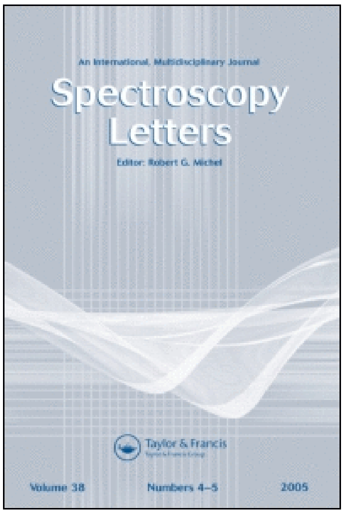

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Tetrafluoro-*p*-Benzoquinone Radicals: Chemical Exchange as Evidenced by Cidep

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TETRAFLUORO-*p*-BENZOQUINONE RADICALS: CHEMICAL EXCHANGE AS EVIDENCED BY CIDEP

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ABSTRACT

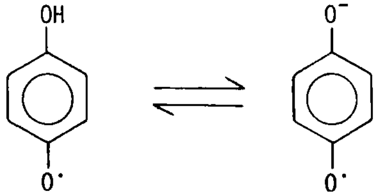
The CIDEP characteristics of radicals derived from tetrafluoro-*p*-benzoquinone have been studied. An alternating linewidth effect in the time-resolved CIDEP spectra was observed when a hydroxylic/non hydroxylic solvent mixture was used. The results are discussed in terms of chemical exchange between the neutral and anionic quinone radicals.

INTRODUCTION

In recent years the phenomenon of Chemically Induced Dynamic Electron Polarization (CIDEP) has provided both a theoretical and experimental advancement in the understanding of mechanisms and molecular dynamics pertaining to the reactions of free radicals in solution. The areas that have been covered span the simple type of protonation–deprotonation[1] reactions to processes such as degenerate electron and proton exchange which may be identified by the nature of the alternating phase effects of the hyperfine lines in a time-resolved CIDEP experiment[2,3].

One class of compounds which has been very useful in elucidating the molecular mechanisms responsible for the development of polarization from free radicals in solution is the quinones[4]. While the parent *p*-benzoquinone has recieved considerable experimental and theoretical consideration, less intensive investigations have been conducted for the halogenated analogues.

We have previously analysed[1] the time-resolved CIDEP characteristics at delay times of 0.5-2.5 μs after the laser irradiation for *p*-benzoquinone and have noted that on this time scale one can clearly observe the reaction;



which, manifested as a superposition of the spectra of both the neutral and anionic semiquinone radicals occurs on a μs time scale.

The existence of the neutral and anionic radicals derived from 2,3,5,6-*tetra*-fluorobenzoquinone (TFBQ) have also been noted and indeed under certain conditions both species may be formed in solution simultaneously[5,6]. However, unlike the situation with the parent molecule, when the anionic and neutral radicals derived from TFBQ exist together they are in rapid equilibrium with the result that the observed cw epr spectrum exhibits an anomalous linewidth and intensity distribution.

In this work we investigated the CIDEP characteristics of radicals derived from TFBQ in a variety of solvents and identify an alteration in the intensity distribution and linewidths of CIDEP spectra which arises as a consequence of a chemical interaction between two radicals in solution. This is the first time this type of chemical exchange has been noted in the CIDEP experiment and it is rather interesting to note that the time evolved hyperfine dependent phenomena characteristic of degenerate electron and proton exchange previously noted[2,3] for radical ions in solution, is not manifested here. Thus we have yet another example in which the phenomenon of CIDEP may be used to unravel radical dynamics and reactions in solution.

EXPERIMENTAL

Tetrafluoro-*p*-benzoquinone (TFBQ) and tetrafluoro- hydroquinone ($TFBQH_2$) were purchased from Aldrich and sublimed before use. All solvents were reagent grade and redistilled, solutions were purged with nitrogen prior to experimentation. The laser flash photolysis system and time-resolved CIDEP experiment have been described in detail previously[7,8]. U.V./visible spectra were recorded on a Hewlett Packard 8451A diode array spectrophotometer.

