1,3-Dimethyl-1,2,3,4-tetrahydrobenzofuro[2′,3′:5,6]pyrazino[2,3-*d*]pyrimidine-2,4-dione (4f). A stirred solution of **2f** (0.50 g, 1.61 mmol) in 10 mL of nitrobenzene was heated at reflux for 54 h. After this period, the reaction mixture was filtered through a silica gel pad, eluting successively with methylene chloride and 1:1 methylene chloride/ethyl acetate. The second fraction was evaporated under reduced pressure, and the residual burnt sienna soil was triturated with methylene chloride to afford 0.21 g of a pale tan solid. The filtrate was passed through a silica gel column, eluting with 1:1 ethyl acetate/methylene chloride to give 0.16 g of additional solid. The products were combined to give 0.37 g (82%) of a tan solid: mp 298–300 °C; ^{1}H NMR ($CDCl_3$) δ 8.26 (d, J = 8.1 Hz, 1 H), 7.82–7.73 (m, 2 H), 7.57–7.52 (m, 1 H), 3.89 (s, 3 H), 3.60 (s, 3 H); HRMS calcd for $C_{14}H_{10}N_4O_3$ m/z 282.0753, found m/z 282.0751. Anal. Calcd for $C_{14}H_{10}N_4O_3$: C, 59.57; H, 3.57; N, 19.85. Found: C, 59.35; H, 3.64; N, 19.71.

1,3-Dimethyl-6-*p*-tolyl-7-azalumazine (5). A mixture of 6-amino-1,3-dimethyl-5-nitrosouracil[14] (1.64 g, 8.9 mmol), *p*-tolylaldehyde (1.20 g, 11.1 mmol), and anhydrous hydrazine (0.32 g, 10.0 mmol) in 50 mL of dimethylformamide was heated at reflux for 5 h. After this period, the solvent was removed by distillation, and the residue was triturated with ethanol. Recrystallization from isopropyl alcohol gave 1.54 g (61%) of a yellow solid: mp 291–292 °C; ^{1}H NMR δ 2.47 (s, 3 H), 3.59 (s, 3 H), 3.94 (s, 3 H), 7.37 (d, J = 8.2 Hz, 2 H), 8.49 (d, J = 8.2 Hz, 2 H); HRMS calcd for $C_{14}H_{13}N_5O_2$ m/z 283.1069, found m/z 283.1069. Anal. Calcd for $C_{14}H_{13}N_5O_2$: C, 59.36; H, 4.63; N, 24.72. Found: C, 59.11; H, 4.69; N, 24.45.

Registry No. 1, 18969-84-1; **2a**, 114996-94-0; **2b**, 114996-95-1; **2c**, 114996-96-2; **2d**, 114996-97-3; **2e**, 114996-98-4; **2f**, 114996-99-5; **4a**, 114997-00-1; **4b**, 114997-01-2; **4c**, 114997-02-3; **4d**, 114997-03-4; **4e**, 114997-04-5; **4f**, 114997-05-6; **5**, 65358-01-2; $HO(CH_2)_2C{\equiv}CH$, 927-74-2; $HOCH(Et)CH_2C{\equiv}CH$, 19780-84-8; $HOCH(Ph)CH_2C{\equiv}CH$, 1743-36-8; $HO(CH_2)_2C{\equiv}CMe$, 5390-04-5; 4-amino-1-butyne, 14044-63-4; 2-cyanophenol, 611-20-1; 6-amino-1,3-dimethyl-5-nitrosouracil, 6632-68-4; *p*-tolylaldehyde, 104-87-0; hydrazine, 302-01-2.

π-Acceptor-Induced Reactions: Unusual Selectivity in Bond-Cleavage Reactions through the Use of Photochemical Excitation

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Received January 8, 1988

Bond-cleavage reactions of benzyl ether (BE) and 4,4′-dicyanobenzyl ether (DCBE) can be induced in the presence of various π-acceptor compounds. π-Acceptors used in this study are 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 7,7,8,8-tetracyanoquinodimethane (TCNQ). The products of these reactions are the corresponding benzaldehydes and benzyl alcohols regardless of the π-acceptors used in this study. Activation of these reactions can be achieved either thermally or photochemically. The relative reactivities of benzyl phenyl ether (BPE) and BE with these π-acceptors have been determined for both thermal and photochemical activation. BE is more reactive under all conditions than BPE. The selectivity of the BE bond-cleavage reaction initiated by photochemical excitation of DDQ is increased by 2 orders of magnitude when compared to thermal activation. $\Delta\Delta H^{\ddagger}$s for the bond-cleavage reactions of BE and BPE as induced by DDQ and $TCNQF_4$ have been determined. These results are interpreted with respect to the stability of the ionic intermediates and the tightness of ion pairing.

Introduction

Even though the transfer of electrons occurs in almost all chemical reactions, the dynamics of electron transfer are probably the least understood of all chemical processes. Given the importance of electron-transfer processes in a large variety of chemical reactions such as photosynthesis[1] and bond-cleavage reactions,[2] a great deal of theoretical[3] and experimental work[4] has been directed toward a better understanding of the relative rates of electron-transfer processes and the chemical processes that occur around them.[5]

A long-standing question concerns the interactions of quinones with various hydride donors.[6-10] The reactions of quinones have attracted a great deal of attention because of their role in a large variety of chemical and biochemical processes. The possible interactions of quinones with various hydrides are shown in eq 1. Although quinones

$$DH + Q \rightleftarrows DH\cdots Q \rightleftarrows DH^{\bullet+}/Q^{\bullet-} \rightleftarrows D^{\bullet}/QH^{\bullet} \rightleftarrows D^{+}/QH^{-} \quad (1)$$

are generally regarded to be good hydride acceptors,[8] a critical question concerns whether this reaction occurs in a single reaction step or in a stepwise fashion.[9,10] A continuum of reaction possibilities exist that form part of what electrochemists have referred to as an electrochemical, chemical, electrochemical (ECE) mechanism.[10] For a chemical oxidizing reagent, in which the oxidation is occurring in solution through single electron transfer (SET) reagents, geminate ion pairs are produced when electrons are transferred from the substrate to the oxidant. Proton transfer would lead to a geminate radical pair, while a

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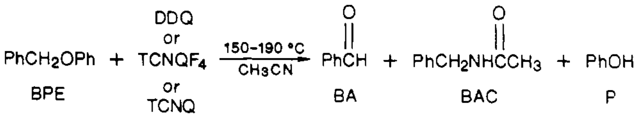
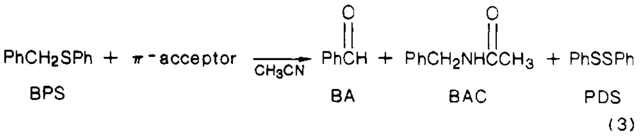
second electron transfer would produce another set of geminate ion pairs. The reactions characteristic of each of these geminate pairs would originate from the relative rates of ion pair or radical pair separation, reversion of the geminate pair to form starting materials, and the rates of the subsequent reactions to form the next intermediates. If diffusion from the geminate pair to form solvent separated species occurs at a rate faster than subsequent reactions, then the reactions of quinones need not occur via a complete hydride transfer. Thus, reactions characteristic of the radical cation of the substrate (produced via SET) or reactions characteristic of the radical (produced by H-atom transfer) may be observed. Evidence has been presented that, in some cases, the reactions may proceed via an initial rate-determining electron transfer reaction.[6,11] Alternatively, evidence has been gathered to support rate-determining H-atom transfer[12] while in other systems, hydride transfer has been argued to be rate determining.[7,14]

As part of our effort to explore new ways to cleave bonds, attention has been directed recently to the reactions initiated by electron acceptors.[13-15] Work in our laboratories has been concentrated on the development and understanding of bond-cleavage reactions, with particular interest to fuel and environmental concerns. We have reported earlier that 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$) were capable of initiating bond-cleavage reactions[13] as shown in eq 2 and 3. These reactions were possible only when the solutions were heated to higher temperatures such as 190 °C.



$$\underset{\text{BPE}}{PhCH_2OPh} + \text{DDQ or } TCNQF_4 \text{ or TCNQ} \xrightarrow[CH_3CN]{150-190\ °C} \underset{\text{BA}}{PhCH{=}O} + \underset{\text{BAC}}{PhCH_2NHC({=}O)CH_3} + \underset{\text{P}}{PhOH} \qquad (2)$$

