Mesolytic Scission of C–C Bonds as a Probe for Photoinduced Electron Transfer Reactions of Quinones

Przemyslaw Maslak* and William H. Chapman, Jr.

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Photoinduced electron transfer reactions of chlorinated benzoquinones are investigated using bibenzylic donors that undergo rapid fragmentation upon oxidation. The fragmentation rates and the quantum yields are used to probe the dynamics of back-electron transfer (BET) in two types of radical ion pairs. The triplet ion pairs formed by interception of excited state quinones give products with high quantum yields. The singlet ion pairs formed by irradiation of the charge-transfer (CT) complexes between the quinones and the donors undergo reactions with significantly lower efficiency. The advantage of the first method (triplet quenching) over the CT-irradiation depends on the energetics of BET. It is large for reactions with relatively small ΔG_{et} for BET and it decreases for reactions with more negative ΔG_{bet}. The indirectly obtained rates of BET are in excellent agreement with literature data for similar, but unreactive systems, and the rates of C–C bond scission in radical cations generated in these systems are consistent with the thermodynamics of these processes.

Photoinduced electron transfer (PET) between neutral donors and acceptors leads to generation of ion pairs.[1–3] Dynamics of these ions determines the efficiency of many photoreactions. There are two main methods to generate the radical ions. One method involves deposition of light energy into acceptor or donor molecules, converting them into potent redox reagents that undergo electron transfer (ET) with ground state substrates.[1,2] In the second method the ground-state charge-transfer (CT) complexes are irradiated leading to promotion of an electron within the complex.[3] The method of generation presets the stage for the competition between the energy-wasting back electron transfer (BET) and product-forming processes of radical ions,[4] such as proton transfers, adduct formations, rearrangements, or fragmentations.[5] Usually, in the first method (where one of the components serves as sensitizer) solvent separated ion pairs (SSIPs) are formed (especially in polar solvents) with spin multiplicities depending on the nature of the excited-state quenched (singlet or triplet). On the other hand, according to the Mulliken theory,[6] irradiation of CT complexes gives, at least initially, contact ion pairs (CIPs) in a singlet state.

Once generated, the ion pairs undergo a multitude of processes that include change of solvation status (from CIP to SSIP to free ions) and intersystem crossing that are superimposed on the competition between BET and product-forming reactions. All these processes often occur on similar time scales. The understanding of all these elementary processes that constitute PET systems has increased dramatically in recent years,[1–5] especially for organic molecules. Kinetic data obtained by time resolved techniques and refinements of theory[7] allow chemists to make at least semiquantitative predictions about systems not studied previously.

We present here an investigation of PET systems testing such predictions. In our design, a simple unimolecular C–C bond scission in radical cations (mesolytic cleavage[8]) serves as a model of a product-forming reaction, and provides, at the same time, an internal probe of PET dynamics.[9,10] The experimental system selected

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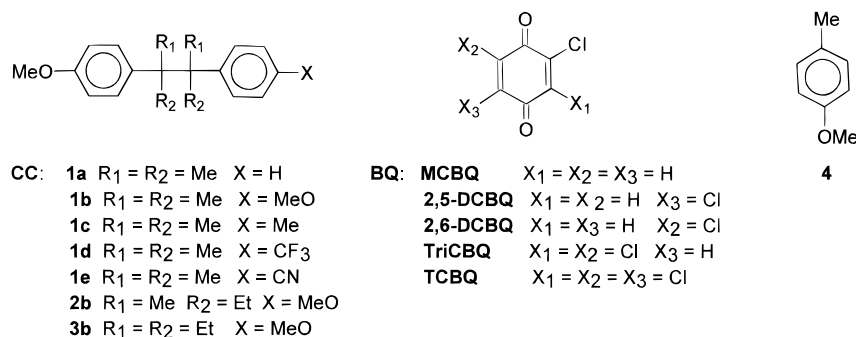
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Scheme 1

CC: **1a** $R_1 = R_2 = Me$ $X = H$
     1b $R_1 = R_2 = Me$ $X = MeO$
     1c $R_1 = R_2 = Me$ $X = Me$
     1d $R_1 = R_2 = Me$ $X = CF_3$
     1e $R_1 = R_2 = Me$ $X = CN$
     2b $R_1 = Me$ $R_2 = Et$ $X = MeO$
     3b $R_1 = R_2 = Et$ $X = MeO$

BQ: **MCBQ** $X_1 = X_2 = X_3 = H$
     2,5-DCBQ $X_1 = X_2 = H$ $X_3 = Cl$
     2,6-DCBQ $X_1 = X_3 = H$ $X_2 = Cl$
   **TriCBQ** $X_1 = X_2 = Cl$ $X_3 = H$
     TCBQ $X_1 = X_2 = X_3 = Cl$

here is based on our previous work[9] and involves methoxybicumenes (CC = **1a–e**, **2b**, or **3b**), serving as electron donors, and chlorinated 1,4-benzoquinones (BQ), serving as electron acceptors (Scheme 1). The methoxyphenyl moiety in all the donors provides essentially electronically-invariant reservoir of electrons while the benzylic and remote (X) substitutions introduce variability into the lifetimes of the corresponding radical cations.[9] The quinones (MCBQ, 2,5-DCBQ, 2,6-DCBQ, TriCBQ, and TCBQ) serve as efficient electron acceptors with redox potentials spanning 0.35 eV. In these bicumene/quinone systems the light energy can be deposited directly into the quinone chromophore, or it can be used to promote the electron within the bicumene/quinone CT complexes ($[CC\cdots BQ]_{CT}$). A direct comparison of the two modes of excitation is, therefore, possible[9c] (Scheme 2).

Chlorobenzoquinones have been reported to act as electron acceptors in a variety of photoinduced electron-transfer reactions.[11] Similarly to other ketones, the excitation of quinones rapidly produces relatively persistent triplets with lifetimes (τ) in the ms range. Following the Weller approach[12] we can estimate the free-energy for the electron transfer to the triplet excited state, as well as the rate constant for the process. The oxidation potential of alkylanisoles[13] is ca. 1.6 V vs SCE. The triplet energies (E_T) of chloroquinones are in the 2.37–2.13 eV range[14] with the less substituted compounds having larger E_T values. The differences between the triplet state energies are partially compensated by the differences in the reduction potentials (E^r) of the quinones, providing large, and nearly constant driving force[15] ($\Delta G_{et} \approx -0.4$ to -0.5 eV) for the forward ET, assuring that in all cases the radical ion pairs are generated with a diffusion-limited rate constant, $k_q = 2.0$ ($\pm$ 0.5) $\times 10^{10}$ M^{-1} s^{-1}. Indeed, numerous time-resolved

Scheme 2
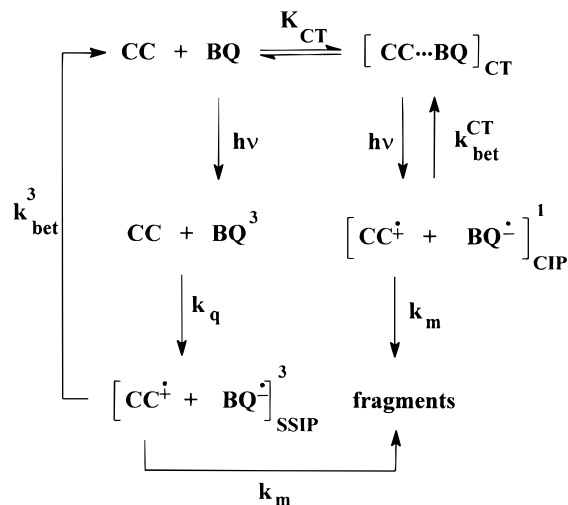
absorbance[16] and CIDNP studies[17] have shown that the triplet quinones generate triplet ion pairs with aromatic donors with high quantum efficiency.

