

PROTON TRANSFER REACTIONS OF PHOTOGENERATED CYANOAROMATIC- METHYLAROMATIC RADICAL ION PAIRS†

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Abstract—The photochemical reactions of a number of cyanoaromatic (acceptor) and methylaromatic (donor) molecules have been investigated. These reactions can result in the formation of photosubstitution products or benzyl radical coupling products. A survey of our results and previously published data indicates that exergonic photostimulated electron transfer is a necessary but not sufficient condition for the observation of reaction products. The efficiency of proton transfer from the donor cation radical to the acceptor anion radical is determined by the kinetic acidity and basicity of the radical ion pair. Mechanistic evidence is presented which indicates that proton transfer requires diffusion apart and re-encounter of the initially formed radical ion pair. Predominant radical pair combination is observed for anion radicals which yield electron-deficient free radicals upon protonation, whereas predominant cage escape and benzyl radical coupling is observed for anion radicals which yield electron-rich free radicals upon protonation.

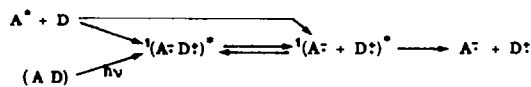
Photoinduced electron transfer between neutral electron donor (D) and acceptor (A) molecules results in the formation of a pair of radical ions, $A^{\cdot -}$ and $D^{\cdot +}$.^{1,2} Radical ion pair formation in polar solvents is exergonic when the electronic excitation energy of the locally excited molecule ($A^* + D^*$) exceeds the sum of the donor oxidation and acceptor reduction potentials.³ The role of radical ion pairs as intermediates in photochemical reactions was first recognized by Guttenplan and Cohen,⁴ who proposed that the photoreduction of triplet benzophenone by amines occurs via initial one-electron transfer, followed by photon transfer from the amine cation radical to the benzophenone anion radical to yield a radical pair. Electron transfer mechanisms have subsequently been proposed for a large number of photochemical reactions, many of which involve subsequent proton transfer steps.⁵

As is the case of classical ion pairs, it is possible to distinguish spectroscopically or chemically between contact radical ion pairs (exciplexes), solvent-separated ion pairs, and free radical ions.⁶ Time-resolved spectroscopic investigations have established that the encounter complex ($A^* + D$) of an electronically excited acceptor molecule and a ground state donor molecule in a polar solvent can directly form either a contact radical ion pair, ${}^1(A^{\cdot -}D^{\cdot +})^*$, or a solvent-separated radical ion pair, ${}^1(A^{\cdot -} + D^{\cdot +})^*$. These radical pairs may interconvert, dissociate to free radical ions (Scheme 1), decay to ground state reactants, or undergo chemical reactions.

Only recently have attempts been made to identify the specific radical ion pair or free radical ion intermediates involved in photochemical reactions. Using

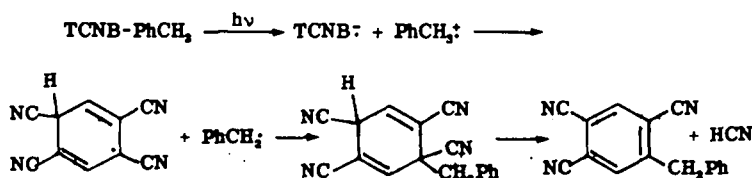
the exciplex fluorescence quenching technique pioneered by Caldwell and Creed,⁷ it has been established that many cycloaddition reactions occur via singlet exciplex intermediates. Mattes and Farid⁸ have demonstrated that electron-transfer sensitized dimerization of certain electron-rich olefins can occur via reaction of the radical ion pair, olefin free cation radical, or olefin triplet with ground state olefin. Recently, Simon and Peters⁹ observed by picosecond absorption spectroscopy that proton transfer from tertiary amine cation radicals to benzophenone anion radicals occurs via the contact radical ion pair and not the solvent separated ion pair. Photochemical kinetic results from this laboratory indicate that proton transfer from amine cation radicals to *trans*-stilbene¹⁰ and cyanophenanthrene¹¹ cation radicals occurs via the contact radical ion pair to yield a radical pair which can either couple or diffuse apart. In contrast, the contact radical ion pair formed from 9-cyanophenanthrene and 2,3-dimethyl-2-butene does not undergo proton transfer, but the free olefin cation radical is deprotonated by solvent to yield an allylic radical which either dimerizes or adds to the anion radical of 9-cyanophenanthrene.¹²

