Direct Comparison of Photoefficiencies of C–C Bond Scission in Radical Cations generated by Photosensitized Electron Transfer and by Irradiation of Charge-transfer Complexes

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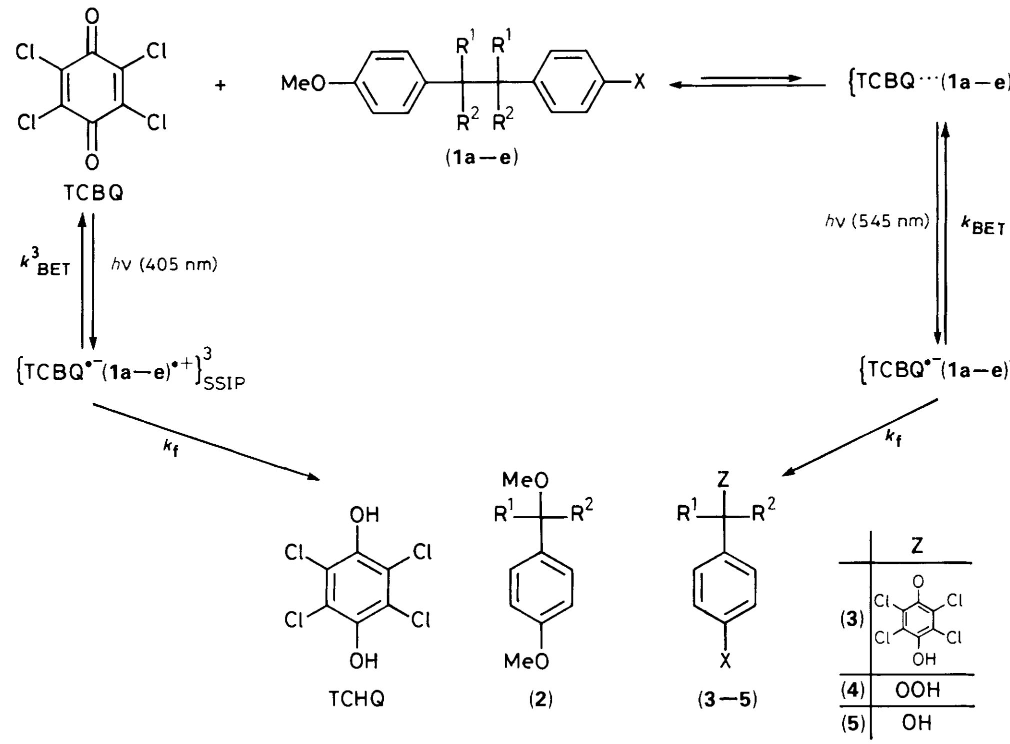
Quantum yields for C–C bond scission are at least 50 times larger in radical cations of methoxybicumenes ($\mathbf{1}^{\cdot+}$) generated by quenching of the *p*-tetrachlorobenzoquinone (TCBQ) excited state (a process that results in triplet solvent-separated ion pairs) than in those obtained by the irradiation of [TCBQ···(**1**)] charge-transfer complexes (a reaction that yields singlet contact ion pairs).

There are two common methods of photogeneration of radical ions. One method involves deposition of light energy in acceptor or donor molecules to form potent redox reagents[1,2] which may undergo electron transfer (ET) with ground-state substrates. In polar media, the electron transfer leads initially to solvent-separated ion pairs[3,4] (SSIP). Alternatively, ET may be induced by irradiation of charge-transfer (CT) bands of donor–acceptor pairs.[3,5—8] Such irradiation produces contact ion-pairs (CIP) in high quantum yields.[6] By determining the quantum yields of a follow-up reaction, we present here the first direct comparison between the radical ion pairs generated in these two ways.[3,8] We show that photoefficiencies of C–C bond scission[9] in radical cations of (**1a**—**e**) generated by ET to photoexcited *p*-tetrachlorobenzoquinone (TCBQ) are much higher than those measured for irradiation of CT-complexes between TCBQ and (**1a**—**e**) (Scheme 1). We



Scheme 1

Table 1. Quantum yields for disappearance of (**1a**—**e**) in the TCBQ/(**1a**—**e**) system.[a]