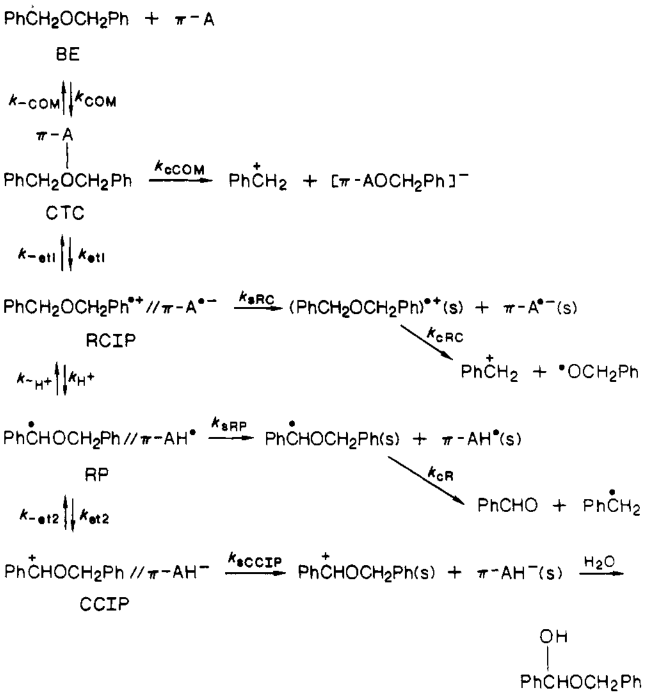


$$\underset{\text{BPS}}{PhCH_2SPh} + \pi\text{-acceptor} \xrightarrow[CH_3CN]{} \underset{\text{BA}}{PhCH{=}O} + \underset{\text{BAC}}{PhCH_2NHC({=}O)CH_3} + \underset{\text{PDS}}{PhSSPh} \qquad (3)$$

The purpose of the present study was to examine the possible role of radical intermediates deriving from an ECE reaction of the quinones with the ethers. Recent evidence suggested that the radical cleavage reaction of benzyl ether (BE) as shown in eq 4 proceeded at an extremely high rate and with only a small thermodynamic barrier to reaction.[16] We reasoned that the reaction of BE with π-acceptors might serve as a test of the relative electron-transfer rates and radical-pair separation.

$$Ph\dot{C}HOCH_2Ph \rightarrow PhCHO + Ph\dot{C}H_2 \qquad (4)$$

Scheme I. Complete ECE Mechanism for Bond Cleavage Reactions of BE



The full ECE mechanism for the reaction of BE with π-acceptors is shown in Scheme I. Charge-transfer complex formation (k_{com}) may be expected to be followed by an electron-transfer process (k_{et1}) to form a radical cation/anion geminate ion pair (RCIP). Proton transfer (k_{H^+}) or pair separation (k_{SRCIP}) may be expected to result from RCIP. The geminate radical pair has a similar set of reactions available with electron transfer (k_{et2}) and separation (k_{SRP}) as possible reactions. Electron transfer would produce a fully hydride transferred species (CCIP) which may undergo separation to yield reaction products. We have intentionally neglected possible reactions of the geminate pairs with external reagents in order to simplify the analysis. By our definition, a bond-cleavage reaction such as shown in eq 4 proceeding within the geminate radical pair followed by electron transfer from the benzyl radical to the semiquinone radical would be equivalent to a second electron transfer followed by its subsequent steps. CCIP might also be envisioned to add water in the ion pair. However, the ultimate products from such processes appear to be those of a complete hydride transfer process. The critical question of interest is the relative rate of separation of the radical pair vs all other processes leading to a second electron transfer step. In order to confirm that any observed reactivity trend is due to the change in these relative reaction rates, we utilized a variety of π-acceptors with varying reduction potentials to initiate the bond-cleavage reactions. This follows from the expectation that electron-transfer rates should be influenced by changes in the redox potentials of the partners.[17] We describe here our results of thermal and photochemical activation of the reactions of BE with π-acceptors.

Results

Thermal Reactions of BE and DCBE. We report here that heating BE in the presence of various π-acceptors yields benzaldehyde (BA) and benzyl alcohol (BOH) as shown in eq 5. The acceptors used in this study were

$$\underset{\text{BE}}{PhCH_2OCH_2Ph} \xrightarrow[CH_3CN]{\pi\text{-acceptor}} \underset{\text{BA}}{PhCHO} + \underset{\text{BOH}}{PhCH_2OH} \qquad (5)$$

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),

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Table I. Product Yield Data for the Thermal Reactions of BE

starting material	π-acceptor	E_r	product yield, mol % BA[a]	 BOH[a]	temp, °C	time, h	% conversion
BE	$TCNQF_4$	0.53[c]	157	53	150	3	19
BE	DDQ	0.51[d]	119	80	150	0.25	27
BE	TCNQ	0.13[c]	115	82	190	2	8
BE					200	27	2

starting material	π-acceptor	E_r	product yield, mol % CBA[b]	 CBOH[b]	temp, °C	time, h	% conversion
DCBE	$TCNQF_4$	0.53[c]	89	111	190	1	4
DCBE	DDQ	0.51[d]	139	55	190	4	40
DCBE	TCNQ	0.13[c]	133	63	190	48	25
DCBE					230	5	0.2

[a] Product yield data determined by GC analysis with *n*-octyl cyanide as an internal standard. Yields are accurate to ±10%. [b] Product yield data determined by HPLC analysis with phenyl benzoate as an internal standard. Yields are accurate to ±10% for the aldehyde and ±25% for the alcohol. [c] V vs SCE.[57] [d] V vs SCE.[58]

2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$), and 7,7,8,8-tetracyanoquinodimethane (TCNQ). These acceptors were used because of their known ability to form charge-transfer complexes[18] and because of their known ability to effect bond-cleavage reactions in benzyl phenyl ether (BPE) and benzyl phenyl sulfide (BPS).[13a] Our general procedure for effecting these thermal reactions has been previously described.[13a] In brief, BE (0.01 M) and the π-acceptor (0.01 M) are mixed in freshly distilled acetonitrile. This mixing is carefully performed in the dark to ensure that all reactions are the result of thermal reactions and not photochemical reactions. The reaction solution is then sealed in base-washed Pyrex tubes[19] after degassing by three freeze–pump–thaw cycles. In all cases, only BA and BOH were formed as products in the reaction. These products were identified by GC–MS analysis and independent coinjection on three different GC columns. Additionally, BA was identified by isolation and derivatization with (2,4-dinitrophenyl)hydrazine (2,4-DNP). A mixed melting point of the 2,4-DNP derivative from the reaction mixture and a 2,4-DNP derivative made from authentic BA confirmed the identity of this product to be BA. The results of quantitative analyses of these reactions are shown in Table I. In all cases, the total product yields are within experimental error of a quantitative mass balance. HPLC analysis of the DDQ reactions confirmed that the products are only BA and BOH.

A control experiment in which no π-acceptor was added to the solution showed very little reaction as can be seen in Table I. This is in reasonable agreement with the 48 kcal/mol activation energy for the uncatalyzed C–O bond cleavage of BE.[20] Thus, the reactions are initiated by the π-acceptor. Extensive efforts were made to find bibenzyl and/or toluene, which would be products of a radical cleavage pathway yielding benzyl radicals (note eq 4). However, no evidence could be found for these products.

Bond cleavage reactions of 4,4′-dicyanobenzyl ether (DCBE) were also found to be induced by the same π-acceptors. The products of this reaction were found to be similar to those formed for BE, i.e., 4-cyanobenzaldehyde (CBA) and 4-cyanobenzyl alcohol (CBOH). These products were established by methods similar to those used for BE product identification. The product yields are given in Table I. Although the yield of products determined for the DCBE/$TCNQF_4$ reactions are higher than quantitative, this derives from the low conversion amounts in the reaction and the insensitivity of the UV detector of the HPLC to CBOH, introducing a large error into the determination of this product. The reactions of DCBE with these π-acceptors are described by eq 6.

$$\underset{\text{DCBE}}{NCC_6H_4CH_2OCH_2C_6H_4CN} \xrightarrow[CH_3CN]{\pi\text{-A}} \underset{\text{CBA}}{NCC_6H_4CHO} + \underset{\text{CBOH}}{NCC_6H_4CH_2OH} \quad (6)$$

Table II. Relative Rate Data for Thermal Reactions of BPE and BE

π-acceptor	substrate BPE	 BE	temp, °C
$TCNQF_4$	1	2.2	190
	1	4.7	160
	1	5.7	130
	1	8.8	100
DDQ	1	6.3	210
	1	12	160
	1	24	130
	1	31	100
TCNQ	1	3.0	210

The thermal reactions of BPE have been previously reported[13a] and are depicted in eq 2.