As part of a continuing investigation of the role of exciplex and radical ion intermediates in photochemical reactions,¹³ we have investigated the photochemical reactions of several cyanoaromatic with alkylaromatic molecules. The photophysics of the 1,2,4,5-tetracyanobenzene (TCNB)-alkylbenzene charge-transfer complexes have been investigated in considerable detail, thus providing a basis for the analysis of photochemical results.



Scheme 1. Formation of radical ion pairs and free radical ions.

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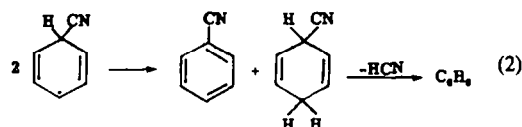
Scheme 2. Ohashi mechanism for photosubstitution.

SCOPE OF THE REACTION OF CYANOAROMATIC WITH METHYLAROMATIC MOLECULES

The photochemical reaction of TCNB in toluene solution was initially investigated by Ohashi and co-workers,¹⁴ who observed the formation of the substitution product 1-benzyl-2,4,5-tricyanobenzene and trace amounts of bibenzyl. On the basis of their mechanistic investigations, the photosubstitution reaction pathway outlined in Scheme 2 was proposed. The two initial steps in this reaction are photostimulated electron transfer followed by proton transfer to yield a radical pair. Coupling of the radical pair yields an adduct which is thermally labile and loses HCN to yield the substitution product. Analogous reactions were observed between TCNB and xylene, mesitylene, halogenated toluenes, and toluonitrile, but not *p*-methoxy- or *p*-aminotoluenes.

We have investigated the photochemical reactions of TCNB, dicyanobenzene (DCNB), and benzonitrile (BN), with several methylated arenes in acetonitrile solution. Irradiation ($\lambda > 300$ nm) of TCNB with toluene, *p*-xylene, mesitylene, durene, and hexamethylbenzene (both reactants 0.03 M in deoxygenated acetonitrile solution) results in the formation of substitution products and only trace amounts of bibenzyls. Similar results were obtained upon irradiation of *p*-DCNB with *p*-xylene or durene at 254 nm. No reaction was observed upon irradiation of TCNB or DCNB with 1-methylnaphthalene or 9-methylantracene. Irradiation of *o*-DCNB with *p*-xylene yielded *ca* 85% substitution and 15% bixylyl

while irradiation of *m*-DCNB with xylene yielded BN and bixylyl but no substitution product. Similarly, irradiation of BN with *p*-xylene, durene, or 1-methylnaphthalene yielded benzene and bibenzyl type products, but no substitution products. Combination of two benzyl radicals (Eq. 1) and disproportionation of two cyanocyclohexadienyl radicals (Eq. 2) can



account for the formation of these products. No reaction was observed upon irradiation of BN with toluene or 9-methylantracene. The results of the chemically productive reactions which we have investigated are summarized in Table 1.

During the course of our investigation, a series of papers by Albini and co-workers¹⁵ on the reactions of cyanonaphthalenes with methylbenzenes has appeared. While the product mixtures obtained in these reactions are complex, electron transfer followed by proton transfer are the proposed initial steps of the reaction mechanism. Substitution and addition product formation is observed upon irradiation of 1,4-dicyanonaphthalene with toluene, xylene, and mesitylene but not with *p*-methoxytoluene. Irradiation of 1- or 2-cyanonaphthalene with durene

Table 1. Product ratios and quantum yields for the reactions of cyanobenzenes with methylbenzenes