Benzoquinones, especially the highly potent tetrachloro derivative, TCBQ, have been reported to form charge-transfer complexes with various electron donors.[11b,18] The absorbance properties of the CT complexes formed between a model compound, 4-methylanisole (**4**) and the quinones ($[4\cdots BQ]_{CTC}$) make it clear that exclusive excitation of the CT band is possible (see below). Excitation of $[4\cdots TCBQ]_{CTC}$ has been reported[19] to give directly observable radical anions of the quinone and the radical cations of **4**. Similar ion pairs were observed upon irradiation of CT complexes of TCBQ (and other acceptors) with various organic donors.[20]

Both methods of irradiation are, therefore, expected to efficiently produce CC$^{\bullet+}$/BQ$^{\bullet-}$ ion pairs. The ion pairs

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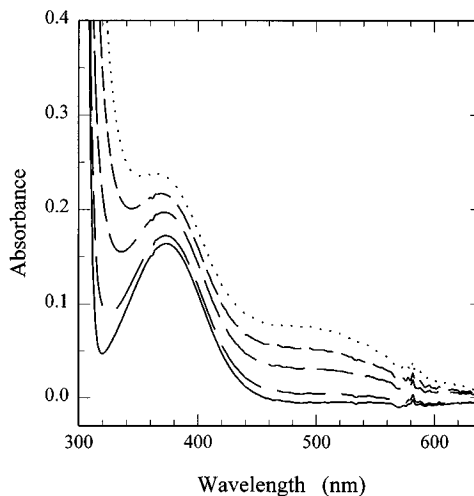
Table 1. Electron-Transfer and Fragmentation Reactions of Methoxybicumene Radical Cations Generated in Photochemical Reactions with TCBQ

	$\Phi_S{}^a$	$k_m{}^b$ (s^{-1})	$k^3{}_{bet}{}^c$ (s^{-1})	$\Phi_{CT}{}^d$	$k^{CT}{}_{bet}{}^e$ (s^{-1})	$k_q \times 10^{-9}$ (M^{-1} s^{-1})^f	E^b (V vs SCE)^g
1a	0.29	2.4×10^7	6.0×10^7			7.50	1.64
1b	0.58	6.0×10^8	4.3×10^8	0.001	6.0×10^{11}	8.89	1.59
1c	0.36	1.2×10^8	2.1×10^8			8.01	1.62
1d	0.084	1.6×10^6	1.7×10^7			6.44	1.67
1e	0.058	2.6×10^6	4.3×10^7			6.95	1.67
2b	0.73	1.2×10^9	4.3×10^8	0.005	2.3×10^{11}		
3b	0.91	4.4×10^9	4.3×10^8	0.020	2.2×10^{11}		

^{a} Quantum yields for disappearance of bicumenes in reaction with TCBQ irradiated at 407 or 435 nm where the quinone absorbs the light. Estimated errors are ca. 5%. ^{b} Rate constants for fragmentation of methoxybicumene radical cations measured in quenching experiments (Figure 4). The values in italics are based on extrapolated $k^3{}_{bet}$ (see text). ^{c} Rate constants for back electron transfer in triplet ion pairs calculated from the observed quantum yields. The values for dimethoxy derivatives (**1b**, **2b**, **3b**) were estimated from a linear relationship between the oxidation potential and $k^3{}_{bet}$ values for **1a,c,d,e**. ^{d} Quantum yields for disappearance of bicumenes in the CT complexes irradiated at 532 or 545 nm. The remaining values were too low to measure accurately. Estimated errors are ca. 5%. ^{e} Rate constants for back electron transfer in singlet ion pairs calculated from the quantum yields and k_m values. ^{f} Rate constants for quenching fluorescence of DCA* measured in CH_2Cl_2 containing 0.5% MeOH v/v (Figure 6). ^{g} Oxidation potentials of the bicumenes estimated from the Weller plot (Figure 5).

formed will differ in their solvation and spin status.[21,22] The sensitizer method (irradiation of the quinone) should give triplet SSIPs. The CT-excitation will generate singlet CIPs. The interconversion of CIPs to SSIP in a solvent of medium polarity[22] takes place within several nanoseconds, and it is practically irreversible[23] (even in CH_2Cl_2). The separation of SSIP to free ions is relatively slow in CH_2Cl_2 (several microseconds).[24] These solvation processes should contribute little to the observed efficiency of the reaction that will be determined by competition of the two faster (see below) processes, BET (k_{bet}) and the fragmentation reactions of CC$^{•+}$ (k_m).

The rates of back electron transfer in triplet ion pairs ($k^3{}_{bet}$) may be controlled by the dynamics of triplet–singlet intersystem crossing, or may follow the Marcus expression.[16,25] In the later case, based on data available[16d]

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Figure 1. Visible spectra of TCBQ (0.65 mM) with varying concentrations of **1a** (0, 0.14, 0.28, 0.54, 0.83 M) in CH_2Cl_2.

for radical cations of anisole ($E^b = 1.76$ V) or 1,2,3-trimethoxybenzene ($E^b = 1.42$ eV) and radical anions of TCBQ, one may predict $k^3{}_{bet} \approx 4 \times 10^7$ s^{-1} for our CC$^{•+}$/TCBQ$^{•-}$ system. Since the lifetimes of the bicumene radical cations vary with substitution[9] and are in the subnanosecond to submicrosecond range, we should observe quantum efficiencies (Φ_S) approaching unity for the most rapidly cleaving CC$^{•+}$ and perhaps reaching 10% for the most slowly fragmenting radical cations.

A different situation is predicted for BET in singlet CIPs ($k^{CT}{}_{bet}$). In CH_2Cl_2, the first order rate of decay of the **4**$^{•+}$/TCBQ$^{•-}$ ion pair generated by irradiation of [**4**···TCBQ]$_{CT}$ was found[19] to be 4×10^{10} s^{-1}. An estimate based on extensive data obtained by Mataga[20] suggests a rate constant of ca. 2×10^{11} s^{-1} for BET within a CIP composed of aromatic radical ions with the driving force for BET similar to that calculated for our system. Under these conditions, only the most rapidly fragmenting radical cations of bicumenes have a chance to compete with BET, and even for these species the quantum yields (Φ_{CT}) are going to be small, perhaps reaching a few percent.