One final point of note concerns the relative rates of reaction as caused by the different π-acceptors. As can be seen from the qualitative data in Table I, the stronger π-acceptors ($TCNQF_4$ and DDQ) cause a much faster reaction than the weaker π-acceptor TCNQ. This signifies that reasonable reaction rates are obtained at lower temperatures for DDQ and $TCNQF_4$ than could be obtained for TCNQ. Thus, the bond-cleavage reactivity is in accord with the one electron reduction potentials of the π-acceptors as has been noted previously.[17]

Relative Thermal Reactivity Data. The relative rates of reaction of BPE and BE were determined as a function of the π-acceptor. These rates were determined by competition experiments in which equimolar amounts (0.01 M) of BPE and BE were mixed with the π-acceptor (also 0.01 M). The relative reaction rates were determined by monitoring the disappearance of the starting ethers. Conversion amounts were kept to a low value to ensure that the observed relative rate data were not affected by changes in the concentration of the starting ethers. The values recorded in Table II represent the average of at least three independent experiments with different conversion amounts. Notice that different ratios are obtained for the same acceptors under different temperature conditions. The reactions at 100 °C for $TCNQF_4$ and DDQ required

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Scheme II. Intermolecular Reaction Pathways Leading to Fast BE Reactions

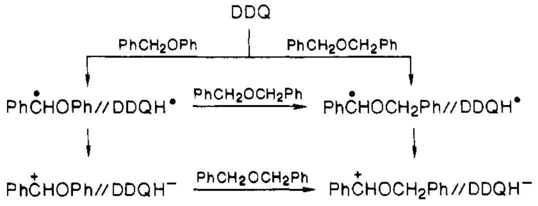

Table III. Relative Rate Data for Thermal Reactions of DCBE and BE

π-acceptor	substrate DCBE	substrate BE	temp, °C	reaction time
$TCNQF_4$	1	7.8	190	5 min
DDQ	1	5.6	190	5 min
TCNQ	1	1.5	200	2 h

several days for accurately measurable conversion of both BE and BPE. Since the reaction of TCNQ at 190 °C was much slower than the reactions of $TCNQF_4$ and DDQ, the relative reaction rates of BE and BPE with TCNQ were not measured at different temperatures.

One explanation for the selectivity observed in the reactions involved intermolecular interactions. At these concentrations, either reactions of the BPE radical with BE or reactions of the BE carbocation with the BPE carbocation could lead to a faster reaction of BE than BPE. These possibilities are depicted in Scheme II. Such reactions would be thermodynamically favorable (vide infra) and may proceed with high bimolecular reaction rates. However, control experiments showed that the same relative rate ratios were obtained whether the BPE and the BE were contained in the same reaction solution or were in different solutions which were treated under similar temperature and concentration conditions.

Relative reactivity data for the thermally activated reactions of DCBE and BE are displayed in Table III. In all cases, the reactions of BE were faster than the corresponding reaction of DCBE.

The above-mentioned reaction rates have been measured as relative reaction rates. We have measured the absolute reaction rates of the DDQ induced bond cleavage reaction of BE at 130, 150, and 170 °C by plotting 1/[BE] vs time. In this fashion, we have measured rate constants of (2.2 ± 0.2), (2.1 ± 0.2), and (2.5 ± 0.2) × 10^{-2} M^{-1} s^{-1} for these temperatures. We do not put too much weight on these determinations, since the formation of BOH during the course of the reaction allows a competitive reaction pathway for the DDQ, thus decreasing its concentration at a relatively faster rate. However, the determination of these absolute reaction rate constants allows extrapolation to absolute reaction rates of BPE and DDQ.

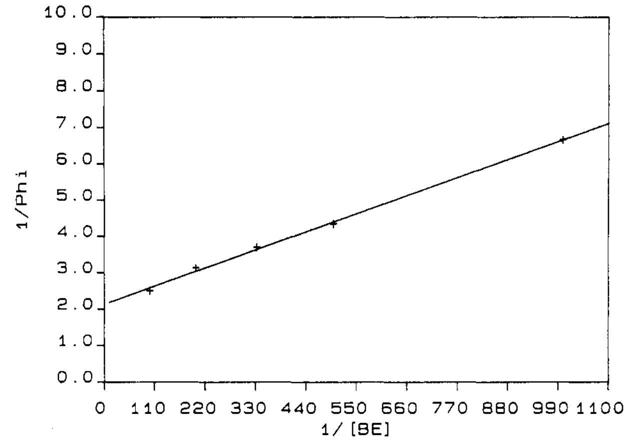

Figure 1. Stern–Volmer plot for the reaction of BE and DDQ.

Photochemically Initiated Bond Cleavage Reactions. Irradiations of solutions of BE and the π-acceptors were performed such that the π-acceptors absorbed all of the incident light. This was accomplished through the use of 350-nm light. In all cases, the same bond-cleavage products (i.e., BA and BOH) were observed. The product yields are listed in Table IV. Control experiments without light established that absolutely no reaction occurred on the time scale of the photochemical experiments. Note that the product ratios are slightly different than those obtained under thermal conditions. Additionally, the product ratios are dependent upon the length of the photochemical reaction time as would be expected if the primary products of the irradiation were undergoing secondary photochemical reactions.

Irradiations of solutions containing π-acceptors and DCBE were similar to the reactions of BE. Product yield data are given in Table IV. Additionally, the irradiations of solutions containing π-acceptors and BPE yielded similar reactions. These data are also shown in Table IV.

Photochemical Quantum Efficiency Data. The absolute quantum efficiency for BE and DDQ was determined in a merry-go-round apparatus with valerophenone actinometry using 300-nm light. The optical density of the valerophenone solution was carefully adjusted to match that of the DDQ solution in order to ensure that all sam-

Table IV. Product Yield Data for the Photochemical Reactions

starting material	π-acceptor	product yield, mol % BA[a]	product yield, mol % BOH[a]	light source	time, h	% conversion
BE	DDQ	180	23	room light	20	14
BE	DDQ	149	48	350 nm	1	52
BE	DDQ	156[b]	43[b]	350 nm	2	52
BE	TCNQ	122	77	350 nm	13	3
starting material	π-acceptor	product yield, mol % CBA	product yield, mol % CBOH	light source	time, h	% conversion
DCBE	DDQ	124	73	350 nm	7	22
starting material	π-acceptor	product yield, mol % BA	product yield, mol % PhOH	light source	time, h	% conversion
BPE	DDQ	61	50	350 nm	42	30
		94[c]	93[c]	350 nm	24	72

[a] Product yield data determined by GC analysis with *n*-octyl cyanide as an internal standard. Yields are accurate to ±10%. [b] Product yield data determined by HPLC analysis with bibenzyl as an internal standard. [c] Heated to 190 °C for 1 h folllowing photoreaction.