Reactants ^a	Substitution (%)	Bibenzyl (%)	Φ^b
TCNB-toluene	100 ^c		0.048
TCNB-xylene	100		0.026
TCNB-mesitylene	100		0.014
TCNB-durene	100		0.007
TCNB-hexamethyl benzene	100		0.002
<i>p</i> -DCNB-toluene	100		0.014
<i>p</i> -DCNB-xylene	100		0.014
<i>p</i> -DCNB-durene	95	5	
<i>o</i> -DCNB-xylene	85	15	
<i>m</i> -DCNB-xylene		100 ^c	0.012
BN-xylene		100	
BN-durene		100	0.012

^a Solution 0.03 M in donor and acceptor in deoxygenated acetonitrile solution irradiated at 313 nm (TCNB) or 254 nm (DCNB, BN).

^b Quantum yields determined at less than 10% conversion of reactants.

^c Less than 5% bibenzyl formation.

^d No photosubstitution product detected.

(but not with lower homologues) results in biduryl formation but no addition or substitution products. We have briefly examined the irradiation of several higher cyanoaromatic molecules (9-cyano- and 9,10-dicyanoanthracene, 9-cyano- and 3,9-dicyanophenanthrene) with durene in deoxygenated acetonitrile solution and failed to detect product formation or reactant consumption.

Ignoring for the moment differences in the reaction products, methylaromatic-cyanoaromatic donor-acceptor pairs can be classified as either reactive or nonreactive. Representative results for five donor methylaromatics and six acceptor cyanoaromatics are given in Table 2. Also given in Table 2 are the singlet energies and redox potentials (measured in acetonitrile solution vs SCE) taken from literature sources and the approximate free energy for electron transfer calculated from the Weller equation (Eq. 3).³ The singlet energy (E_S) used in these calculations is the lower of the donor-acceptor pair

$$\Delta G_{ET} = -E_S - E_{A+}^{red} + E_D^{ox} - 0.06 \text{ eV} \quad (3)$$

values. In all cases where photochemical reactions are observed (upper left and middle sections of Table 2), ΔG_{ET} is exergonic or only slightly endergonic, in accord with the proposal of electron transfer as the initial step in the photochemical reaction mechanism. However, in cases where no photochemical reactions are observed, ΔG_{ET} can be either endergonic (lower left section of Table 2) or exergonic (right section of Table 2). Thus exergonic photostimulated electron transfer is a necessary but not a sufficient condition for electron transfer.

The failure of chemical reactions to occur in cases where electron transfer is exergonic may reflect slow proton transfer vs non-radiative decay of the radical ion pair intermediates. The rate of proton transfer will depend upon the kinetic acidity of the cation radical and basicity of the anion radical. The acidity of methylbenzene cation radicals has been the topic of considerable interest. Recent estimates of the pK_a of toluene cation radical in acetonitrile or dimethyl sulfoxide solution are in the range -10 to -17 .^{16,17} Rate constants for cation radical deprotonation in aqueous solution decrease from $1 \times 10^7 \text{ s}^{-1}$ for toluene to 2×10^4 for pentamethylbenzene.¹⁸ Relative pK_a s for several methylbenzene cation radicals also increase with increasing alkylation.¹⁹ Electron-releasing groups such as methoxy would also be expected to decrease the kinetic acidity of the toluene cation radical. Bausch¹⁷ has estimated pK_a values in dimethyl sulfoxide solution for the cation radicals of toluene (-17), 1-methylnaphthalene (-10), and 9-methylanthracene (-4). Thus both kinetic and equilibrium acidities for the cation radicals of the donors in Table 2 decrease with decreasing donor oxidation potential (increasing cation radical stability).

