words, membranes *could be* chiral at phosphorus, and the configuration at phosphorus could be important in membrane structures. It should not be presumed that the phosphorus is achiral (as in state I) in membranes without experimental proof. In the interaction of phospholipids with membrane proteins or enzymes, it is not impossible that the phosphate group may function as a chiral recognition site.[13]

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(13) Although this concept may be difficult to be envisioned in membranes, we have already found that the phosphate group of phospholipids in the form of micelles functions as a chiral recognition site in the catalysis of phospholipase A$_2$. This enzyme hydrolyzes the C-2 carboxylic ester, which is five bonds away from the phosphorus center. However, it specifically takes the isomer B of DPPsC as a substrate.[5]

Chemically Induced Dynamic Electron Polarization (CIDEP) of Some Sulfur-Containing Cation Radicals: Evidence of the Charge-Transfer Processes between Quinone Cation Radicals and Sulfur Heterocyclic Compounds

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Although cation radicals have been extensively studied by ESR,[1-3] many of the reactions leading to the formation and observation of these radical cations in solution are complex and often incompletely understood. The recent elegant studies of alkane radical cations at 77 K in CFCl$_3$ or similar solvents[4-8] have utilized beautifully a simple charge-transfer mechanism to produce such interesting radical cations. The concept of charge transfer involving organometals in organic reactions has long been recognized,[9,10] and recently we were able to demonstrate the potential of the combined ESR and CIDEP (chemically induced dynamic electron polarization) technique in providing unequivocal evidence of the nature of the charge-transfer processes in the photochemical reactions between quinones and organotins.[11,12] In this report, we establish a model CIDEP system in charge-transfer studies in solution that involves the use of a unique charge transfer between the well-defined benzoquinone cation radicals and several sulfur-containing heterocycles in trifluoroacetic acid at room temperature. Historically, organosulfur cation radicals have occupied a prominent place both in ESR and organic chemistry literature.[13] The choice of organosulfur radical cations as our initial model CIDEP study will be of much wider general interest.

Table I. ESR Parameters and CIDEP Observations for Some Organosulfur Cation Radicals in Trifluoroacetic Acid and in the Presence of BQ$^{+\cdot}$

organosulfur cation radical	g factor ±0.001	a_X, mT	T_1 ± 0.5, μs (temp, °C)
thianthrene	2.0085	0.128 (4 H)	1.5 ± 0.5 (−10)
		0.89 (^{33}S)	
phenothiazene	2.0051	0.634 (N)	1.8 (23)
		0.729 (H–N)	
		0.113 (2 H)	
		0.050 (4 H)	
		0.249 (2 H)	
thioxanthen-9-one	2.0072	0.367 (4 H)	2.1 (−10)
		0.110 (2 H)	
		0.092 (2 H)	
dibenzothiophene	2.0070	unresolved	1.7 (23)
4,4′-thiodiphenol	2.0068	0.135 (4 H)	1.3 (23)
thianaphthalene	2.0047	unresolved	
BQ$^{+\cdot}$	2.0038	0.299 (4 H)	4.6 (−10)

Trifluoroacetic acid was used as solvent for these reactions since its acidity and low nucleophilicity[14] contribute to the stabilization of the cation radicals formed in solution. Irradiation of 1,4-benzoquinone in trifluoroacetic acid with a 200-W super-pressure mercury lamp produced a radical species with the following ESR parameters: $g = 2.0038 \pm 0.0001$; $a_H = 0.229$ mT (4 H). This species can be reasonably assigned to the benzoquinone radical cation, BQ$^{+\cdot}$. At room temperature and in trifluoroacetic acid solvent, BQ$^{+\cdot}$ radical cations are persistent up to an hour after irradiation. This fact afforded the use of BQ$^{+\cdot}$ in trifluoroacetic acid as a definitive charge-transfer agent when other electron-donor molecules are added that do not form radical cations by themselves in trifluoroacetic acid. Thus, irradiation of benzoquinone in trifluoroacetic acid followed by the addition of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) from a separated side arm configuration resulted in the immediate formation of the well-known TMPD$^{+\cdot}$ cation radical. Another example of this model system is diphenylamine, which formed the well-resolved diphenylamine radical cations in the presence of BQ$^{+\cdot}$. Neither TMPD nor diphenylamine yields radical cations by themself in trifluoroacetic acid.

