corrected for the polarization due to the biradical adduct. The lines shown are calculated using eq 5 for $(t \times {}^3k_q)^{-1} = 3 \times 10^{-3}$ and 1.5×10^{-3} mol L⁻¹ for 8 and 20 kG.

discussed here, the quencher concentration dependence of the polarization (Figure 10), when corrected for the presence of biradical polarization (vide supra), indicates that the lifetimes at 8 and 20 kG are different. The curve obtained at 20 kG is identical within experimental error with that measured at low field (Figure 4, left) whereas the 8 kG data clearly indicate a shorter "lifetime".

The fact that the results are field dependent is reminiscent of the field dependence expected for the electron relaxation time, ${}^3T_{1e}$. However, the ratio, $t_{20}/t_8 \approx 2$, suggested by the data of Figure 10 is too small to be accommodated by any reasonable correlation time. This apparent discrepancy can be resolved if the electron relaxation time, ${}^3T_{1e}$, at intermediate fields is of the same order of magnitude as the triplet lifetime, ${}^3\tau$. In this case, the transfer of polarization from triplet to doublet would be limited not only by the electron relaxation but also by the decay of the triplet to the ground state. At low fields the electron relaxation would be limiting whereas at high fields the triplet decay would be the limiting factor. In the model, this situation can be accommodated by substituting the relaxation rate, ${}^3T_{1e}^{-1}$, by the combined rates of relaxation and decay, ${}^3T_{1e}^{-1} + {}^3\tau^{-1}$.

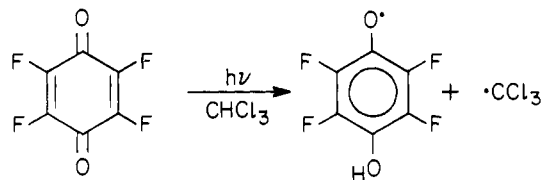
On the basis of these considerations we have chosen a value of ${}^3T_{1e} \approx 1 \times 10^{-7}$ s for the electron relaxation time at 8 kG. Assuming a zero-field splitting, $D = 0.06$ cm⁻¹, slightly smaller than the value of triplet benzoquinone ($D = 0.074$ cm⁻¹),²⁰ this corresponds to a rotational correlation time, $\tau_r = 1.7 \times 10^{-10}$ s, for the triplet state, significantly larger than the value assigned to the radicals, $\tau_r = 10^{-11}$. The value of B_{zz}^{eff} was set to 50 G, slightly larger than the value derived from the known isotropic hyperfine couplings according to $B_{zz} = 2.4a^2$.

Other values used in our simulation include: ${}^3k_q = 2 \times 10^9$ L mol⁻¹ s⁻¹; ${}^3\tau = 2 \times 10^{-7}$ s; and a light intensity of 3×10^{18} photons s⁻¹ cm⁻³ as determined in our apparatus according to Yang and Murov.²¹ Furthermore, a term describing the g factor anisotropy^{2a} was included in this simulation. A value, $\delta g = 0.004$, was used for this parameter, essentially the same as that used by Adrian et al.^{2a} The δg term improves the fit at high fields.

The resulting theoretical field dependence curve (Figure 9) reproduces the absolute enhancement factors and the general trend of the experimental field dependence quite well. Comparable fits can be obtained when both B_{zz} and τ_r are somewhat reduced (e.g., to 45 G and 1.3×10^{-10} s, respectively). Nevertheless, it is clear that relatively high values for these parameters are essential to achieve a reasonable fit.

The satisfactory agreement between experiment and theory leads us to conclude that the polarization generated in the photoreaction of tetrafluorobenzoquinone with tetrafluorohydroquinone can be ascribed to the triplet-Overhauser mechanism. Provided that the assumptions incorporated into the above simulation are not invalidated by new experimental findings or theoretical insights, the system TFBQ–TFHQ would be the second system for which this mechanism is firmly established.

Tetrafluoroquinone Polarization in Chloroform. The magnetic field dependence has also been useful in identifying the mechanism responsible for the strong ¹⁹F emission observed during the irradiation of tetrafluorobenzoquinone in chloroform. This reaction



almost certainly proceeds via hydrogen abstraction producing semiquinone radicals paired with trichloromethyl radicals. This view is supported by the reduced lifetime of the quinone triplet state in CHCl₃ (209 ns) and in CDCl₃ (521 ns) relative to the lifetime in acetonitrile (2.1 μs).

The observed signal direction is compatible with the radical-pair mechanism²² as well as with the triplet-Overhauser mechanism. This polarization had been ascribed to the latter mechanism because of the dependence of the CIDNP intensity on the plane of polarization of the incident light.³ However, the plane of polarization dependence has since been eliminated as a useful criterion for the triplet-Overhauser mechanism.²⁴ As a result, the polarization mechanism operative in this system remains uncertain.

We have examined the magnetic field dependence of this polarization and have found it to be similar to that observed for the reaction of TFBQ with TFHQ. This result is compatible with the triplet-Overhauser mechanism and is quite incompatible with the field dependence expected for the radical-pair mechanism as calculated according to Adrian² for $\Delta g = 0.0045$ ($g_{\text{CCl}_3} = 2.0091$; $g_{\text{C}_6\text{H}_4\text{O}_2\text{H}} = 2.0046$). We note that this conclusion confirms the earlier assignment by Vyas and Wan.³

Conclusion

In summary, a careful study of the nuclear spin polarization generated in the system 1–2 in benzene and of the magnetic field dependence of these effects has revealed contributions due to three independent polarization mechanisms: a radical-pair mechanism involving S–T_± mixing, a biradical polarization mechanism, and the triplet-Overhauser mechanism. These studies indicate that the field dependence may reveal important mechanistic features, especially when used in connection with other criteria such as the quencher concentration dependence. The involvement of two polarization mechanisms at high magnetic fields could not have been derived from the results obtained at either constant field or constant quencher concentration alone. Only when the variations of both parameters were considered was the composite nature of the overall effect discovered.

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Registry No. 1, 527-21-9; 2, 771-63-1; 3, 24719-25-3; 4, 83060-46-2; F₂, 7782-41-4; CHCl₃, 67-66-3; •CCl₃, 3170-80-7; H, 1333-74-0; C₆H₆, 71-43-2; acetonitrile, 75-05-8; mesitylene, 108-67-8.

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