Less information is available concerning the basicity of cyanoaromatic anion radicals. The conjugate acids of the anion radicals of BN and DCNB are reported to have pK_a values of 7 and ≤ 0 , respectively.²⁰ While kinetic data for protonation of cyanoaromatic anion radicals are not available, rate constants for protonation of unsubstituted aromatic hydrocarbon anion radicals in 2-propanol solution decrease from 6×10^5 for naphthalene to 4×10^2 for tetracene.²¹ Thus both kinetic and equilibrium basicities for the

Table 2. Correlation of the free energy for electron transfer with product formation^a

Acceptor	E_S (eV)	$-E_{1/2}$ (V)	Donor	Toluene	<i>p</i> -Xylene	Durene	1-Methyl-naphthalene	9-Methyl-anthracene
			E_S (eV)	4.6	4.5	4.4	3.9	3.2
			$E_{1/2}$ (V)	2.3	1.9	1.8	1.9	1.5
Tetracyanobenzene	3.8	0.7		-0.9 (+)	-1.3 (+)	-1.4 (+)	-1.3 (-)	-1.0 (-)
<i>p</i> -Dicyanobenzene	4.1	1.6		-0.2 (+)	-0.6 (+)	-0.7 (+)	-0.4 (-)	-0.1 (-)
1,4-Dicyanonaphthalene	3.5	1.3		+0.1 (+)	-0.3 (+)	-0.4 (+)	+0.2 (+)	+0.5 (-)
Benzonitrile	4.5	2.3		+0.1 (-)	-0.3 (+)	-0.4 (+)	0 (+)	0 (+)
1-Cyanoanthracene	3.7	2.0		+0.5 (-)	+0.1 (-)	0 (+)	-0.1 (-)	-0.5 (-)
9,10-Dicyanoanthracene	2.9	0.9		+0.3 (-)	-0.1 (-)	-0.2 (-)	-0.1 (-)	-0.5 (-)

^a Values of ΔG_{ET} calculated using Eq. 3 and the lower E_S value for each donor-acceptor pair. (+) and (-) indicate the occurrence of photochemical reactions or lack thereof.

anion radicals in Table 2 are expected to decrease with decreasing (less negative) acceptor reduction potential (increasing anion radical stability).

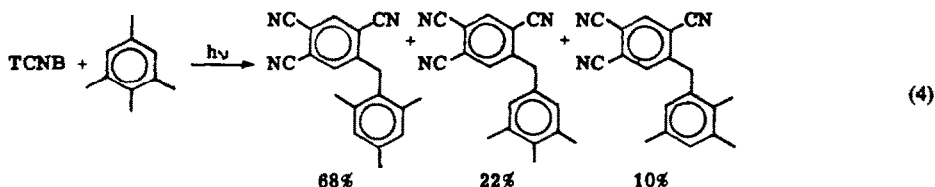
In summary, the observation of product formation upon irradiation of the donor-acceptor pairs in Table 2 is dependent upon both the energetics of electron transfer (Eq. 3) and the kinetics of proton transfer. Highly delocalized acceptors (9,10-dicyanoanthracene) or donors (9-methylanthracene or *p*-methoxytoluene) fail to undergo proton transfer reactions due to their low kinetic basicity or acidity. While proton transfer is not observed in such cases, other radical ion reactions, such as the 9,10-dicyanoanthracene sensitized photooxygenation of toluene,²² can occur.

MECHANISTIC STUDIES

Reaction selectivity and efficiency

In the preceding discussion, we have assumed that the reactions of cyanoaromatics and methylaromatics proceed via photostimulated electron transfer followed by proton transfer from the cation radical to the anion radical, as initially proposed by Ohashi and co-workers.¹⁴ Such reactions are known to display small deuterium isotope effects on both reaction kinetics and product quantum yields.¹¹ Due to ground state complexation, standard Stern-Volmer kinetic analysis is not possible for the donor-acceptor systems under investigation. We have measured a quantum yield ratio $\Phi_H/\Phi_D = 1.5$ for photosubstitution from the TCNB-xylene vs xylene-*d*₁₀ system. Such a small isotope effect is more consistent with quantum yield-determining proton vs hydrogen atom transfer.¹¹ However, since xylene deuteration is known to increase the lifetime and fluorescence quantum yield of the TCNB-xylene system in the vapor phase,²³ the observed isotope effect cannot be simply interpreted.