RESULTS AND DISCUSSION

The CIDEP spectrum of TFBQ in isopropanol at 1.5 μs after the laser flash consists of a predominantly emissive quintet signal (Fig. 1a, a_F = 4.08 Gauss) consistent with the formation of the radical anion of TFBQ[5,6,9] and indicative of the triplet mechanism of polarization characteristic of aromatic carbonyl compounds[8]. The relative intensity distribution of the hyperfine lines in this spectrum deviates significantly from the 1:4:6:4:1 quintet expected on the basis of spin density considerations. By reducing the incident laser light intensity to 30% of the original value we find that although there is an overall reduction in the signal intensity the relative magnitude of the centrally located line approaches more closely what would be expected on the basis of structural considerations. Similarly by progressively lowering the temperature we observed a gradual reduction in the relative intensity of the central line in the CIDEP spectrum of TFBQ until at −50°C the observed spectrum conforms to what would be expected for the CIDEP spectrum of this radical when both the emissive triplet mechanism polarization and an E/A signal from ST_0 radical pair mechanism polarization

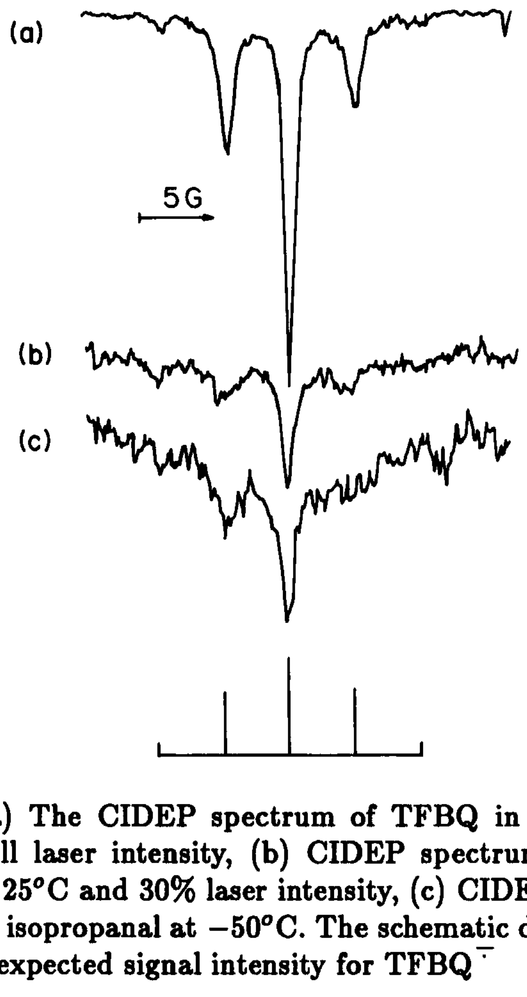


Fig. 1. (a) The CIDEP spectrum of TFBQ in isopropanal at 25°C, full laser intensity, (b) CIDEP spectrum of TFBQ recorded at 25°C and 30% laser intensity, (c) CIDEP spectrum of TFBQ in isopropanal at −50°C. The schematic diagram represents the expected signal intensity for $TFBQ^{\overline{\cdot}}$

(RPM) are superimposed. Increasing the delay time results in a more marked E/A pattern in the polarization spectrum further verifying the existence of the RPM in this system. Conversly on photolysis of TFBQ in solvents such as toluene or THF although the intensity of the centrally located line indicates that an exchange process is also occurring in this solvent the polarization spectrum consists of a triplet (a_F = 13.2 Gauss) of triplets (a_F = 3.3 Gauss) consistent with the formation of the fluorinated semiquinone neutral radical[5]. In a mixed solvent system such as IPA/toluene 3:7 v/v or THF/IPA 3:7 v/v the observed spectrum is considerably different than that observed for either the neutral or anionic radicals. Indeed, as has been previously reported[6] in the cw epr spectrum of TFBQ, what we are observing in this case is an admixture of both the anion and neutral radical of TFBQ. In Fig. 2 spectra observed for TFBQ under each of the solvent conditions listed above are shown along with a stick diagram to represent the effect of the chemical exchange in a system where both the anionic and neutral species co-exist. A theoretical analysis to account for this linewidth alternation has previously been proposed[6] and was based on the variation in the signs of the hyperfine splitting constants for the neutral and the anionic radicals. The observation of this effect in the CIDEP experiment implies that the rate constant for the deprotonation–protonation equilibrium (Eq. 1)