Results

Charge-transfer complexes formed between the quinones and methoxybicumenes showed characteristic absorption spectra above 400 nm (Figures 1 and 2). All the donors (**1a**–**e**, **2b**, **3b**) and the model compound (**4**) exhibited similar behavior with all the quinones (MCBQ, 2,5-DCBQ, 2,6-DCBQ, TriCBQ, and TCBQ). No correlation was found between λ_{max} of the CT absorbance for [**1a**–**e**···TCBQ]$_{CT}$ and the nature of the substituent (X). The CT complexes have been characterized in more detail using the model compound (**4**). In all cases the dependence of the intensity of the new absorbance on the concentration of the donor was found to fit the Benesi–Hilderbrand equation[26] (Figure 3), confirming the existence of a 1:1 CT complex between the quinones and the donors. No chemical change was observed by NMR

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Table 2. Photoinduced Electron-Transfer Reactions of Chlorinated Quinones

quinone	λ_{max} (nm)[a]	K_{CT}[b] (M^{-1})	ϵ_{CT}[c]	E^r (V)[d]	Φ_S[e]	k^3_{bet}[f] (s^{-1})	Φ_{CT}[g]	k^{CT}_{bet}[h] (s^{-1})
MCBQ	415	0.034	521	-0.318	0.026	9.0×10^8	0.0703	1.6×10^{10}
2,5-DCBQ	438	0.069	926	-0.162	0.072	3.1×10^8	0.0114	1.0×10^{11}
2,6-DCBQ	425	0.23	380	-0.166	0.14	1.4×10^8	0.0391	2.9×10^{10}
TriCBQ	470	0.28	668	-0.118	0.23	8.1×10^7	0.0077	1.5×10^{11}
TCBQ	500	0.78	600	$+0.038$	0.29	6.0×10^7	0.0052	2.3×10^{11}

[a] Absorbance maxima of CT complexes between **4** and quinones in CH_2Cl_2. [b] Formation contants for CT complexes of **4** and quinones measured with the Benesi−Hildebrand technique (Figure 3) in CH_2Cl_2. [c] Extinction coefficients (in M^{-1} cm^{-1}) for the CT complexes of **4** with quinones measured at 510 nm (MCBQ, 2,6-DCBQ) or 520 nm. [d] Reduction potentials measured by cyclic voltammetry at a Pt disk electrode in CH_2Cl_2 containing 0.1 M TBAP, reported vs SCE. [e] Quantum yields for disappearance of **1a** in reaction with quinones irradiated at 407 or 435 nm under conditions where only the quinones absorb the light. Estimated errors are ca. 5%. [f] Rate constants for back electron transfer in triplet ion pairs calculated from the quantum yields (Φ_S) using k_m for **1a**[•+] from Table 1. [g] Quantum yields for disappearance of **2b** in CT complexes with quinones irradiated at 532 or 550 nm. Estimated errors are ca. 5%. [h] Rate constants for back electron transfer in singlet ion pairs calculated from quantum yields (Φ_{CT}) and k_m for **2b**[•+] from Table 1.
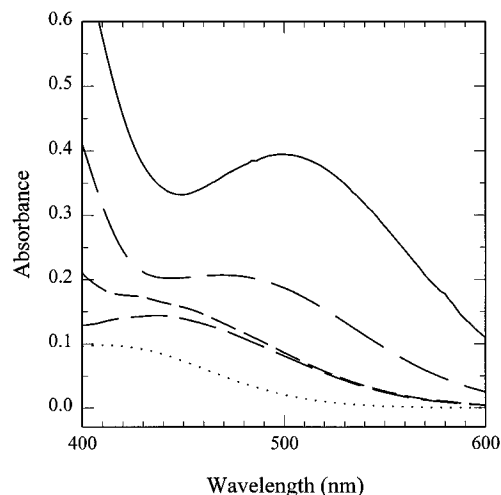

Figure 2. CT-bands of $[4{\cdots}BQ]_{CT}$ complexes in CH_2Cl_2. From the bottom to the top, the spectra correspond to BQ = MCBQ, 2,5-DCBQ, 2,6-DCBQ, TriCBQ, and TCBQ. In all cases the concentration of quinone was 0.02 M and that of **4** was 0.041 M.
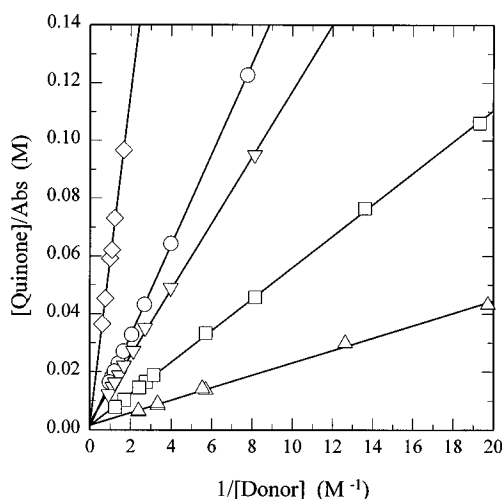

Figure 3. Benesi−Hildebrand plots for $[4{\cdots}BQ]_{CT}$ complexes in CH_2Cl_2. From the steepest to the least steep, the titration lines correspond to MCBQ (510 nm), 2,5-DCBQ (520 nm), 2,6-DCBQ (510 nm), TriCBQ, and TCBQ (both at 520 nm).

or GC upon combining the donors with TCBQ in the dark. The data on the CT complexes of the quinones are collected in Table 2.

Products of irradiation of the CC/BQ mixtures at room temperature were derived from the cleavage of the central C−C bond and were accompanied by the forma-

tion of the corresponding hydroquinones. The same products were observed when the irradiation was carried out at wavelengths where only the CT complexes absorbed the light ($\lambda > 520$ nm) and at the wavelengths where both the complexes and the quinones absorbed ($\lambda > 400$ nm). No light was absorbed by the bicumenes under these conditions. The efficiency of the photoreaction was, however, strongly dependent on the irradiation wavelength (see below). The long-wavelength reactions were inefficient, while the irradiation of quinones led to highly efficient destruction of the bicumenes.

A quantitative NMR analysis of the products was carried out for **1a**−**c**, **2b**, and **3b** with TCBQ as the acceptor in THF-d_6 containing 20% CD_3OD, using uranium-glass filtered light (the only absorbing species are the quinones and CT complexes). In the case of **1b**, **2b**, and **3b**, the corresponding α,α-dialkyl-4-methoxybenzyl methyl ethers were the exclusive bicumene-derived products (>93% yields). The unsymmetrical donors **1a,c** also gave high yields (86% and 75%, respectively) of the *p*-methoxycumyl methyl ethers. The X-substituted half of these bicumenes reappeared in one of two forms: electron-donating substituents (such as in **1c**) favored the formation of the analogous methyl ethers (83% of α,α-dimethyl-4-methylbenzyl methyl ether and 51% of α,α-dimethylbenzyl methyl ether were formed), and the electron-withdrawing substituents (such as in **1d**) favored the formation of addition products with the quinone (26% of 4-(cumyloxy)-2,3,5,6-tetrachlorophenol, **5a**, was formed from **1a**). Under the oxygen atmosphere, the reaction of **1a**/TCBQ yielded cumyl alcohol (7%) and cumyl hydroperoxide (41%), in addition to cumyl methyl ether (14%), 4-methoxycumyl ether (71%), and a small amount of **5a** (7%). Similar reaction of **1b**/TCBQ under oxygen gave *p*-methoxycumyl alcohol (23%) and *p*-methoxycumyl methyl ether (69%). Identical products were observed in CH_2Cl_2/MeOH mixtures containing 5% or 0.5% (v/v) of alcohol. Analogous products were observed by NMR and GC for other bicumenes and quinones, but no quantitative product analysis was undertaken in these cases. In all cases hydroquinones were produced in addition to the bicumene derived products.