Baciocchi *et al.*²⁴ have proposed the use of isodurene (1,2,3,5-tetramethylbenzene) oxidation as a chemical probe for electron transfer-proton transfer vs hydrogen atom abstraction from methylbenzenes. They report a reactivity order ${}^2\text{CH}_3 > {}^3\text{CH}_3 > {}^{13}\text{CH}_3$ for chemical oxidation with one-electron oxidants (Ce(IV), Mn(III), Co(III)), and a reactivity order ${}^2\text{CH}_3 > {}^{13}\text{CH}_3 > {}^3\text{CH}_3$ for bromination with NBS. Relative reactivity is controlled by charge distribution (kinetic acidity) in the former reactions and free radical stability in the latter. We have investigated the reaction of TCNB with isodurene and observe the formation of three substitution products (Eq. 4). The



order of methyl group oxidation selectivity is the same as that for chemical one-electron oxidants, thus supporting an electron transfer-proton transfer mechanism.

Quantum yields for product formation from several of the donor-acceptor systems that we have investigated are reported in Table 1. The measured values

Table 3. Concentration dependence of quantum yields for product formation^a

Acceptor, M	Donor, M	Φ
TCNB, 0.03	Mesitylene, 0.03	0.014
		0.06
		0.12
		0.03
		0.03
BN 0.03	Durene, 0.03	0.012
		0.06
		0.15
		0.30
		0.03

^aSee footnotes to Table 1 for conditions for quantum yield measurement.

are uniformly low (0.002–0.048), as is the value reported by Ohashi and Nakayama^{14c} for the reaction of TCNB in toluene solvent (0.024) and the limiting quantum yields for reaction of 1,4-dicyanonaphthalene with toluene, mesitylene, and durene (0.03–0.07) reported by Albini *et al.*^{15b} Quantum yields for photosubstitution from the TCNB-mesitylene system and biduryl formation from the BN-durene system increase modestly with increasing donor concentration but not acceptor concentration (Table 3). Since the acceptors absorb more strongly than the donors at the excitation wavelengths, the concentration dependence may reflect more efficient quenching of the locally excited acceptor by ground state donor. Light absorption by weak ground state complexes may also be responsible for product formation.²⁵ Uncertainty concerning the light-absorbing species precludes kinetic analysis of the quantum yield data.

Quantum yields for substitution product formation from TCNB-methylbenzene systems (Table 1) decrease with decreasing donor ionization potential (Table 2). As discussed in the preceding section, this trend can be explained by decreasing cation radical acidity with increasing methylation. Quantum yields for ionic photodissociation of the weak ground state complexes of TCNB with a number of donors in acetonitrile solution have been determined by Mataga and co-workers.²⁶ Their results for several methylbenzenes and 1-methylnaphthalene are shown in Fig. 1 along with our quantum yield data plotted vs donor oxidation potential. The observed decrease in ionic

photodissociation yield with decreasing donor oxidation potential is attributed to an increase in the rate of radical ion pair decay to the ground state.²⁷ The latter process is subject to an energy gap law, as predicted by the Marcus equation. The observed parallel between quantum yields for ionic photodissociation and photosubstitution (Fig. 1) suggests that the two

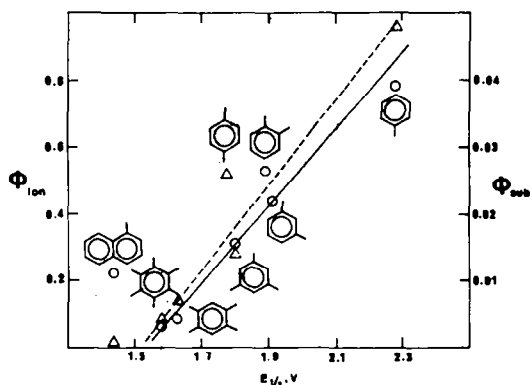


Fig. 1. Quantum yields for ionic photodissociation (O) and photosubstitution (Δ) of TCNB vs donor oxidation potential.

processes are related either by having a common precursor (radical ion pair) or by free radical ions serving as the precursor for product formation. Decreases in both photodissociation yield and cation radical acidity with decreasing donor oxidation potential may account for the smaller slope for photosubstitution vs photodissociation data in Fig. 1.