Scheme III. Energies of BPE Reaction Intermediates

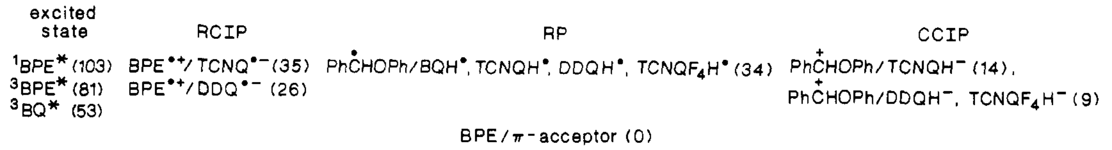

Table V. Photochemical Quantum Yields

ether	ether concn, M	π-acceptor	π-acceptor concn, M	λ, nm	Φ
BE	0.003	DDQ	0.003	300	0.27
BE	0.01	DDQ	0.003	350	0.40
BE	0.005	DDQ	0.003	350	0.32
BE	0.003	DDQ	0.003	350	0.27
BE	0.002	DDQ	0.003	350	0.23
BE	0.001	DDQ	0.003	350	0.15
BE	0.01	TCNQ	0.01	300	<0.02
BPE	0.01	DDQ	0.01	350	0.0027

Table VI. Relative Photochemical Quantum Yields

	substrate		
π-acceptor	BPE	BE	wavelength, nm
$TCNQF_4$	1	1.9	350
DDQ	1	98	350
DDQ	1	53[a]	350
TCNQ	1	2.1	350

	substrate		
π-acceptor	DCBE	BE	wavelength, nm
DDQ	1	3.5	350

[a] 65 °C.

ples absorbed the same amount of light. Thus, the absolute quantum yield for the reaction of 0.003 M DDQ with 0.003 M BE was determined to be 0.27. Varying the concentration of BE showed that the relative reaction efficiency obeyed Stern–Volmer kinetics. As can be seen in Figure 1, a double-reciprocal plot of $1/\phi$ vs $1/[BE]$ gave a straight line with a slope of 4.53×10^{-3} and an intercept of 2.14. For concentrations of BE higher than 0.01 M, a diminished quantum efficiency was observed, suggesting that quenching of the photochemical reaction is accomplished by a sufficient concentration of BE or interference through direct absorption of light by the charge-transfer complex leading to less efficient photochemical reactions.

Although the absolute efficiency of the BPE reaction was not determined, the efficiency relative to BE was determined with 350-nm light (note Table VI). When a competition experiment was performed in which the BE and the BPE were contained within the same reaction solution, a relative efficiency of 82:1 was obtained. When the BE and the BPE were contained in separate solutions (note Scheme II), an even higher relative efficiency of 98:1 was obtained. Since the quantum efficiency of bond cleavage of BE was shown to diminish at higher BE concentrations, we believe that the determination of 98:1 is more accurate and is used in subsequent analysis. In any case, the high selectivity of the photochemical reactions is highly unusual, particularly when compared to the thermal reaction selectivities. Interestingly, the photochemical reaction of DDQ and BPE did not display Stern–Volmer kinetics. Within experimental error, the same relative quantum efficiency was obtained as the concentration of BPE was changed from 0.001 to 0.01 M BPE. Since the quantum efficiencies of BE and BPE are 98:1, the absolute quantum efficiency for the reaction of 0.01 M BPE with 0.01 M DDQ is 2.6×10^{-3}.

The relative photochemical efficiencies of the BE/DDQ and the DCBE/DDQ photochemical reactions were measured by a competition experiment using 350-nm light. BE was found to react with a higher efficiency than DCBE by a factor of 3.5:1.

Discussion

Product Formation. Reactions of BE and DCBE with these π-acceptors yield in all cases only two products, an aldehyde and an alcohol, BA and BOH. As can be seen in Tables I and IV, all of the material in the reaction (within experimental error) is accounted for in the formation of these products. Since 2 mol of products are formed for every 1 mol of starting material, 200 mol % product yield would be anticipated. All of the analyses were carried out under low conversion conditions to ensure that secondary reactions of the products were minimized. Both high-pressure liquid chromatography (HPLC) and gas chromatography (GC) were used to check for the formation of either benzylacetamide (BAC) or (*p*-cyanobenzyl)acetamide (CBAC). We estimate that we would have been able to detect a 1% amount of either acetamide. However, none could be found. Even though the majority of the reactions were analyzed by gas chromatography, HPLC was used to verify that the products of the reactions initiated by DDQ were not those of thermal decomposition of the "true" products. Note that the agreement of the HPLC and GC results is well within the experimental error of the measurement (Table IV). Thus, we believe that we have accounted for all of the products of the reaction.

In these reactions, the aldehyde is always formed in greater yield than the alcohol. At first glance, this seems surprising, but is easily explained by the fact that the alcohol can react with these π-acceptors to form the aldehyde under the reaction conditions. A similar observation has been made in many previous oxidative cleavages of BE.[21-23] In fact, the oxidation of benzylic alcohols seems to proceed more readily than the oxidative cleavage reactions of benzylic ethers for a wide variety of reagents including [bis(trifluoroacetoxy)iodo]benzene,[21] Co(III),[22] and TPP·Mn^{IV}.[23] The more rapid reaction of benzylic alcohols with π-acceptors is further supported by the fact that 1-phenyl-1-propanol is converted to 1-phenyl-1-propanone by DDQ upon heating at 60 °C for 2 h.[24] Indeed, we have verified that BOH reacts 1.3 times faster than BE under our reaction conditions. Therefore, the higher yields of aldehyde relative to the alcohol derive simply from a faster reaction rate of BOH relative to BE.

Energetics of Potential Reaction Intermediates. A point to begin a discussion of the mechanism of these reactions is the consideration of the relative energetics of the potential intermediates. The exact thermodynamic energies of these species cannot be determined with precision for two reasons. First, there is a lack of relevant thermodynamic data on the isolated species that we postulate to be involved in the reaction. Second, the energies of the ion pairs that must exist in these reactions will differ

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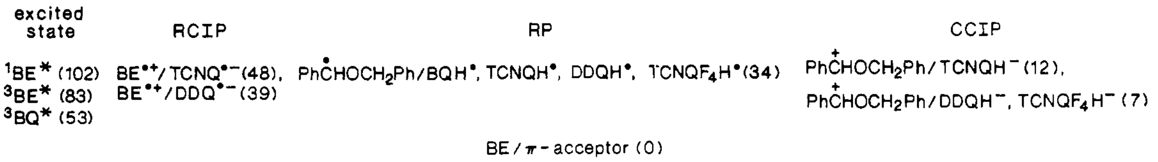
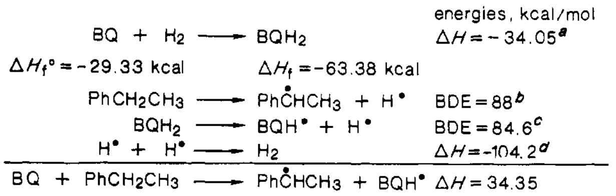
[24] Ohki, A.; Nisiguchi, T.; Fukuzumi *Tetrahedron Lett.* **1979**, *35*, 1737.

Scheme IV. Energies of BE Reaction Intermediates



Scheme V. Energetics of Radical Pairs



[a] Reference 59. [b] Reference 60. [c] Reference 61. [d] Reference 62.

from that of the solvated ions in solution. Thus, the energetic scheme developed here should be considered to be only a guide for determining the possible intermediates in the reaction. Energies for the intermediates that may be involved in the reactions of BPE and the π-acceptors are shown in Scheme III while energies for the intermediates that may be involved in the reactions of BE and the π-acceptors are shown in Scheme IV.

Our method for determining the energies of the BPE intermediates is as follows. All energies are relative to an arbitrary ground-state energy that we define to be a zero energy state consisting of BPE and the relevant π-acceptor. The triplet excited state of BQ is known to be 53 kcal/mol.[25] Although some variation in the excited-state energy of substituted quinones is expected, the triplet excited state of dichlorobenzoquinone has been reported to be 53 kcal/mol.[25] Since, the addition of two chlorines to the quinones causes only a slight change in the triplet state energy, we believe that the triplet excited state energies of DDQ will be similar to the excited state energy of BQ. The energies of the π-acceptors are below that of the excited states of BPE which have been assigned the excited state energies of anisole (103 and 80.8 kcal, respectively[26]). It is readily apparent that all photoreactions must proceed via the excited state of the π-acceptor and not via an excited state energy transfer process from the quinone to BPE.

The energy of the species formed from an initial single electron transfer is computed through the use of the oxidation potential for BPE (E_{ox} = 1.67 V vs SCE)[27] and the corresponding one electron reduction potentials for the π-acceptors (note Table I). The energy of the radical pair formed from BPE and BQ is calculated by the thermochemical cycle shown in Scheme V. This value seems amazingly low. The low value derives from the exothermicity of the reduction reaction of BQ to form BQH_2. Although the absolute value for this reaction may be questionable, it is not entirely unreasonable. We have also calculated ΔH_f for BQ (−33.11 kcal/mol) and BQH_2 (−74.05 kcal/mol) by MNDO and find ΔH for the reaction to be −40.94 kcal/mol. Inclusion of this value makes the energy of the radical pair even lower. Our major point in this argument is that the energy of the radical pair is below that for a single electron transfer in the case of BE reactions with these π-acceptors. Even a 10-kcal adjustment in the energy of the overall reduction reaction of BQ to form BQH_2 leads to a prediction that the energy of the radical pair is below that of the RCIP. Strengthening our argument is the fact that the ether functionality should give a further stabilization to the radical pair. This factor has not been included numerically in our energy calculations.