The reversibility of fragmentation of photogenerated radical cations of the bicumenes was probed with diastereomerically pure *erythro*-**2a**, enriched **2b** (11.8:1 mixture of *meso* and *d,l* isomers) and optically active 2,3-dimethyl-2-phenyl-3-(4′-methoxyphenyl)pentane. These donors were combined with TCBQ in THF/MeOH (20%) and irradiated as described above. The starting materials were isolated at 50 ± 5% conversion (as determined by GC) and examined by either NMR or polarimetry. In

all cases studies, the starting materials were recovered unchanged, indicating that the fragmentation reaction is irreversible under the conditions studied.

Quantum yields for destruction of donors were measured independently under conditions where the quinones or the CT complexes absorbed the light. The quantum yields for destruction of **1a**−**e**, **2b**, and **3b** in the presence of TCBQ are presented in Table 1. The triplet excited state quinone was generated by irradiation at 407 or 435 nm (Xe or Xe/Hg arc lamp) and CT complexes were excited at 532 (YAG laser) or 550 nm (Xe or Xe/Hg arc lamp). The concentration of the donor was adjusted to quench more than 99% of the excited-state quinone. The quantum yield for disappearance of **1a** measured at 435 nm in THF with 20% MeOH was identical to that measured in CH_2Cl_2/MeOH (either 5% or 0.5%). The measurements of quantum yields were not influenced by the exclusion of atmospheric gases from the samples.

The quantum yields for destruction of **1a** with the excited triplet states of quinones (MCBQ, 2,6-DiCBQ, 2,5-DiCBQ, TriCBQ, and TCBQ) were measured at 407 and 435 nm. For the charge-transfer excitation, **2b** was used as the donor, and the samples were irradiated at 532 and 550 nm. The data for the quinones are displayed in Table 2, and the details of quantum yield measurements are provided in the Experimental Section.

Rate constants for fragmentation of radical cations were measured in a bimolecular quenching experiments utilizing TCBQ as the electron acceptor.[27] The experiment is based on a competition reaction between the unimolecular fragmentation process (k_m) and a bimolecular electron-transfer reaction of the radical cations (k_q[Q]). The chosen quencher (1,2,4-trimethoxybenzene, TMB) is expected to react with the triplet excited state of TCBQ and with the radical cations of methoxybicumenes with diffusion limited rates ($k_q \approx 2 \times 10^{10}$ M^{-1} s^{-1}, see below). In the absence of quencher, the quantum yield of the sensitized reaction ($\Phi_S = k_m/(k_m + k^3_{bet})$) is governed by the competition between the fragmentation reaction of the radical cation (k_m) and the back-electron transfer process from TCBQ$^{\bullet-}$ to the radical cation (k^3_{bet}). The quantum yield in the presence of the quencher ($\Phi_{SQ} = Ak_m/(k_m + k^3_{bet} + k_q[Q])$) is diminished by the interception of the triplet state quinone ($A = k_q$[bicumene]/(k_q-[bicumene] + $k_q[Q]$)) and the radical cation by the quencher. Under these conditions, $A\Phi_S/\Phi_{SQ} - 1 = \Phi_S k_q$-[Q]/$k_m$, and the measured quantum yields for destruction of the bicumene as a function of quencher concentration (Q = TMB) yield k_m values. Quantum yield data collected for the reactions of **1a**,**c**,**d**,**e** with triplet excited-state TCBQ in the presence of varying concentrations of TMB are plotted in Figure 4, and the rate constants determined are presented in Table 1. In these experiments the samples were irradiated with white light (uranium-glass filtered) in a way which guaranteed that each sample received the same dose. The reaction of **1d** was also run with monochromatic light ($\lambda = 435$ nm), and the results were identical to those obtained with the white light source. The quenching technique did not yield k_m values for the more labile radical cations (*i.e.*, those derived from **1b**, **2b**, and **3b**) due to their short lifetimes.

Redox potentials of methoxybicumenes were not available directly from cyclic voltammetry (CV) measurements due to the rapid fragmentation of the radical cations (see above). However, the oxidation potentials could be estimated from the rates of electron transfer of
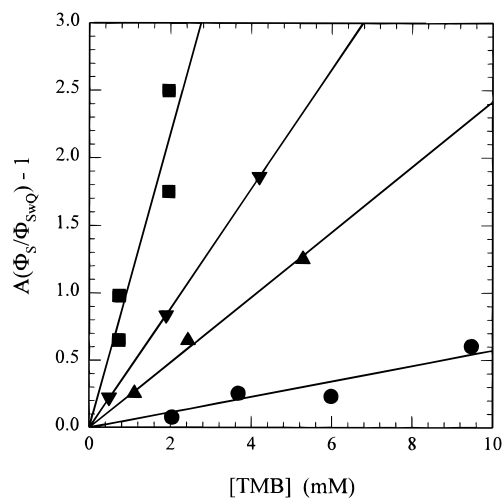

Figure 4. The relative quantum yields for destruction of BB with triplet TCBQ with added quencher (TMB) corrected for quenching of triplet TCBQ by TMB (see text). From the steepest to the least steep, the slopes correspond to the rate of mesolysis ($k_m = \Phi_S k_q$/slope, where $k_q = 2 \times 10^{10}$ M^{-1} s^{-1}) of **1d**$^{\bullet+}$, **1e**$^{\bullet+}$, **1a**$^{\bullet+}$, and **1c**$^{\bullet+}$.

Table 3. Oxidation Potentials of Electron Donors and Their Rates of Electron Transfer to DCA* and ANT*

donor	acceptor	E^b (V)^a	$k_q \times 10^{-9}$ (M^{-1} s^{-1})^b	ΔG_{et} (eV)^c
p-anisidine	DCA*	0.832	20.8	−1.22
	ANT*	0.832	20.4	−0.56
4-*tert*-butyl-*N,N*-dimethyl-aniline	DCA*	0.805	18.8	−1.07
	ANT*	0.805	15.4	−0.40
N,N-dimethylaniline	ANT*	0.831	12.7	−0.38
triphenylamine	DCA*	1.026	20.0	−0.85
1,2,4-trimethoxybenzene	ANT*	1.157	9.5	−0.05
tris(2,4-dibromophenyl)amine	DCA*	1.527	10.9	−0.33
1,3,5-trimethoxybenzene	DCA*	1.559	9.3	−0.32
hexaethylbenzene	DCA*	1.696	9.9	−0.18

^{a} In V vs SCE, measured at a Pt disk in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate. ^{b} Obtained from the Stern−Volmer equation using independently determined fluorescence lifetimes: $\tau_{DCA^*} = 13.7$ ns, $\tau_{ANT^*} = 2.30$ ns. The lifetimes and the fluorescence quenching data were measured in CH_2Cl_2 containing 0.5% MeOH v/v. ^{c} Free-energy of electron transfer to the excited state acceptors calculated using measured reduction potentials (CH_2Cl_2, 0.1 M tetrabutylammonium perchlorate) and the singlet energies E^r (DCA) = −0.984 V, E^{oo} (DCA) = 2.86 eV, E^r (ANT) = −2.114 V, and E^{oo} (ANT) = 3.31 eV.

these substrates to fluorescent electron acceptors. The rates of fluorescence quenching of 9,10-dicyanoanthracene (DCA) and anthracene (ANT) by various aromatics with known oxidation potentials were determined using the Stern−Volmer technique[28] (Table 3). A relationship between the quenching rates and the free energy change (Weller equation) for electron transfer (Figure 5) was used to calculate the oxidation potentials of the methoxybicumenes (Table 1).