A significant exception to the parallel between ionic photodissociation and photosubstitution (Fig. 1) is provided by the TCNB-1-methylnaphthylene system. The observation of moderately efficient ionic photodissociation is in accord with exergonic electron transfer (Table 2). Thus the failure to observe photosubstitution must be due to the low kinetic acidity of the 1-methylnaphthalene cation radical rather than rapid ion pair decay to the ground state.

Solvent polarity dependence

Picosecond time-resolved spectroscopy of TCNB in toluene solution indicates that the initially formed Franck-Condon excited state of the TCNB-toluene donor-acceptor complex undergoes reorientational relaxation with a time constant of *ca* 5 ps to form a fluorescent contact radical ion pair.²⁸ Increasing solvent polarity results in a decrease in the fluorescence intensity and lifetime of the contact radical ion pair from 1.9 ns in dichloroethane to 320 ps in acetonitrile solution.²⁹ This decrease in lifetime is accompanied by an increase in the quantum yield for ionic photodissociation as shown in Fig. 2.^{6,30} Both the rate of solvation of the contact radical ion pair to yield a solvent-separated radical ion pair and the rate of diffusion of A^- and D^+ beyond the Coulomb radius are expected to increase with increasing solvent polarity. The latter process is apparently insensitive to the nature of A^- and D^+ having a value of *ca* $5 \times 10^8 \text{ s}^{-1}$ for numerous radical ion pairs in acetonitrile solution.⁵⁶

Increasing solvent polarity also results in an increase in the quantum yields for photosubstitution. Our results for photosubstitution in the TCNB-mesitylene system in mixed ethyl acetate-acetonitrile solution are compared to those of Mataga and co-workers.^{6,30} for ionic photodissociation of the TCNB-toluene system in Fig. 2. The observed similarities in these plots provide additional evidence of the formation of substitution products via either free radical

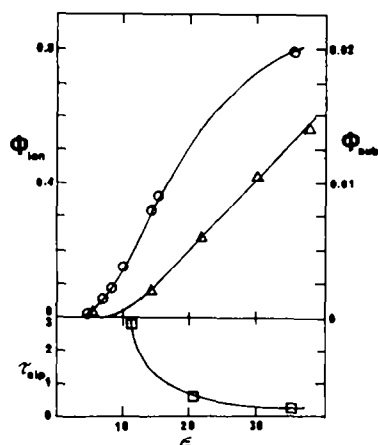


Fig. 2. Solvent polarity dependence of the quantum yields for ionic photodissociation from TCNB-toluene (O), photosubstitution from TCNB-mesitylene (Δ), and TCNB-toluene contact radical ion pair lifetimes (\square).

ions or their precursors, the contact or solvent-separated radical ion pairs. Formation of products directly from the contact radical ion pair state would require a marked increase in the rate of reaction with solvent polarity in order to compensate for the decrease in contact radical ion pair lifetime (Fig. 2). The solvent dependence for the quantum yield of product formation from the DCNB-xylene systems and BN-durene systems is shown in Fig. 3. The results for the former system in mixed ethyl acetate-acetonitrile are similar to those for the TCNB-mesitylene system (Fig. 2). The quantum yield measured in pure propionitrile solution falls below the line for mixed solvents, indicating that dielectric constant may not provide the only relevant solvent parameter. No reaction is observed upon irradiation of the DCNB-xylene system in dimethyl sulfoxide solution ($\epsilon = 46.7$). Since this solvent is more readily oxidized (*ca* $E_{1/2} = 1.5 \text{ V}$)