The energy of the intermediates derived from the formal transfer of a hydride can be estimated through the use of relevant oxidation and reduction potentials for the corresponding radical species. The reduction potential for the semiquinone radical has been reported to be −0.13 V vs SCE.[28] Although no oxidation potential data are available for $Ph\dot{C}HOPh$, we estimate its oxidation potential from data for $Ph\dot{C}H_2$ and $Ph\dot{C}(CH_3)_2$ for which values of 0.73 and 0.13 V vs SCE have been reported.[29] Since the oxidation potentials of α-alkoxy radicals are known to be lower than those of alkyl radicals by ca. 0.5 V,[29b] we assume that the oxidation potential for a $Ph\dot{C}HOR$ is 0.5 V less than $Ph\dot{C}HCH_3$ (0.37 V vs SCE) or −0.13 V. In this fashion, an energy value for the CCIP/BQH^- ion pair of −0.26 V or 6 kcal/mol more stable than the radical pair is derived. If one assumes that the changes in the one electron reduction potentials of the π-acceptors are the same magnitude as the corresponding one electron reduction potentials of the semiquinone radicals, then the energies for the CCIPs pairs are given approximately in Scheme III.

The energies for important BE intermediates are given in Scheme IV. The energies were derived in a similar fashion to that utilized for BPE, with the following modifications to properly evaluate the relative thermodynamics of the species. Since the oxidation potential of BE is unknown, we have utilized the known correlation between photoelectron gas phase ionization energies and solution oxidation potentials of methylarenes to provide an estimate of the oxidation potential for BE.[31] The highest occupied molecular orbital of benzyl alcohol is known to be an aromatic π-orbital, rather than the oxygen lone pair orbitals.[30] For BE, containing only nonconjugated oxygen lone pair electrons and aromatic π-orbitals, the oxidation must occur from the aromatic π-orbitals. An estimate of the oxidation potential of BE can be obtained from the oxidation potential of ethyl benzene (2.27 V vs SCE).[31] We note that our overall conclusion that a single electron transfer cannot account for the relative reaction rates (vide infra) is not changed by a change in the oxidation potential of ca. 0.1 V (ca. 2.3 kcal/mol). An additional modification to the relative energetics depicted in these two schemes concerns the energies of the hydride transferred species. Since the OCH_3 substituent has a σ^+ value of −0.78 and the OPh substituent has a σ^+ value of −0.5,[32] the carbocation derived from BE should be more stable than the

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(26) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

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(31) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasine, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

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corresponding carbocation derived from BPE. We have arbitrarily chosen a 2-kcal stabilization energy. This value is in line with the $\Delta\Delta G$ value expected from a ρ value of -2 for an arbitrary reaction and a temperature of 100 °C.

Relative Thermal Reaction Rates. As seen in Table II, BE has a higher reaction rate than BPE with every π-acceptor. To account for this observation, we refer to the notation introduced in Scheme I.

The first mechanistic pathway available for the cleavage of BE induced by these π-acceptors consists of CTC formation followed by a rate-determining cleavage to form a benzyl cation and an alkoxy-π-acceptor complex. If the rates of cleavage for BE and BPE are similar in these complexes, the equilibrium constant for charge-transfer complex formation may determine the relative reactivities of these two compounds. We were unable to measure the equilibrium constants for charge-transfer complex formation for BE and these π-acceptors since the UV absorbance of the acceptors obscures the region where the charge-transfer absorbance might be expected. However, we have measured the equilibrium constants for complex formation of these ethers with tetracyanoethylene (TCNE) since a correlation of the equilibrium constants for complex formation between anthracene and TCNE and between anthracene and chloranil has been noted previously.[33] The equilibrium constants for charge-transfer complex formation in the solvent methylene chloride for TCNE and BPE or TCNE and BE are 0.74 and 1.2, respectively.[34-37] This ordering is in agreement with estimates of the complexing ability of zinc halides (e.g., $ZnCl_2$),[38] which have also been used to induce bond-cleavage reactions of BE and BPE. The greater complexing ability of BE must derive from the greater basicity of the aliphatic ether linkage of BE as compared to BPE.

Although the magnitude of the equilibrium constants predicts that BE should react more rapidly than BPE, the lack of formation of BAC in the reaction of BE and these π-acceptors suggests that the benzyl cation is not formed in these reactions. The formation of BAC has been observed previously in the reactions of BPE with several of these π-acceptors.[13a] Further, the formation of BAC has previously been shown to be a general product of the benzyl cation in acetonitrile.[39] Since we have demonstrated our ability to detect BAC and it is not formed in these reactions, we conclude that the benzyl cation is not an intermediate in this reaction.

A further point in support of the lack of direct reaction from the charge-transfer complex is the kinetic isotope effect which was observed in the oxidation of 1-phenyl-1-propanol.[24] In this work, the relative reaction rates of $PhCH(OH)CH_2CH_3$, $PhCH(OD)CH_2CH_3$, $PhCD(OH)CH_2CH_3$, and $PhCD(OD)CH_2CH_3$ were found to be 8.9:9.1:1.0:1. This signifies that the rate-determining step of benzylic alcohol oxidation by quinones involves the transfer of a hydrogenic species. Thus, we believe that the rate-determining step occurs farther along the reaction coordinate than the charge-transfer complex.

A second mechanistic alternative involves the cleavage of the radical cation formed upon single electron transfer. This pathway also cannot be involved in this reaction. Note Schemes III and IV where we have explicitly given the energies of the RCIPs. A crude estimate of the relative activation energies for cleavage of the BPE and BE radical cations can be made through the use of thermochemical cycles. If the activation energy for cleavage of the radical cation is assumed to be near the energy of formation of the benzyl cation and the oxy radical, an estimate of the activation energies is available. These cycles predict nearly identical activation energies for the $BPE^{\bullet+}$ and $BE^{\bullet+}$ cleavages with the increased oxidation potential for BE offset by a stronger C–O bond in this species.[40] These energies are ca. 20 kcal/mol greater than the energy required for the electron-transfer reaction from either ether to the relevant π-acceptor. The high-energy demand of this reaction pathway, coupled with our inability to observe BAC in the BE reactions indicates that the radical cation is not involved in the reaction pathway.

A third mechanistic alternative involves the formation of the radical pair (RP), followed by radical pair separation and subsequent reaction. This pathway would be expected to yield a larger rate of reaction for BE when compared to BPE. This results from the expectation that BPE has no low-energy pathways available leading to the products observed in the reaction. A high-energy pathway involving phenyl carbene and the phenoxy radical can be envisioned, but seems unfeasible. We have extensively searched in the BE reactions for bibenzyl (BB) as a reaction product that would be expected to arise from coupling of two benzyl radicals. This product was detected in trace amounts in the Co(III) oxidation of BE.[22] Among our experiments have been the reaction of both DDQ or BQ with BE at higher concentrations, thereby hoping to generate a higher steady-state concentration of the benzyl radicals if they were formed in the reaction. However, we have been unable to find this product to date. In order to definitively examine the influence of the radical reaction pathway in this reaction, DCBE was prepared. This species would be expected to yield a more stable radical than BE. If electron transfer proceeds to give the CCIP, then BE should react more rapidly than DCBE. As seen in Table III, BE reacted more rapidly than DCBE for these π-acceptors. Thus, the radical pair cannot be involved as the rate-determining intermediate in these reactions.

The final mechanistic alternative is that in which hydride is transferred from the ether to the π-acceptor. Hydride abstraction would be expected to yield a faster reaction rate from BE than from BPE. As shown in Schemes III and IV, the energies of the CCIPs are exceedingly low. In fact, for all π-acceptors used in this study, our crude estimate of the energetics predicts that hydride transfer is the low-energy pathway. Thus, we speculate that this is the easiest rationale for explaining the reaction dynamics. The data generated from DCBE support this hypothesis. The more rapid reaction of BE relative to DCBE suggests that hydride transfer is the rate-determining step in the reaction.

Effect of the Acceptor upon the Photochemical Reaction Efficiency of BE. An alternative explanation for the reaction behavior is radical cleavage in the radical pair, followed by rapid electron transfer. Therefore, we desired to generate the radical pair directly and observe the subsequent reactions in order to fingerprint the re-

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[33] Lofti, M.; Roberts, R. M. G. *Tetrahedron* **1979**, *35*, 2123.