$$TFBQH^{\cdot} \rightleftharpoons TFBQ^{\overline{\cdot}} \qquad (1)$$

occurs on a time scale which is rapid compared to the time resolution of the experiments (*i.e.* 1 μs). Indeed the ability to observe this chemically averaged polarization spectrum, implies that the rate of chemical exchange exceeds the difference in hyperfine frequencies for the fluorine splitting, which is of the order of 45 MHz.

Therefore for TFBQ, by varying the nature of the solvent or by using a solvent mixture it is indeed possible to alter the nature of the observed polarization spectrum. For example when isopropanol is the solvent, even at short delay times only the anion radical is observed, this is in contrast to the situation for the parent *p*-benzoquinone where one observes the formation of the neutral semiquinone radical at short delay times (1 μs) in isopropanol, as a result of H abstraction from the alcohol. At longer delay times this species deprotonates forming the radical anion and we observe a superposition of the spectra of both of these species. It has previously been proposed[9] that TFBQ

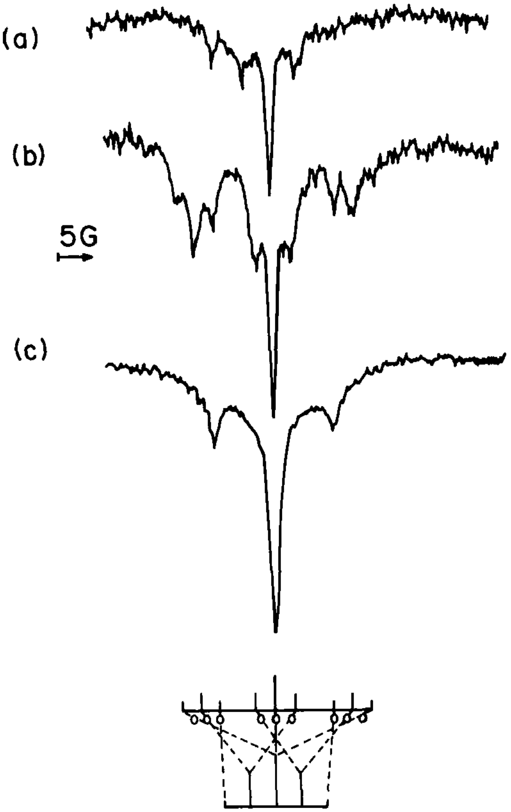


Fig. 2. (a) CIDEP spectrum of TFBQ in isopropanol, (b) CIDEP spectrum of TFBQ in toluene and (c), CIDEP spectrum of TFBQ in isopropanol/toluene 3:7 v/v. All spectra were recorded at 1.5 μs after laser firing. The schematic diagram depicts the mechanism of exchange broadening predicted for these radical species.

forms an anion radical directly in ethanol as a consequence of the increase in the electron affinity of the fluorine atoms in TFBQ relative to benzoquinone itself.

In order to establish the mechanism leading to the formation of the TFBQ radical anion in isopropanol and the stability of TFBQH in this solvent we conducted an experiment with tetrafluorohydroquinone in isopropanol in the presence of *t*-butylperoxide. On photolysis the peroxide molecule undergoes homolytic cleavage to form the very reactive peroxy radical which would rapidly abstract an H atom from the hydroquinone molecule to form the neutral $TFBQH^{\cdot}$ thus minimizing the possibility of radicals being derived from an interaction of the quinone with the alcohol solvent. Under these conditions we observed only the formation of the radical anion, indicating that the rate of deprotonation of TFBQH in isopropanol must be extremely fast. When the solvent was changed to ethanol a similar phenomenon was observed, however by the addition of acetic acid one could stabilize the neutral radical and a cw spectrum consistent with the presence of both the neutral and anionic forms of this semiquinone was observed.