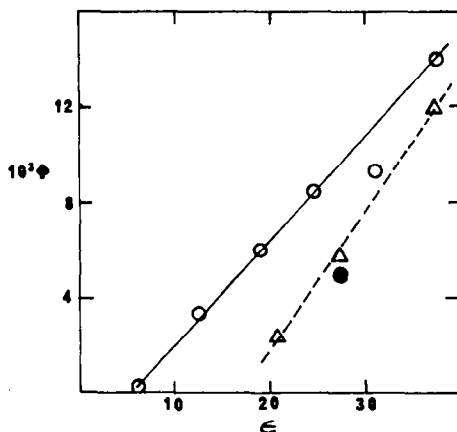


Fig. 3. Solvent polarity dependence of the quantum yield for photosubstitution from DCNB-xylene in ethyl acetate-acetonitrile mixed solvents (O) and in propionitrile (●) and for biduryl formation from BN-durene in nitrile solvents (Δ).

than xylene, reduction of the xylene cation radical by solvent should occur and thus preclude proton transfer to DCNB⁻. The quantum yields for biduryl formation from BN-durene measured in acetonitrile, propionitrile, and isobutyronitrile solution also increase with increasing solvent polarity, suggestive of a reaction mechanism related to that for photosubstitution.

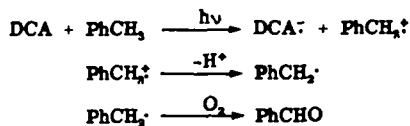
Oxygen and salt dependence

Irradiation of the donor-acceptor systems in Table 1 in the presence of O₂ (1 atm) results in complete inhibition of substitution or bibenzyl formation. In the case of the DCNB-toluene system, irradiation in the presence of oxygen results in the oxidation of toluene to benzaldehyde without consumption of DCNB. The quantum yield for benzaldehyde formation is 0.052, somewhat larger than the value for photosubstitution in the absence of oxygen.

Saito *et al.*²² have previously reported that irradiation of dicyanoanthracene (DCA) with alkylbenzenes in the presence of oxygen results in selective oxidation of the alkyl side chain without consumption of DCA. They proposed that photooxygenation occurs via photostimulated electron transfer from the alkylbenzene to DCA to form a radical ion pair. Deprotonation of the alkylbenzene cation radical (possibly by superoxide ion) yields a benzyl radical which undergoes classical free-radical chain auto-oxidation (Scheme 3). We assume that the DCA and DCNB sensitized photooxygenation of alkylbenzenes occur via analogous mechanisms.[†]

The effect of O₂ on the formation of TCNB⁻ from the TCNB-toluene systems in acetonitrile solution has been investigated by Mataga and co-workers.²² They report an accelerated rate of decay, presumably due to electron transfer from TCNB⁻ to O₂. However, the initial yield of TCNB⁻ is essentially the same in oxygenated vs degassed solutions. Thus oxygen apparently does not inhibit photosubstitution by intercepting the contact or solvent-separated radical ion pairs prior to ionic dissociation. By a process of elimination, oxygen inhibition of photosubstitution must result from the reaction of oxygen either with free radical ions or with the free radical intermediates formed by proton transfer in radical ion pairs prior to cage escape or radical pair combination (Scheme 2).

Addition of the salt NaClO₄ to acetonitrile solutions of the donor-acceptor systems in Table 1 causes a decrease in the quantum yield of substitution and bibenzyl products. Typical results are shown in Fig. 4 for the effect of salt concentration on the quantum yield of substitution from the DCNB-toluene system and biduryl formation from the BN-durene system. A large decrease in quantum yield is observed upon addition of less than 0.1 M NaClO₄, but little further decrease is observed at higher salt concentrations. In contrast to the effect of salt upon photosubstitution, quantum yields for DCNB-sensitized photooxygenation of toluene increase with added salt concentration (Fig. 4).



Scheme 3. Saito mechanism for photooxygenation.