[34] The Foster-Hammick-Wardley modification[35] of the Scott equation[36] was used to measure these equilibrium constants in the solvent methylene chloride. In this method, the equilibrium constant (K) is determined as the negative slope of the plot of $A/[D]_0[A]_0$ against $A/[A]_0$ where A is the optical absorbance of the solution at a particular wavelength of light, and $[D]_0$ and $[A]_0$ are the initial donor and acceptor concentrations.

[35] Foster, R.; Hammick, D. L.; Wardley, A. A. *J. Chem. Soc.* **1953**, 3817.

[36] Scott, R. L. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 787.

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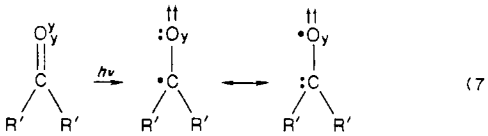
[40] Penn, J. H. GRI 1987 Annual Report (available through NTIS).

Scheme VI. Kinetic Analysis of the DDQ Reaction with BE

$$\begin{aligned} \mathrm{DDQ} &\xrightarrow{h\nu} \mathrm{DDQ^*} \\ \mathrm{DDQ^*} + \mathrm{BE} &\xrightarrow{k_i} \mathrm{DDQ{\cdots}BE} \\ \mathrm{DDQ^*} &\xrightarrow{k_{dt}} \mathrm{DDQ} \\ \mathrm{DDQ{\cdots}BE} &\xrightarrow{k_s} \mathrm{DDQ} + \mathrm{BE} \\ \mathrm{DDQ{\cdots}BE} &\xrightarrow{k_r} \text{products} \end{aligned}$$

activity of the radical pair. It has previously been shown that the lowest energy excited state of BQ is an n–π* excited state by both experimental[41] and theoretical[42] methods. The Zimmerman notation of the electronic configuration of n–π* excited states is shown below diagramatically in eq 7.[43] Upon photoexcitation, an electron



(7)

from one of the oxygen lone pairs (designated by y) is promoted to the antibonding orbitals of the π system. This excitation results in an alkoxy radicaloid type species since the electron in the π* orbital is extensively delocalized, while the remaining lone-pair electron is localized on the oxygen atom. This electronically excited state has previously been shown to correlate to the reactivity of *tert*-butoxy radicals.[44] The expectation that the excited state of BQ readily initiates H-atom abstraction reactions has been confirmed. BQ* readily abstracts a hydrogen atom from 2-propanol.[45]

A further point of note about this excited state is that generation of CCIP requires two full steps. This follows from the fact that the two electron holes in the n–π* excited state are in orthogonal orbitals. Whether the photoreaction occurs by an initial electron transfer to yield solvent-separated ion pairs[46] followed by H-atom transfer or the photoreaction occurs by initial H-atom transfer (vide supra) followed by a second electron transfer, two steps resulting in geminately coupled intermediates are involved in reactions originating from n–π* excited states. In contrast, the tetracyanoquinodimethanes have only a π–π* excitation available to them. This excited state does not have the same restrictions as the n–π* excited state and may be expected to undergo reactions via a single hydride transfer step if that is the lowest energy pathway.

As can be seen in Table IV, bond cleavage reactions of BE were observed from all of the π-acceptors. In all cases, 350-nm excitation was used to directly excite only the π-acceptor. In this fashion, neither BE nor the CTC should receive a significant amount of light. In all cases, BA is formed in a much greater amount than BOH, similar to the thermal reactions. Note the case of room light irradiation of DDQ where 180% BA is formed. Here the nature of the excitation is not so clear. Either DDQ or the charge-transfer complex may be irradiated with such broad-band excitation. The large amount of BA formed in this reaction gives credence to the much faster reaction rate of BOH with DDQ or DDQ*. Thus, the larger amount of BA formed in these reactions is not particularly disturbing.

As noted above, the reaction of BE and DDQ follow Stern–Volmer kinetics (Figure 1). In order to put this reaction into physical reality, we refer to the mechanistic analysis shown in Scheme VI. Thus, a photon of light may be used to create an excited state of DDQ. The DDQ excited state (DDQ*) may either decay naturally to the ground state by internal conversion, by fluorescence, or by phosphorescence. The rates for all of these processes have been included together and are represented by k_{dt}. The alternative process for the excited state of DDQ is to interact with a molecule of BE. This is represented by k_i. The interaction of BE and the excited state of DDQ may not lead to a reaction, but may produce an alternative pathway for dissipation of excited-state energy that we define as k_s. The desired pathway that gives a reaction product is termed k_r. Since the quantum yield for reaction is given as the product of the probabilities of reaction, the quantum yield of reaction (Φ) is given by eq 8 where P_i is the probability of interaction of the BE with the excited state of DDQ and P_r is the probability of reaction once an interaction has taken place. The quantum yield for the reaction is given by eq 9 while rearrangement in the Stern–Volmer fashion yields eq 10. From the data shown in Figure 1, an intercept of 2.1 is obtained. Thus, the rate of return to starting material (k_s) is 1.1 times the rate of reaction to yield products. Using the slope of 4.53 × 10^{-3} and a diffusion rate constant in acetonitrile (2 × 10^{10} $\mathrm{M^{-1}\,s^{-1}}$)[26] one can obtain an intrinsic lifetime for DDQ* of 11 ns.

$$\Phi = P_i P_r \qquad (8)$$

$$\Phi = \left(\frac{k_i[\mathrm{BE}]}{k_{dt} + k_i[\mathrm{BE}]}\right)\left(\frac{k_r}{k_r + k_s}\right) \qquad (9)$$

$$\frac{1}{\Phi} = \left(\frac{k_r + k_s}{k_r}\right)\left(\frac{k_{dt}}{k_i[\mathrm{BE}]} + 1\right) \qquad (10)$$

An important part of this analysis concerns the fact that all the light is absorbed by the quinone and not by a charge-transfer complex (BE–Q) formed between BE and the quinone. Several observations are relevant to this point. First, the magnitude of the equilibrium constant (*K*) for charge-transfer complex formation between BE and TCNE is 1.2 in the solvent CH_2Cl_2. If $K_{\mathrm{BE\text{-}TCNE}} \approx K_{\mathrm{BE\text{-}BQ}}$ or $K_{\mathrm{BE\text{-}DDQ}}$, then the maximum complex concentration ([BE–Q]) under our photochemical reaction conditions (0.01 M in both BE and DDQ) is 1.2 × 10^{-4} M. Thus, [BE–Q] is ca. 100 times less than [Q]. Further, the effect of more polar solvents has been shown to generally decrease the magnitude of *K*.[47] Thus, it may be expected that our estimate of [BE–Q] is conservatively high. The complex would absorb only 1% of the incident light if the magnitude of the extinction coefficients (ε) for BE–Q and Q were the same. We have measured the value of ε for DDQ to be 780. This number is of the proper order of magnitude for those ε found for charge-transfer complexes. Since all of these estimates are conservative, we argue that the absorption of light by the charge-transfer complex is at best a minor contributor to the observed photochemistry. In further support of this argument is the concentration range over which the Stern–Volmer plot is linear. The concentrations cited above are maximal, while the linearity of the Stern–Volmer plot continues to lower

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[41] Galaup, J. P.; Trannsdorff, H. P. *J. Mol. Struct.* **1980**, 325.

[42] Lichtenbelt, J. H.; Wiersma, D. A.; Jonkman, H. T.; Van der Velde, G. A. *Chem. Phys.* **1977**, 297.

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[47] Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969; p 182.

concentrations of BE ([BE] = 0.001 M).

The lack of Stern–Volmer reactivity of BPE is somewhat surprising. However, the overall low quantum yield ($\Phi \approx 3 \times 10^{-3}$) allows for a small alternative reaction pathway to give a larger quantum efficiency than the desired pathway of interception of DDQ* by BPE. Thus, we suggest that the observed photochemical bond cleavage reaction of BPE proceeds through the weak absorbance of a charge-transfer species. A higher energy charge-transfer absorbance is often noted for interactions of aromatics and quinones.[48] Absorbance by this species would not require diffusional encounters and may result in a low but constant quantum efficiency.