The U.V./visible absorption spectrum of TFBQ has been shown to be very solvent dependent[5]. In alcohol solvents such as ethanol, methanol and isopropanol the spectrum has one main peak around 250-280nm (π–π^*) (depending on alcohol) with a second less intense shoulder around 350-360nm ($n\pi^*$). On irradiation a new band appears around 418nm which may be attributable to the semiquinone radical anion[10,11]. However the spectra of TFBQ in non hydroxylic solvents such as toluene, THF, dioxane or acetone reveal only one broad absorption (having λ_{max} dependent on the solvent). It has been shown previously that TFBQ will indeed form electron donor-acceptor complexes with toluene and several other molecules such as durene and *p*-xylene in the ground state[12] and that the formation of these complexes results in a bathochromic shift in the absorption spectrum.

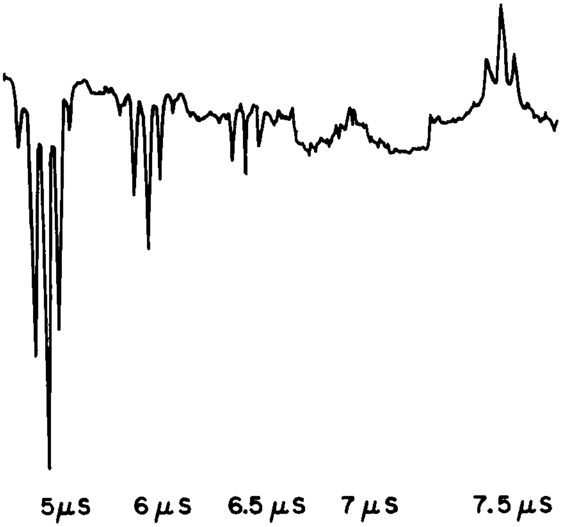


Fig. 3. The CIDEP spectra of *p*-benzoquinone radical anion as a function of delay time after the laser firing. This reversal of phase is typical in systems which exhibit degenerate electron exchange.

Numerous epr studies have been conducted to clarify the effect of halogen substitution on the spin density of C atoms in hydrocarbon radicals[13,14,15]. For TFBQ it has been shown that indeed there is very little variation expected in both the spin density of the ring C atoms or the carbonyl oxygens as compared to benzoquinone. Although perhaps somewhat surprising in view of the proposed differences in the physicochemical properties of fluorinated hydrocarbons[15], on the basis of the spin density studies for the carbonyl oxygens one would not expect to see very great differences in the dynamics of the epr characteristics of TFBQ relative to the parent benzoquinone. However, as mentioned previously TFBQ has a propensity to interact with other hydrocarbon molecules to form charge transfer and π type complexes; the electron withdrawing nature of the F atoms tends to increase the strength of these complexes relative to the parent molecule[16].

The phase inversion phenomenon which has been observed in CIDEP spectra of BQ (Fig. 3) and several other free radical intermediates was not observed for TFBQ or TFBQH radicals.

It would appear that the ability to observe a composite spectrum corresponding to both the neutral radical and the radical anion in TFBQ simultaneously depends strongly on the solvent system employed, thus in isopropanol it is easily shown that the neutral radical deprotonates on a time scale that is fast compared with the time resolution of the experiment, however in a mixed solvent system such as IPA/toluene the neutral radical is stablized by interaction with toluene and is thus capable of participating in a proton exchange reaction with the radical anion most readily.

It is with great interest that we study the reactions of quinone molecules and it is never surprising that this class of compounds can reveal many different phenomena that allow us to further unravel the possible mechanisms by which free radical species form and interact. Thus we are suggesting that indeed it is the chemical modifications and environmental interactions that determine the variations in the epr characteristics of TFBQ. We have noted previously that fluorinated solvents can have a profound effect on the formation and stability of radicals in solution, it may therefore be very interesting to compare the properties of various fluorine substituted compounds to assess their CIDEP characteristics.

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