The redox potentials for the compounds in Table 3 were obtained by CV in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate (TBAP) serving as electrolyte. The Stern−Volmer quenching experiments of DCA* and ANT* were carried out in CH_2Cl_2 containing 0.5% MeOH. The rate constants for quenching were calculated using the fluorescent lifetimes measured independently in the same solvent with time-resolved fluorescence spectroscopy. The values of k_q are presented in Table 3, and the free-energy relationship is plotted in Figure 5. The solid
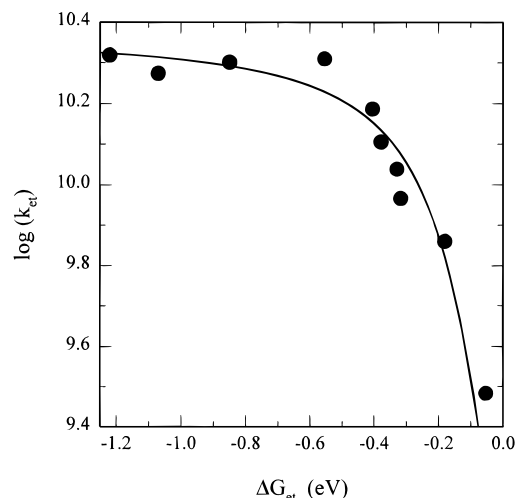
Figure 5. The relationship between fluorescence-quenching rates of DCA* and ANT* by aromatic donors (Table 3) and ΔG for electron transfer. The solid line represents the Weller equation with $\Delta G(0) = 0.13$ eV.
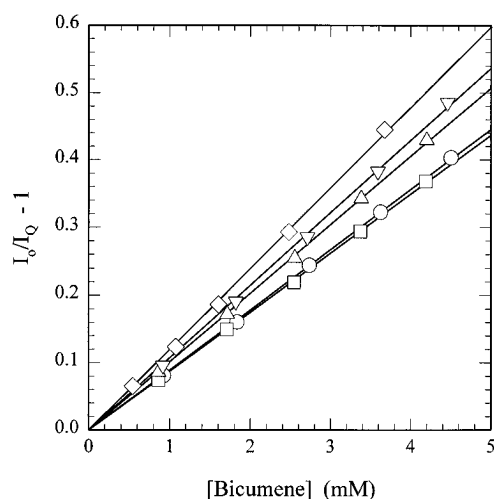

Figure 6. Stern−Volmer plots for the quenching of fluorescence of DCA with (from the steepest) **1b**, **1c**, **1a**, **1e**, and **1d**.

line in Figure 5 was calculated from the Weller equation[12] with $\Delta G(0) = 0.13$ eV. The oxidation potentials of bicumenes were obtained from the quenching rates measured for these compounds (Figure 6) with DCA*, using the ascending part of the plot ($\Delta G_{et} < -0.5$ eV) in Figure 5.

Discussion

In all cases studied, irradiation of CC/BQ mixtures resulted in fragmentation of the central carbon−carbon bond in the bicumenes. The overall efficiency of the process strongly depended on the nature of substituents in bicumenes and quinones, as well as, on the method of irradiation. TCBQ provided an experimentally convenient system to probe the products and kinetics of fragmentation in a quantitative fashion. The mechanistic details of product formation are expected to be the same throughout the studied series, as suggested by the results of qualitative studies, showing that the identity of the products remain independent of the quinone used or method of radical cation generation.

Regardless of the spin multiplicity and solvation status, the radical cations of the donors (CC•+) undergo frag-

mentation to give carbon-centered X-substituted cumyl radicals and MeO-substituted cumyl cations. This electron apportionment is consistent with the relative thermodynamic stability of the fragments.[10b] The cationic fragments react with MeOH to produce ethers. The radical fragments appear in the product mixture in one of two forms: (1) as the corresponding X-substituted methyl ethers, or (2) as adducts with the quinones. The reduction potential of TCBQ is comparable to the oxidation potentials of the more electron rich cumyl radicals.[29] Thus, TCBQ is expected to convert the easily oxidized radicals to cations, which then react with MeOH to form the ethers. In the case of the more difficult to oxidize radicals (or when quinones are not as potent oxidants) a well-precedented addition[30] reaction is observed (instead of an electron transfer process), yielding phenyl ethers.

The formation of cumyl radicals was further confirmed by their interception with oxygen. The oxygen derived products (alcohols and hydroperoxides) were detected for **1a,b** (X = H or OMe). The presence of these products indicates that dioxygen is able to successfully compete with the quinone (or semiquinone) for these radicals.

The question of reversibility of the fragmentation reaction was probed with stereodistinct substrates. The cleavage reaction of bicumene radical cations are nearly thermoneutral[31] ($\Delta G_m = -2$ to 3 kcal/mol), and therefore, no complication due to reaction reversibility was expected. Indeed, the tested substrates showed no detectable scrambling of stereochemistry, even in the case of the most sensitive probe, the optically active substrate (see above). Although the rejoining of the cumyl carbocations with cumyl radicals within the solvent cage without any relative reorientation cannot be excluded by such tests, for all mechanistic purposes the reaction can be treated as irreversible.

As can be seen in Table 1, both the strain energy in the scissile bond[9,32] and the remote X-substituent affected the quantum yields (Φ_S) in a way consistent with the proposed mechanism of product formation. The decrease of the donor's homolytic bond strength[32,33] (from **1b** to **2b** to **3b**) resulted in the increase in the quantum yield for destruction of CC. Electron-withdrawing substituents (X) lowered and electron-donating groups increased the quantum yield for disappearance of bicumenes. These trends closely followed those observed[9] for the reaction of CC•+ produced with singlet 1,4-dicyanobenzene (DCB*) or by irradiation of CC/tetranitromethane charge-transfer complexes ([CC···TNM]$_{CT}$) and are analogous to those observed in the directly-observable radical cations of (dimethylamino)bicumene derivatives.[32]

The relatively high efficiencies of CC/TCBQ reactions ($\Phi_S = 0.06-0.91$) allowed us to indirectly obtain a measure of kinetics of radical cation fragmentation, using an additional quencher. The role of the added quencher (TMB) is to, at least partially, intercept the radical cations of the bicumene under study in a diffusion-

(29) (a) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132. (b) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635.
(30) Jones, G. II; Haney, W. A.; Phan, X. T. *J. Am. Chem. Soc.* **1988**, *110*, 1922.
(31) Maslak, P.; Vallombroso, T. M.; Chapman, W. H., Jr.; Narvaez. J. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 73.
(32) (a) Maslak, P.; Asel, S. *J. Am. Chem. Soc.* **1988**, *110*, 8260. (b) Maslak, P.; Chapman, W. H. Jr.; Vallombroso, T. M., Jr.; Watson, B. A. *J. Am. Chem. Soc.* **1995**, *117*, 12380.
(33) (a) Kratt, G.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1984**, *117*, 1748. (b) Kratt, G.; Beckhaus, H.-D.; Lindner, H. J.; Rüchardt, C. *Chem. Ber.* **1983**, *116*, 3235.