Several sulfur-containing compounds undergo similar charge-transfer reactions with BQ$^{+\cdot}$ in trifluoroacetic acid, and the ESR parameters of some of these organosulfur radical cations observed are reported in Table I. Previous CIDEP studies of the quinone system in this laboratory usually dealt with the semiquinone radical or the radical anion, and indeed this is the first time we observed CIDEP from a benzoquinone cation radical. Two organosulfur radical cations, thianthrene and phenothiazine, were chosen for detailed CIDEP characterization. However, the use of the BQ$^{+\cdot}$ charge-transfer technique permitted observations of CIDEP from other less stable radical cations such as the thianaphthene. Thianthrene and phenothiazine both form radical cations thermally in trifluoroacetic acid, but their concentrations are further enhanced upon addition of benzoquinone. On the other hand, thianaphthene radical cations are produced only when BQ$^{+\cdot}$ is present.

We have pointed out previously[15] that CIDEP is a powerful tool in mechanistic and kinetic studies of photochemical reactions. In the present model system, the organosulfur radical cations formed thermally cannot exhibit *initial* polarization, which arises only from a photochemical triplet mechanism.[15] On the other hand, secondary thermal reactions involving polarized primary BQ$^{+\cdot *}$ formed photochemically can lead to polarization transfer from BQ$^{+\cdot *}$ to the organosulfur cation radical, provided the secondary reaction takes place before the destruction of polarization of BQ$^{+\cdot *}$ by spin–lattice relaxation:

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$$\mathrm{BQ}^{+\cdot *} + \mathrm{S} \rightarrow \mathrm{BQ} + \mathrm{S}^{+\cdot *} \qquad (1)$$

It is also feasible, however, that polarization of the sulfur radical cation derives directly from a primary photochemical charge-transfer reaction:

$$\mathrm{BQ} + \mathrm{S} \xrightarrow{h\nu} \mathrm{BQ}^{-\cdot *} + \mathrm{S}^{+\cdot *} \qquad (2)$$

Indeed, much of our previous effort in CIDEP studies of quinone/organometal systems[11,12] involves such a primary charge-transfer mechanism. Nevertheless, in the present model sulfur system $\mathrm{BQ}^{-}\cdot$ and the semiquinone radical have not been observed in all the experiments. Furthermore, in a majority of the experiments, both $\mathrm{BQ}^{+\cdot *}$ and $\mathrm{S}^{+\cdot *}$ radical cations are clearly observable simultaneously, since their g factors are substantially different. Both $\mathrm{BQ}^{+\cdot *}$ and $\mathrm{S}^{+\cdot *}$ exhibit the totally emissive polarization, consistent with the photochemical triplet mechanism and the secondary polarization transfer in (1).

All experiments were performed at room temperature except in cases in which T_1 of the organosulfur cation radicals are too short for CIDEP measurements. Samples were contained in Pyrex tubings and sealed off under high vacuum. ESR observations were made on a Varian E3 X-band spectrometer with 100-kHz field modulation for cw experiments. Time-resolved CIDEP experiments were carried out by using a megawatt nitrogen laser and direct ESR detection, as previously described.[16] The transient polarization was analyzed to obtain T_1. The detailed analysis reported earlier[16,17] showed that the ESR signal $h(t)$ at time t from a CIDEP spectrometer with a unique exponential response is

$$h(t) = b_1 + b_2e^{-\lambda_1 t} + b_3e^{-\lambda_2 t} + b_4e^{-t/\tau}$$

where constants b_1, b_2, b_3, and b_4 are related to the initial polarization, the equilibrium polarization, the amplitude B_1 of the microwave magnetic field, the instrument response time τ, and the parameters λ_1 and λ_2. The λ_1 and λ_2 respectively approach T_1^{-1} and T_2^{-1} as the microwave power approaches zero. In our experiments when T_1 is significantly longer than T_2 and τ, an estimate of T_1 can be reliably obtained by extrapolating measured decay times for a sequence of low microwave powers to zero power.