Relative Photochemical Efficiencies of BE and BPE. The relative reaction efficiencies of BE and BPE were determined at two different temperatures. These data are collected in Table VI. Interestingly, the difference in efficiencies at room temperature is so large that different concentrations of BE and BPE were necessary in order to determine accurately the relative quantum efficiencies. Even though BE and BPE have been shown to give bond-cleavage reactions upon photochemical excitation,[49] the chemical reactions seen in this work cannot result from an excited state of BE or BPE. The triplet excited state energy of xylene is 80.4 kcal/mol[26] and the triplet excited state energy of anisole is 80.8 kcal/mol.[26] These compounds should reasonably model the excited-state energies of BE and BPE, respectively. Since the excited-state energy of BQ is only 53 kcal/mol,[25] and the wavelength of irradiation (350 nm) is such as to produce only the excited state of BQ, then energy transfer from the triplet state of BQ to the higher energy excited states of BE or BPE would be expected to be highly inefficient. Although the excited-state energy of DDQ is unknown, it should be similar in energy to that of BQ.[25] Thus, the DDQ reactions must also proceed via H-atom or hydride transfer. Additionally, BE would be expected to have almost no absorption at the wavelength of irradiation (350 nm) and give the most efficient reaction. The reactions occur through interaction of the acceptor with the ether.

Note the relative efficiencies of these π-acceptors in promoting C–O bond cleavage reactions. Since the light is absorbed directly by the π-acceptors, the excited-state lifetimes would be expected to be most important in determining the efficiency of the reaction. This follows from the fact that reaction with BE represents a competition situation with decay of the excited states. Although no lifetime data are available for these compounds, predictions of relative lifetimes are easy in this series of compounds. Both TCNQ and $TCNQF_4$ have dicyanomethylene units that are capable of dissipating excited-state energy through the well-known "free-rotor" effect.[50] These compounds should have extremely short excited-state lifetimes and therefore are much less likely to intercept a molecule of BE during the lifetime of the excited state. This is exactly in accord with the experimental observations whereby TCNQ has a dramatically lower quantum efficiency than DDQ.

Selectivity Effects in the Photochemical Reactions of BE and BPE. We reasoned that the relative photochemical reaction efficiencies of BE and BPE would allow a reactivity profile of the potential radical pairs that would be generated through excitation of the π-acceptor. The use of different π-acceptors with differing electronic demands would serve as a test of the relative rate of electron transfer in the radical pair vs the rate of the α-cleavage reaction of the radical.

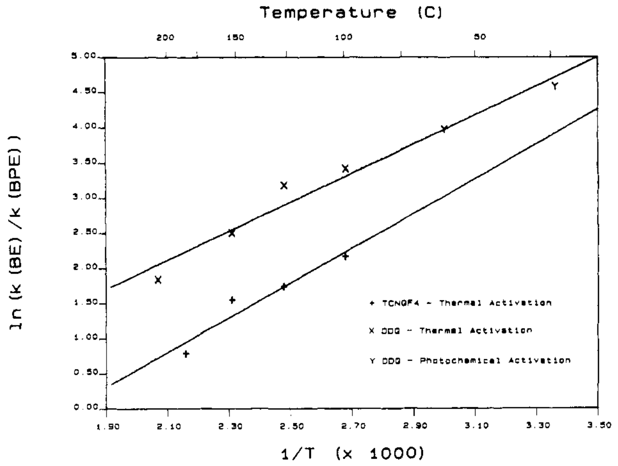

Figure 2. Arrhenius plot for BE/BPE competition reactions.

A reasonable correlation is found between the relative photochemical reaction efficiencies of BE and BPE as initiated by DDQ and the relative thermal reaction rates as initiated by DDQ. This is shown in Figure 2 where the relative reaction efficiencies are treated as reaction rates and plotted in an Arrhenius fashion together with the relative rate data from Table II. Such an enhancement of reaction selectivity is not unusual in thermal reactions. It is well known that larger kinetic isotope effects are obtained at lower temperatures. This effect may be ascribed to differences in activation energies for the corresponding reactions. The correlation of the photochemical efficiencies with thermal reaction rates is highly unusual. Previously such correlations of photochemical and thermal reactions have been used to note common intermediates along the reaction coordinate.[50] We suggest that the thermal and photochemical reaction of BE as induced by DDQ possesses identical intermediates, regardless of whether the excitation occurs via thermal or photochemical means. For the reaction of DDQ, a correlation coefficient of 0.99 is obtained for the relative reactivities at six temperatures, giving a $\Delta\Delta H^{\ddagger}$ of 3.5 kcal/mol. In agreement with this picture are the data for the $TCNQF_4$ reactions that are also shown in Figure 2. Although only four points are available for this reaction due to the inefficient photochemical reaction, an apparent enthalpy difference of $\Delta\Delta H^{\ddagger}$ of 4.6 kcal/mol is obtained for the reaction induced by $TCNQF_4$ ($r = 0.96$). We consider this agreement to be excellent.

A skeptical observer may note that the correspondence of the relative reaction rates of BE and BPE as initiated by DDQ is not exact. Since the DDQ*-induced bond cleavage of BPE did not exhibit Stern–Volmer behavior, the photochemically induced bond cleavage of BPE may not follow the same mechanistic course as the photochemically induced bond cleavage of BE, allowing for a slight discrepancy in the observed efficiency for BPE bond cleavage. The ratio of the efficiencies for BE/BPE would be lower than expected if the observed efficiencies of the BPE reaction was artificially high as induced by a competing reaction mechanism. The observed selectivity would then represent a lower value for the possible selectivity in this reaction. Extrapolation of the thermal activation data to 25 °C would predict a value of ca. 1000 for the selectivity in the reaction, if the same mechanism were followed for each reactant.

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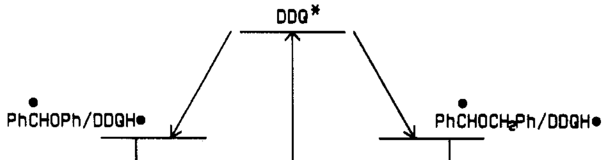

Figure 3. Reaction pathways for BE/BPE DDQ reactions.

An alternative rationale for the incomplete correspondence of the photochemical and thermal relative reaction data derives from the geometries of approach of the reagents. Differing approach geometries would lead to differing geminate pairs in the thermal and photochemical reactions. Since different dynamics would be expected for different geometries or interactions, the correspondence of the photochemical efficiencies and thermal reaction rates observed here is indeed surprising. In any case, an extremely high selectivity is observed at lower temperatures.

We rationalize this selectivity with the crude reaction coordinate diagram shown in Figure 3. Either thermal excitation or photochemical excitation leads to the CCIP intermediates, since these are the lowest energy intermediates in all cases. It is easily seen that the initially formed radical pairs should be subject to a high electron-transfer rate within the RP for either BE or BPE. This is in accord with the large exothermicity of the electron-transfer process. Although recent experimental[4] and theoretical predictions[5] of electron-transfer rates have shown that an overly exothermic reaction will indeed be slowed, the electron transfer from the benzylic radical to the DDQ semiquinone radical should be exothermic by only about 1 V. This is in the range for optimal electron-transfer rates and, therefore, should be diffusion controlled. Since the radical pair is generated by contact, the electron-transfer rate should be exceedingly high and therefore close to instantaneous. All of the chemistry from BE as initiated by DDQ should proceed through the CCIP rather than RP. This is shown by the correspondence of the selectivity as seen in the variable-temperature reactions. The high selectivity of the photochemical reaction is due to the low-energy states populated by electron transfer. The present experimental evidence does not allow a determination of whether this state consists of contact ion pairs, solvent-separated ion pairs, or some mixture of the two. Thus, the reactions of DDQ derive from the competing reversion of the intermediates to form starting materials or diffusion out of the solvent cage to yield solvated ions. In the case of photoactivation of BE cleavage, the rate of product formation is approximately equal to the rate of return to starting materials.

The $\Delta\Delta H^{*}$ of the π-acceptor-initiated bond cleavage reactions of BPE relative to BE can be explained by two alternative rationales. The first rationale is that reversion of the BPE CCIP to form starting materials proceeds much more rapidly than the reversion of the BE CCIP while product formation occurs at a similar rate from the solvated species. This would be in accord with the higher energetic demands of the BPE CCIP due to the lower stabilization energy of the phenoxy group on the carbocation. A larger fraction of contact ion pairs may be easily envisioned for the BPE CCIP, leading to a faster rate of reversion to starting materials. The second rationale for the observed selectivity is that the rates of return to starting materials are similar for the BPE/DDQ and the BE/DDQ CCIP while the rates of solvation and hence formation of products are vastly different. Either rationale suggests a larger fraction of contact ion pairs for the BPE CCIP than for the BE CCIP.