(1)	R^1	R^2	X	$h\nu_{CT}$[b]/eV	Φ_Q[c] (406 nm)	k_{rel}[d]	Φ_{CT}[e] (545 nm)
a	Me	Me	H	2.55	0.21	1.0	—
b	Me	Me	Me	2.62	0.36	2.1	—
c	Me	Me	MeO	2.51	0.58	5.2	—[f]
d	Me	Et	MeO	2.54	0.73	10.2	0.005
e	Et	Et	MeO	2.52	0.91	38.0	0.020[g]

[a] In tetrahydrofuran (THF)/MeOH (20%) measured against ferric oxalate and Reinecke's salt (ref. 18) actinometers. [**1a**—**e**] = 0.01—0.04 M; [TCBQ] = 0.08—0.12 M. [b] In CCl_4; in THF/MeOH (20%) $\lambda_{max.} \approx 465$ nm. Formation constants of CT complexes were *ca.* 0.9 mol^{-1} dm^3 in CCl_4 (ref. 13) and *ca.* 0.1 mol^{-1} dm^3 in THF/MeOH (non-linear fitting). [c] Irradiated at 406 ± 10 nm; (**1**—**e**$^{\bullet+}$) are produced by quenching of TCBQ.[3] [d] Estimated from Φ_Q assuming equal k_{BET} for all compounds. [e] Irradiation at 545 ± 10 nm where only CT complexes absorb light. [f] Too low to measure accurately. [g] Assuming $k_{BET} = 3\times10^{11}$ s^{-1} (ref. 3), τ(**1e**$^{\bullet+}$) = 2 × 10^{-10} s.

attribute the nearly fifty fold difference in quantum yields to different rates of back-electron transfer (BET) between (**1a**—**e**$^{\bullet+}$) and TCBQ$^{\bullet-}$ within triplet SSIP and singlet CIP, respectively (Scheme 1).

For TCBQ, separate irradiation of the acceptor and its CT-complexes (Table 1) is possible. Direct irradiation of TCBQ leads to the triplet excited state (TCBQ^3) with a microsecond lifetime.[6,8,10] The rate of ET from (**1a**—**e**) to TCBQ^3 is expected[2,10,11] to be diffusion limited.† Thus, millimolar concentrations of (**1a**—**e**) are sufficient to intercept the majority of TCBQ^3 leading to formation of the triplet TCBQ$^{\bullet-}$/(**1a**—**e**$^{\bullet+}$) as SSIP.[3] Also, all donors used in our study form very similar weak CT-complexes[12] with TCBQ (Table 1). Photon absorption by such species leads to ET beween the donor and acceptor molecules[3,6—8] which, in our case, results in formation[3] of singlet TCBQ$^{\bullet-}$/(**1a**—**e**$^{\bullet+}$) as CIP.

Irradiation of both experimental systems results in the same products. For bis-methoxy derivatives (**1c**—**e**), quantitative yields of the corresponding methyl ethers (**2c**—**e**) and tetrachlorohydrobenzoquinone (TCHQ) are observed. For (**1a**—**b**), in addition to (**2c**) and TCHQ, ethers (**3a**—**c**) are formed.[13] These products are consistent with the fragmentation of (**1a**—**e**$^{\bullet+}$) to yield the corresponding *p*-methoxycumyl cation which is trapped by MeOH, and the X-substituted cumyl radical which is covalently trapped by TCBQ (X = H, Me) or is oxidized by TCBQ (X = MeO). This trend corresponds very well to the redox properties of TCBQ (E_{red} = 0.02 V)[14] and cumyl radicals (*p*-MeO: $E_{ox} = -0.14$; *p*-Me: $E_{ox} = 0.04$; *p*-H: $E_{ox} = 0.16$ V).[15] Additional support for these conclusions may be found in product studies performed under O_2. The radicals are now partially intercepted by oxygen, giving hydroperoxide (**4a**) and alcohols (**5a, c**) from (**1a**) and (**1c**), respectively.