controlled ET reaction. The diminished reaction efficiency (after correction for direct quenching of triplet TCBQ by TMB) as a function of quencher concentration provides information about the lifetime of the intermediate of interest (see above). The selection of TMB as quencher proved quite successful. The electron transfer from TMB to the triplet TCBQ and to radical cations of bicumenes is sufficiently exergonic (Table 3) to assure the diffusion-limited rate for both reactions. Also, the diffusion-limited quenching of TCBQ* by CC has essentially identical rate constant, simplifying the analysis even further. The linearity of the experimental data for **1a**,**c**,**d**,**e** in Figure 4 supports the validity of the method. The radical cations of bismethoxy derivatives (X = OMe) underwent fragmentation too rapidly to be intercepted with TMB at experimentally practical concentrations. The fragmentation rate constants determined by this method are consistent with the absolute quantum yields observed for the reaction with TCBQ*, as well as with the relative trends observed in PET reactions of CC with 1,4-dicyanobenzene (DCB) or tetranitromethane.[9] Indeed, the rate constants for fragmentation of the radical cations of **1a** (1×10^7 s^{-1}) and **1d** (7×10^5 s^{-1}) obtained from the time-resolved absorbance experiments carried out by irradiation of CC−tetranitromethane charge-transfer complexes[9] in acetonitrile are in good agreement with the values measured by the quenching technique in CH$_2$Cl$_2$. In accordance with the previously observed transition-state (TS) polarization,[9] wherein part of the positive charge is transferred across the scissile bond, the electron-withdrawing substituents (X = CF$_3$, CN) slow down the fragmentation, while electron-donating substituents (X = CH$_3$, OMe) accelerate the cleavage. The submicrosecond lifetimes (Table 1) of these radical cations are also consistent with the exergonicity[31] of the reaction ($\Delta G_m \approx 1-3$ kcal/mol for **1a−e**).

The fragmentation rate constants in conjunction with quantum yields (Φ_S) allow us to determine the rates of BET within the triplet ion pairs (k^3_{bet}, Table 1). These rates are clearly depended on the nature of X-substituent and vary from 10^7 to 10^8 s^{-1}, in an excellent agreement with the prediction based on the literature data (see above). This dependence suggests that there are minor perturbations in the electronic structure of the methoxyphenyl moiety by the remote substituent, affecting the redox potentials and free energies of ET. This supposition cannot be tested directly, since the radical cations have too short lifetimes for standard electrochemical measurements.

The redox potentials may be estimated, however, using a kinetic approach based on the Weller equation.[12] We have selected two fluorescent excited-state acceptors (ANT* and DCA*) and a series of aromatic donors with known redox potentials (Table 3) to establish a free-energy relationship for ET (Figure 5). The Stern−Volmer method was used to obtain the kinetic data. The experiments with **1a−e** and DCA* are shown in Figure 6. There are small, but systematic and easily measurable differences in the rates of ET between the members of the series (see k_q values, Table 1). The measured rate constants for quenching can be converted with the help of the ascending part of the Weller plot (Figure 5) to redox potentials of the bicumenes (Table 1).

The BET rates (k^3_{bet}) show a correlation with the redox potentials characteristic of the inverted region.[7] The correlation between k^3_{bet} and redox potentials can be used to extrapolate the rate constant for BET between **1b**$^{•+}$

and TCBQ$^{•-}$. Since the change in the driving force is rather small (less than 0.1 eV) a linear approximation is adequate.[34] The extrapolated value of k^3_{bet} for **1b**$^{•+}$/TCBQ$^{•-}$ pair of 4.3×10^8 s^{-1} can then be utilized to obtain the fragmentation rate for **1b**$^{•+}$, using the measured quantum yield (Φ_S). Similarly, the rates of BET for radical cations of **2b** and **3b** may be taken to be equal to that of **1b**$^{•+}$/TCBQ$^{•-}$ system, since the electronic properties of the methoxyphenyl moiety are not significantly affected by side-chain substitutions.[9] Under these assumptions, the fragmentation rates for all CC$^{•+}$ can be obtained (Table 1).

The radical cations of CC have lifetimes spanning the range from several hundred nanoseconds to a few tens of a nanosecond. By choice of the remote substituent (which affects the charge delocalization in TS for fragmentation) or side-chain substituents (which modify the strength of the scissile bond), appropriate probes may be selected that will have similar electronic properties and could be used for processes with varying time scales. We have used **1a** to probe the PET reactions of triplet state quinones and **2b** to explore the photochemistry of CT complexes of BQ (Table 2).

In the photosensitized reactions the quinones with more chlorines gave more efficient reactions. The quantum yields (Φ_S) for disappearance of **1a** increased from under 3% in the case of MCBQ to nearly 30% for TCBQ. Accordingly, the rates of BET within the triplet ion pairs (k^3_{bet}) decreased by a factor of fifteen. In this case the decrease in rates followed the trend in driving forces for ET, i.e. the quinones with the more negative reduction potentials exhibited larger k^3_{bet}. This trend would indicate that the reaction is in the Marcus normal region for ET.[7] An opposite trend was observed for TCBQ when the driving force was varied by the change of bicumene substituent (see above). That reaction series seems to belong to the Marcus inverted region. The driving-force range spanned there only 0.1 eV, and the results should be treated with caution. Nevertheless, these opposite trends obtained by separately varying the redox properties of the donor or the acceptor indicate that BET may be controlled to a different degree by both the thermodynamics of ET and dynamics of spin state interconversion,[16,25] leading to a quite complicated situation. Additional difficulty in interpretation of these trends is the fact that the change in driving force for different bicumenes was obtained with minor modification of the electronic structure of the methoxyphenyl moiety, while the increasing chlorine substitution in quinones was likely to perturb the electronic coupling of the of radical anions of the acceptors with the radical cation of the donor in a more substantial way. Indeed the literature data[16d] obtained for various quinones and other acceptors with similar structures forming triplet ion pairs illustrate that the relation between the kinetics and thermodynamics for ET is only crudely described by a unique Marcus-type parabola. The experimental data are quite scattered[16d] (much more so than those observed for similar singlet ion pairs[35]), and the crossover from the normal to the inverted region is not well defined.

The bicumenes formed CT complexes with all the quinones. The position of the maximum of the CT band of [**1a−e**···TCBQ]$_{CT}$ did not show any correlation with the oxidation potential of the bicumenes. In light of the detectable differences in ET kinetics of these donors and

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(34) The approximation used: $\log(k^3_{bet}) = 35.4 - 16.8E^o$ (Table 1).

their radical cations (see above), the lack of correlation suggests that the remote substituent affects the radical cation significantly more than it perturbs the neutral. This interpretation is consistent with the radical cation structure having an elongated scissile bond that allows for increased transmission of substituent effects from the remote phenyl moiety.[9] A similar, yet more pronounced, effect is responsible for the TS polarization observed in the fragmentation reaction[9] (see above). The electron-donating behavior of the remote methoxy substituent (X = OMe) indeed indicates that the observed effect has resonance, rather than inductive characteristics.