The organosulfur compounds studied in this report include thianthrene, phenothiazine, thioxanthen-9-one, dibenzothiophene, 4,4′-thiodiphenol, and thianaphthene. With the exception of the last compound, all of these radical cations exhibit totally emissive polarization and their T_1's are reported in Table I. For thianaphthene, although no transient CIDEP could be detected, it was clear that reaction 1 took place in cw experiments. The lack of observable polarization in this case could be due to the much shorter T_1 for this sulfur radical cation and/or the slower charge-transfer reaction between $\mathrm{BQ}^{+\cdot *}$ and thianaphthene. It is worth pointing out that in the same system, the polarization from $\mathrm{BQ}^{+\cdot *}$ was indeed observable. T_1's of the other organosulfur cation radicals are also relatively short, as compared to the "smaller" $\mathrm{BQ}^{+}\cdot$ radical cation in the same system. Our earlier theoretical analyses[17,18] showed that T_1 is sensitive to both the molecular size and the number of rings in the semiquinone radicals. This may have some bearing on the difference between the "three-ring" and the "two-ring" sulfur compounds. The comparison between the thianthrene and benzoquinone probably will have to take into account the large spin–orbit coupling of the S atom(s), which could contribute to a shorter T_1.

The ESR and CIDEP results presented here clearly define a useful model reaction using the simple charge-transfer process of a benzoquinone cation radical to organosulfur compounds. The charge-transfer reaction studied here can obviously be applied to other classes of organic donors. In systems where the specific charge-transfer mechanism is complicted by other thermal electron-transfer processes, application of the time-resolved CIDEP technique should be of great help in delineating the mechanism. Current studies include further exploration of the use of related solvents other than trifluoroacetic acid as well as other organic donors including the sulfoxides.

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Absence of an α-Effect in the Gas-Phase Nucleophilic Reactions of HOO^-

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In solution nucleophiles that contain a heteroatom adjacent to the reaction center (HOO^-, ClO^-, $\mathrm{HONH_2}$, etc.) are found to be more reactive toward carbon electrophiles than would be expected from their basicity (the α-effect[2]). For example, in a recent study HOO^- was shown to undergo $\mathrm{S_N2}$ displacement on a methyl group 10 times faster than does $\mathrm{CH_3O}^-$, despite the greater basicity of the latter anion.[3] Even larger effects are found for reactions at unsaturated carbons.[4] The origin of this phenomenon remains a subject of active discussion. Some explanations invoke special solvation effects such as reduced solvation of the α-nucleophile.[5] More commonly, it is proposed that electronic repulsions between the lone pair on the heteroatom and those on the nucleophilic center lead to an increase in reactivity for α-nucleophiles,[6] and a number of workers have advanced quantum mechanical explanations based on this model.[7] However, these explanations have recently been challenged by Wolfe.[8] If the α-effect is an intrinsic property of the anion, as these latter explanations suggest, it should manifest itself in the gas phase, while if it is due to differential solvation, it should not. We report that in the gas phase HOO^- shows no evidence of an enhanced nucleophilicity, as compared to HO^-, toward either saturated or unsaturated carbon.

The α-effect is most pronounced for HOO^-, and the most extensive theoretical work has been reported for this anion.[7c] We have been interested for some time in the chemistry[9] of HOO^- and recently reported measurements of its basicity and electron binding energy.[10] In order to test its nucleophilicity we first

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