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† The diffusion limited quenching of TCBQ^3 assures that (**1a, b**) will undergo ET with the same rates as (**1c**—**e**), despite the fact that the latter have two anisole moieties per molecule.

The photoefficiencies of the two alternative methods are compared by measuring quantum yields for disappearance of the bicumenes (**1a**—**e**) (Table 1). The measured quantum yields should reflect the relative rates of C–C bond scission (k_f) and back ET (k_{BET}) within the corresponding ion pairs [$k_f/k_{BET} = \Phi/(1 - \Phi)$].

In cases where the diffusional ion separation has rates similar to the fragmentation step, k_f will be a composite of rate constants for both these processes.[3] However, different Φ_Q values for (**1a**—**e**) indicate that the rate of C–C bond scission is the limiting factor. Also substituent and strain effects on Φ_Q are consistent with the trends observed in fragmentation reactions of radical cations.[16] If diffusional separation of ions were a dominant factor, all compounds would have shown very similar quantum yields. To assure that Φ_Q values accurately reflect the rate of C–C bond scission the fragmentation reaction has to be irreversible. This requirement is satisfied by employing a large concentration of MeOH in the reaction medium to trap the cumyl cations. The irreversibility is confirmed in experiments with *meso*-(**1d**). As expected, starting material recovered at 50% conversion shows no isomerization to D,L-(**1d**) (<1%). Under such circumstances relative rates for C–C bond cleavage may be estimated assuming identical k_{BET} for all compounds (Table 1).

The rates of BET are determined mostly by thermodynamics,[‡] and to a smaller degree, by ion pairing. Similar electron reservoirs in (**1a**—**e**) (*i.e.*, the *p*-alkylanisole moiety) assures that the thermodynamic driving force will be essentially the same for all the compounds for both modes of radical ion generation, the small differences in ion solvation notwithstanding.[3] Thus, the differences in BET between the two methods of radical ion generation will be due to differences in ion solvation, interionic distances, and spin multiplicity.[3,17]

Irradiation of TCBQ leads to very efficient reactions indicating that BET and C–C bond fragmentation have comparable rates in this system. In contrast, the quantum yields measured for irradiation of CT complexes (Φ_{CT}) are very small. Assuming that the rate of C–C bond scission is largely independent of the ion pairing, these data imply that k_{BET} is at least[§] 500 times larger in a singlet CIP than in a triplet SSIP. As observed[3,17] by Gould and Farid k_{BET} is larger in the singlet CIP than in the singlet SSIP for $-\Delta G_{BET}$ smaller than *ca.* 2 eV. At $-\Delta G_{BET}$ equivalent to that of our system[¶] (1.65 eV), this difference corresponds[3] to a factor of *ca.* 20. The additional difference must therefore be ascribed to the spin multiplicity differences between the radical ion pairs generated by these alternative methods. Apparently, within the triplet ion pair k_{BET} is limited by the rate of intersystem crossing. These observations agree very well with recent ET theories.[3,17] Thus, BET is more facile for CIP where both the distance between ions and solvent-reorganization energy are smaller than for SSIP. Whether a reversal[3] of this trend will be observed for BET with more negative ΔG remains to be explored.

This research was supported by grants from the NSF and the Link Foundation (Fellowship to W. H. C.). P. M. is a recipient of the Camille and Henry Dreyfus Foundation New Faculty Award.

Note added in proof: a similar study by S. Sankararaman, S. Perrier, and J. K. Kochi has appeared (*J. Am. Chem. Soc.*, 1983, **111**, 6448) after submission of our manuscript.

Received, 24th July 1989; Com. 9/03109J

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[‡] The thermodynamic driving force for BET is obtained from E_{ox} (*p*-methylanisole)$-E_{red}$(TCBQ). See refs. 7 and 16. Also compare ref. 3.

[§] In the CT system the interconversion of singlet CIP to triplet CIP (or SSIP) followed by BET may compete with the fragmentation. Thus, Φ_{CT} may reflect the relative efficiency of the spin flip. The quantum yields measurements were carried out in the absence of magnetic fields, which may influence this process.

[¶] The rates of BET between π-substrates of similar size have similar functional dependence on ΔG (refs. 3, 4, and 17).