Although the substitution in bicumenes had no effect on the position of CT bands (with TCBQ), the CT-band maxima of different quinones were clearly affected by the number of chlorine substituents present, as indicated by studies with the model, **4**, (Table 2). As expected, both λ_{max} and the equilibrium constant for the formation of the CT complexes (K_{CT}) increased with the number of chlorine atoms on the quinone moiety. The small differences between the 2,5- and 2,6-dichloro isomers are probably attributable to different electron distribution in these two compounds that may affect the overlap between the components of the CT complexes, as well as solvation of these systems.

In all cases, irradiation of $[CC\cdots BQ]_{CT}$ was possible without deposition of light energy into the quinone chromophore. The photoreaction was dramatically inefficient as compared to the photosensitized reaction (Table 2). In the case of CT complexes of TCBQ only those bicumenes that give the most labile radical cations disappeared with measurable quantum yields (Φ_{CT}, Table 1). For **1a** the quantum yield was only ca. 0.1%, increasing for the more sterically strained **2b** and **3b**. Assuming that the fragmentation rate constants for radical cations are not significantly affected by solvation status of the ion pairs, BET within singlet ion pairs (k^{CT}_{bet}) takes place on the picosecond time scale, in agreement with the literature data[20] for singlet ion pairs with similar driving force. It is worth noticing that the data for both **2b** and **3b** lead to the same estimate for k^{CT}_{bet}, confirming the validity of our analysis. The data for **2a** are a little off, but the low (and a less accurate) value of quantum yield in this case is probably responsible for the deviation.

The quantum yields for different quinones (Φ_{CT} measured with **2b**) showed an opposite trend to one observed for photosensitized reactions (Φ_S, Table 2). The lowest efficiency was observed for the most chlorinated quinone (TCBQ), the highest for the monochloro derivative (MCBQ). Again an "irregularity" was detected for the two isomers of the dichloro derivatives (see above). The observed increase in rates of BET with the increased chlorination of quinones indicates that the reaction takes place in the inverted region.

It is instructive to compare the two modes of radical ion generation. With the strongest acceptor (TCBQ) the reaction generating triplet ion pairs is up to several hundred times more efficient (Φ_S/Φ_{CT}) than the reaction where singlet ion pairs are involved (Table 1). Although, similar quantitative comparison of quantum yields cannot be made for MCBQ (Φ_{CT} is larger than Φ_S, Table 2, but different probes are used), clearly the difference is much less dramatic for reactions with larger driving force for BET. A valid comparison is available for rates of BET in the two systems (Figure 7). In both systems the rate constants for BET vary by a factor of ca. 15, but in triplet ion pairs the fastest rate is observed for the most negative
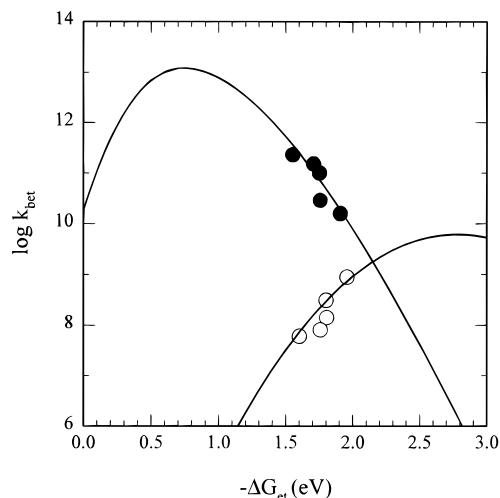

Figure 7. The rates of BET in singlet, contact-ion pairs (filled circles) generated by the excitation of CT complexes, and in triplet, solvent separated ion pairs (open circles) formed in the quenching process. The solid lines represent the Marcus equation[7] for ET with speculative parameters, chosen to illustrate the qualitative trends. For both curves the average vibrational frequency is taken as 1500 cm^{-1}, and the internal reorganization energy is set to 0.2 eV. In the case of singlet ion pairs the electronic matrix element (V) is 230 cm^{-1} and the solvent reorganization energy (λ_s) is 0.6 eV. For the triplet ion pairs $V = 6.6$ cm^{-1} and $\lambda_s = 2.6$ eV.

ΔG_{bet} (MCBQ), while in singlet ion pairs the fastest rate corresponds to the smallest driving force (TCBQ). Thus, ratio k^{CT}_{bet}/k^3_{bet} is dependent on exergonicity of the reaction changing from nearly 20 ($\Delta G_{bet} \approx 2$ eV) to almost four thousand ($\Delta G_{bet} \approx 1.5$ eV).

As indicated above, it is not clear whether k^3_{bet} corresponds to the spin-forbidden electron transfer or whether it represents a rate of intersystem crossing of the ion pairs (or perhaps a combination of the two).[16,25] The literature seem to favor the former,[16,25] and our data may be analyzed in a way that supports that conclusion as well. Although our data span only a narrow range in terms of ΔG_{bet}, we may "fit" them into the Marcus equation[7] with speculative parameters (Figure 7). This presentation emphasizes the differences between the two modes of ion pair generation. In singlet, contact ion pairs generated by irradiation of CT complexes, the solvent reorganization energy accompanying BET is small, and the interaction between ions relatively strong. In triplet, solvent-separated ion pairs formed in the quenching process the solvent reorganization is energetically more costly, and the coupling between the ions is significantly weaker due to the larger interion distance and the spin-forbidden nature of the electron-transfer process. Thus, the solvation status of ion pairs also contributes to the difference in BET dynamics.[21–24,35] It has to be stressed that the specific partition of the observed differences between the triplet and singlet pairs between the two phenomena (differences in spin or solvation status) shown in Figure 7 is highly speculative (because of the narrow range of the data) and requires further study.

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In conclusion, the existing literature data on ET in organic systems within the framework of Marcus theory may be very successfully used to predict dynamic behavior of PET systems unexplored previously. The study presented a series of radical cation probes with variable lifetimes that can be used to explore ET reactions in photogenerated ion pairs. The direct comparison of two methods of ion pair generations clearly showed the advantage of utilizing triplet excited states, but also indicated that this advantage depends on the energetics of BET, being large for reactions with relatively small ΔG_{et} for BET and decreasing for reactions with more negative ΔG_{bet}.

Experimental Section

Materials. The bicumenes were prepared as described previously.[9] Preparation of optically active 2,3-dimethyl-2-phenyl-3-(4′-methoxyphenyl)pentane is described in the supporting information. Tetrachlorobenzoquinone (TCBQ) and 2,5-dichlorobenzoquinone (2,5-DCBQ) were purchased from Kodak. TCBQ was purified by recrystallization from benzene and sublimation. 2,5-DCBQ was purified by sublimation. Chlorobenzoquinone (MCBQ) was prepared by the oxidation of chlorohydroquinone with $Na_2Cr_2O_7$ in aq H_2SO_4 according to a reported procedure,[36] and it was purified by double recrystalization from ethanol, followed by sublimation. The trichlorobenzoquinone (TriCBQ) and 2,6-dichlorobenzoquinone (2,6-DCBQ) were prepared by the CrO_3 oxidation of 2,3,4,6-tetrachlorophenol (purified before use by recrystallization from heptane) and 2,4,6-trichlorophenol, respectively. The procedure used was identical to that reported by Manecke and Beyer.[37] The products were purified by double sublimations.