Implications for Protecting Group Removal. An interesting feature of this work is the highly efficient photochemical reaction of DDQ and BE. This reaction can be completed within 1 h at room temperature. The reaction is quite selective and rapid. Alcohols have frequently been protected in synthetic reaction sequences with benzyl ether or substituted benzyl ethers.[52] Removal of these protecting groups has been accomplished via hydride acceptors (such as DDQ or triphenylmethyl cation) by using thermal activation. A critical concern is the selectivity of cleavage of the protecting group in the presence of other delicate functionality. The present study indicates that further selectivity can be gained by utilizing photochemical excitation. Since the same intermediates (CCIP) are generated by photochemical excitation as generated by thermal excitation with an overall faster reaction rate, photochemical excitation may provide a more selective and more facile removal of the protecting groups. Studies are presently in progress in our laboratories to determine the generality of this phenomenon.

Summary. We have found that π-acceptors induce the cleavage of BE to yield BA and BOH by both photochemical and thermal activation. By comparing the relative photochemical reaction efficiencies of various π-acceptors to induce bond cleavage in BE and BPE, an amazing selectivity has been seen in the DDQ initiated reactions, whereby BE reacts much more rapidly than BPE. A larger fraction of contact ion pairs is suggested to result from the less stable carbocation, leading to a higher percentage of return to starting materials in the BPE bond cleavage reactions relative to the BE bond cleavage reactions.

Experimental Section

Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model 5890A GC equipped with a 10-m 5% phenylmethylsilicone or a Carbowax 20M Megabore column. Integration of the signals was performed by a Hewlett-Packard Model 3390A digital integrator. GC-MS data were measured with a Finnigan Model 4021 quadrapole mass spectrometer equipped with a Model 9610 data reduction system for comparison of mass spectra to those of authentic samples. Acetonitrile was predried over CaH_2 and then distilled from CaH_2 shortly before use. BE was purchased from Aldrich and purified by vacuum distillation prior to use. DCBE was synthesized by literature methods.[53]

Thermal Reactions. General Procedures. All thermal reactions were carried out in sealed tubes at the temperatures indicated. The Pyrex tubes were base-washed by using the procedure of Pasto.[19] Thus, the Pyrex tubes were initially washed with 1 N aqueous hydrochloric acid for 24 h and then 1 N aqueous sodium hydroxide for an additional 24 h. The tubes were then

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rinsed extensively with distilled H_2O and then extensively with methanol. The tubes were then dried at 110 °C.

All operations involving sample preparation and sample analyses were carefully performed in the dark to ensure that the observed products were due to thermal reactions and not to photochemical reactions. A solution of the ether (0.100 mmol) and the indicated acceptor (0.100 mmol) in 10 mL of freshly distilled acetonitrile was prepared and added to several Pyrex tubes. These tubes were degassed by using three freeze-pump-thaw degassing cycles and then sealed under vacuum. The sealed tubes were contained in a Neslab Model EX250-HT constant-temperature bath for the designated time. The product mixtures were then analyzed directly on the GC or the HPLC.

Benzaldehyde (2,4-Dinitrophenyl)hydrazone. A solution of BE (0.198 g, 1.00 mmol) and DDQ (0.340 g, 1.50 mmol) in 10.0 mL of freshly distilled CH_3CN was degassed by bubbling N_2 for 15 min prior to irradiation. The sample was sealed and irradiated with 350-nm light for 2 h. Solvent removal on a steam bath produced an oily solid, which was passed through a short silica gel column with chloroform. The solvent was concentrated and then reacted with (2,4-dinitrophenyl)hydrazine (2,4-DNP) reagent[54] to yield reddish orange benzaldehyde (2,4-dinitrophenyl)hydrazone, mp 238–240 °C (95% EtOH). A mixture melting point of the 2,4-DNP derivative made from authentic BA showed no melting point depression.

4-Cyanobenzaldehyde (2,4-Dinitrophenyl)hydrazone.[55] DCBE (0.0243 g, 0.098 mmol) and DDQ (0.0227 g, 0.100 mmol) were dissolved in acetonitrile (10.0 mL) and treated similarly to the benzaldehyde structure proof to yield yellow-orange 4-cyanobenzaldehyde (2,4-dinitrophenyl)hydrazone, mp 297–299 °C (EtOH). A mixture melting point of this material with the 2,4-DNP derivative prepared from authentic 4-cyanobenzaldehyde showed no melting point depression.

Thermal Competition Experiments. BE (0.0099 g, 0.05 mmol), BPE (0.0092 g, 0.05 mmol), the indicated π-acceptor (0.100 mmol), and *n*-octyl cyanide were dissolved in 10.0 mL of freshly distilled CH_3CN. Portions of this solution were added to several (six to eight) Pyrex tubes (vide supra). These tubes were then degassed by using three freeze-pump-thaw cycles and sealed under vacuum. The sealed samples were placed in the constant-temperature bath at the indicated temperature and analyzed directly on the GC or HPLC.

BE (0.0099 g, 0.05 mmol), DCBE (0.0124 g, 0.05 mmol), the indicated π-acceptor (0.100 mmol), and PBA were dissolved in 10.0 mL of freshly distilled CH_3CN. Portions of this solution were added to several (six to eight) Pyrex tubes (vida supra). These tubes were then degassed by using three freeze-pump-thaw cycles and sealed under vacuum. The sealed samples were then placed in the constant-temperature bath at the indicated temperature and analyzed directly by HPLC.

Photochemical Reactions. General Procedures. A solution of the ether (0.100 mmol) and the indicated π-acceptor (0.100 mmol) in 10.0 mL of freshly distilled acetonitrile was degassed by bubbling He for 15 min prior to irradiation. The samples were then sealed and irradiated with the fluorescent room lights or the 350-nm lamps of a Southern New England Ultraviolet Model RPR-100 Rayonet photochemical reactor. Product analysis proceeded similarly to the thermal reactions.

Photochemical Reaction of BPE with DDQ. A solution of BPE (0.0184 g, 0.100 mmol), DDQ (0.0227 g, 0.100 mmol), and an internal standard, *n*-octyl cyanide (0.0139 g, 0.100 mmol), in 10 mL of freshly distilled acetonitrile was added to several Pyrex tubes. These tubes were degassed by using three freeze-pump-thaw degassing cycles and then sealed under vacuum. The sample was irradiated with 350-nm light for 24 h. The tubes were then placed in a thermostated oil bath at 190 °C for 1 h. GC analysis yielded the results listed in Table IV.

Photochemical Competition Experiments. BE (9.9 mg, 0.05 mmol), BPE (9.2 mg, 0.05 mmol), and the indicated π-acceptor compound (0.10 mmol) were mixed in 10.0 mL of freshly distilled acetonitrile. After degassing by bubbling N_2 for 15 min, the solutions were irradiated with the 350 nm lamps of the Rayonet Reactor. The relative conversions as a function of time give the relative reaction efficiencies.

BE (9.9 mg, 0.05 mmolP), DCBE (12.4 mg, 0.05 mmol), and the indicated π-acceptor compound (0.10 mmol) were mixed in 10.0 mL of freshly distilled acetonitrile. After degassing by bubbling N_2 for 15 min, the solutions were irradiated with the 350-nm lamps of the Rayonet reactor. The relative conversions as a function of time give the relative reaction rates.

Quantum Yield Determinations. Valerophenone actinometry was used.[56] The optical density of the valerophenone sample and the π-acceptor were carefully adjusted to be the same value within 5%. After degassing, irradiations were performed in a merry-go-round apparatus at 300 nm. The quantum yields of disappearance were measured directly in each experiment through the use of hexanenitrile or *n*-octyl cyanide as an internal standard.

Acknowledgment. We gratefully acknowledge the financial assistance of the West Virginia University Energy Research Center for generous financial support of this work. We also acknowledge the assistance of Zhe Lin in the determination of charge-transfer complex formation equilibrium constants of TCNE and BE and BPE and David Griller for a preprint of his experimental results.

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