Determination of Charge-Transfer Complex Formation Constants. Addition of donor molecules **1a**−**e**, **2b**, **3b**, and 4-methylbutylanisole (**4**) to the bright yellow solutions of the quinones in CH_2Cl_2 resulted in a visible darkening of the solutions. The equilibrium constants for formation and extinction coefficients for the complexes were determined by the Benesi−Hilderbrand technique.[26] The quinones were not highly soluble in the solvents employed in this study, so the donors were used in large excess. In a typical run, the quinone (10−30 mg) was weighted into a 25 mL volumetric flask, and the flask was topped to the mark with CH_2Cl_2 (ca. 10 mM solutions). The solution (3 mL) was transferred to a cuvette, and an absorbance spectrum was recorded. The donor was added to the quinone solution, and the change in absorbance of the solution was measured at a wavelength at which the absorbance of the quinone was less than 0.01. The process was repeated several times, controlling the concentration of the donor in a manner such that the measured absorbance at the monitored wavelengths was between 0.1 and 1.0. Each determination consisted of three to four runs. The desired quantities were obtained by linear regression (Figure 3).

Identification of Products and Measurement of Product Yields. Light was provided by the Hanovia lamp fitted with a uranium-glass. The samples (0.03 M in both the donor and acceptor) were contained in either 4 mL Pyrex test tubes or 5 mm o.d. NMR tubes held 5−10 cm from the lamp. Owing to the reactions high quantum yield, the reaction times were short; 5−15 min of irradiation was usually sufficient to consume ca. 50% of the starting **1**, **2**, or **3**. Under these conditions, the temperature of the samples remained at room temperature (ca. 23 °C, copper−constantine thermocouple immersed in the sample). The identity of the products of the photochemical reactions of the donors with the quinones (the corresponding methyl ethers) were determined by isolation and comparison to authentic samples.[9] The phenyl ethers derived from the quinones (**5** and analogues) were found to be difficult to isolate. The structures of these ethers were inferred from

¹H NMR spectra of the reaction mixtures and characteristic decomposition products detected after chromatographic separations. For example, a ¹H NMR spectrum of the reaction of **1a** with TCBQ run in THF containing 20% MeOH (by volume) revealed no α-methylstyrene. However, GC showed the styrene to be present. The α-methylstyrene could also be isolated if the reaction mixture was flash-chromatographed with pentane immediately after solvent evaporation. Yields of the products in all cases were determined by ¹H NMR (vs internal methyl *tert*-butyl ether) or GC (calibrated with authentic samples of products prepared as described previously).

Quantum Yield Measurements. All quantum yield measurements were made with focused light of wavelength 407, 435, 550 nm (±10 nm, with the focused Xe/Hg arc lamp) or 532 nm (YAG laser) with both the single beam and two beam techniques. The procedure employed for the determinations were identical to those used in the previous studies.[9]

Most of the solutions were totally absorbing at 407 and 435 nm. For measuring the quantum yield for destruction of **1** at 407 or 435 nm with the quinones, **1** (20−30 mg), the quinone (50−100 mg), and octadecane (50 mg) were weighed into a 10 mL volumetric flask, MeOH was added, and the flask was topped with CH_2Cl_2. The CC/BQ solution (0.3 mL or 2 mL) was transferred to a 1 mL or a 4 mL, 10 mm path-length cuvette, the cuvette was tightly sealed with Teflon caps, and the solutions were irradiated for 1−6 h. GC analysis after this time (alternatively injecting the irradiated sample with a sample of the original solution stored in the dark) gave the degree of conversion. The light intensity was measured both before and after each run using ferric oxalate actinometry.[38] For illustration: the average value of twelve runs over a three day period was 7.5 (± 0.8) × 10⁻⁶ mol photons/h.

The solutions used for the determination of the quantum yields for destruction of bicumenes under conditions where the CT complexes were irradiated at 532 and 550 nm were not totally absorbing. The corrections based on measured absorbances were applied. Light intensities at 532 were measured with a Coherent light intensity meter (in mJ and converted to photons/h) and were corrected for reflection of the light off the front surface of the cuvette. At 550 nm, light intensities were measured with the $KCr(NH_3)_2(NCS)_4$ actinometer.[39] Measurements made with the beam splitting prism ($\lambda = 532$ nm) were run in 4 mL, 10 mm pathlength cuvettes containing 3 mL of the solution. Single beam experiments were run in the 1 mL, 10 mm pathlength cuvettes containing 0.3 mL of the solution. All mixtures were analyzed as described for the 407 and 435 nm irradiations, except the samples were diluted 10 times before analysis.

Measurement of Fragmentation Rate with the Quenching Technique. The efficiency of consumption of the donor in the photochemical reaction with TCBQ was determined in the presence of varying concentrations of 1,2,4-trimethoxybenzene (TMB, Aldrich, used as received). The general procedure is illustrated with a run for **1a**. Bicumene (**1a**) (155.9 mg, 0.582 mmol), TCBQ (333.9 mg, 1.36 mmol), and octadecane (100 mg) were weighed into a 500 mL volumetric flask, and the flask was topped with CH_2Cl_2/MeOH (spectrophotometric grade, 0.5% v/v MeOH, the final concentrations of **1a** and TCBQ were 1.16 mM and 2.71 mM, respectively). Varying amounts of TMB (18.7 mg, 40.8 mg, 88.7 mg, 169.0 mg) were weighed into four 100 mL volumetric flasks (the final concentrations of TMB were 1.11 mM, 2.53 mM, 5.28 mM, and 10.06 mM, respectively) and each flask was topped with the **1a**/TCBQ/octadecane solution. Samples (2 mL) of each solution were transferred to a set of 4 mL test tubes, and the tubes were sealed with rubber septa (a total of 10 tubes were filled and sealed). One set of tubes was stored in the dark, and the other set was photolyzed (450 W Hanovia, Uranium glass filter) while being rotated on a turntable apparatus (each sample received the same dosage). After 7 min of photolysis,

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the degree of conversion of **1a** was determined by GC. The photolyzed samples were alternatively injected with the samples which were stored in the dark, and the final degrees of conversions were determined by averaging the results of at least two injections. In this specific run, the degree of conversion in the reactor which contained the highest concentration of TMB was to low to measure (<2%). The measured degree of conversion ($\pm 0.3\%$) in the other four reactors was 39.4% (no TMB), 15.9% ([TMB] = 1.11 mM), 7.54% ([TMB] = 2.53 mM), and 2.91% ([TMB] = 5.28 mM). The value of A was taken as [**1a**]/([**1a**] + [TMB]), considering that **1a** (and other bicumenes) has quenched the fluorescence of 1,4-dicyanobenzene with diffusion limited rates (2.0×10^{10} M^{-1} s^{-1}), and TMB quenched the fluorescence of DCA* with the same rate constant. The quenching plots for **1a** and other derivatives are shown in Figure 4.

Supporting Information Available: Preparation of optically active 2,3-dimethyl-2-phenyl-3-(4′-methoxyphenyl)pentane (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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