Added salts are known to both increase the yield of radical ion pair dissociation via ion pair exchange and to prolong the lifetime of free radical ions by slowing down the rate for homogeneous back electron transfer.³³ Added perchlorate salts increase the quantum yields for cation radical chain isomerization of hexamethyl (Dewar benzene)¹⁴ and Z-stilbene,¹⁵ reactions which occur via the free cation radicals. It is important to note that added NaClO₄ increases the quantum yield for DCNB sensitized photooxygenation of toluene (Fig. 4), but decreases the quantum yield for DCA sensitized photooxygenation of Z-stilbene.³⁵ Saito *et al.*²² have suggested that the free radical chain auto-oxidation of toluene (Scheme 3) is terminated by electron transfer from DCA⁻ to peroxy radicals. Ion pairing of Na⁺DCA⁻ should slow down the rate of electron transfer and hence increase the quantum yield for photooxygenation. In contrast, the photooxygenation of stilbene is a non-chain process which requires the reduction of O₂ by DCA⁻.³⁵ Ion pairing of Na⁺DCA⁻ should inhibit reduction of O₂ and hence decrease the yield of stilbene photooxygenation. Use of Bu₄NBF₄ in place of NaClO₄ results in an increase in the yield of stilbene photooxygenation in dimethoxyethane solution,³⁶ presumably due to the small equilibrium constant for DCA⁻ ion pairing with Bu₄N⁺.

The decrease in the quantum yields for product formation from the DCNB-toluene and BN-durene systems with added salt (Fig. 4) could result from either an increased rate of radical ion pair dissociation or a decreased rate of reaction of the free radical ions. If product formation occurred via proton transfer

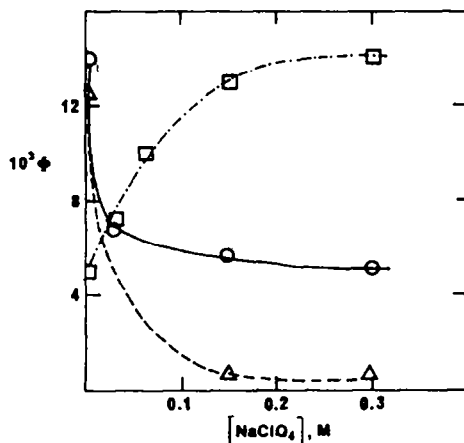


Fig. 4. Salt concentration dependence of the quantum yield for photosubstitution from DCNB-xylene (O), biduryl formation from BN-durene (Δ), and benzaldehyde from DCNB-toluene photooxygenation (□).

[†]Acetone-sensitized photooxygenation of alkylbenzenes has also been reported.³¹

in a contact or solvent-separated radical ion pair (Scheme 2), then salt acceleration of ionic photodissociation could account for the decrease in yield. Alternatively, if product formation occurred predominantly upon homogeneous reencounter of free radical ions, Na^+DCNB^- ion pairing could account for the decrease in product formation. The lower plateau value for BN vs DCNB may reflect stronger ion pairing for the more localized anion radical.

Brønsted acid dependence

Ohashi and Nakayama^{14c} observed that both photo-substitution and contact radical ion pair fluorescence from TCNB in toluene solution were quenched by added trifluoroacetic acid (TFA). While they interpreted this as evidence for product formation from the fluorescent contact radical ion pair state, their observation is also consistent with product formation from a solvent separated ion pair formed via the fluorescent state. Albini *et al.*^{15b} have reported that TFA inhibits the normal photoreactions of 1,4-dicyanonaphthalene with toluene and yields instead 1,2-dihydrodicyanonaphthalene, presumably via protonation of the anion radical. While the mechanism of fluorescence and product quenching by TFA is unknown, TFA is known to stabilize aromatic hydrocarbon cation radicals generated electrochemically^{37a} and may serve to prevent their deprotonations. TFA has recently been reported to form hydrogen bonds with cyanoaromatic molecules.^{37b} Ground state hydrogen bonding could account for fluorescence quenching, the absence of bimolecular photochemical reactions, and the reduction of 1,4-dicyanonaphthalene.

We have investigated the effects of the Brønsted acids TFA, trifluoroethanol (TFE), and water on the photochemical reactions of the DCNB-xylene and BN-durene systems in acetonitrile solution. The results of this investigation are shown in Fig. 5. The

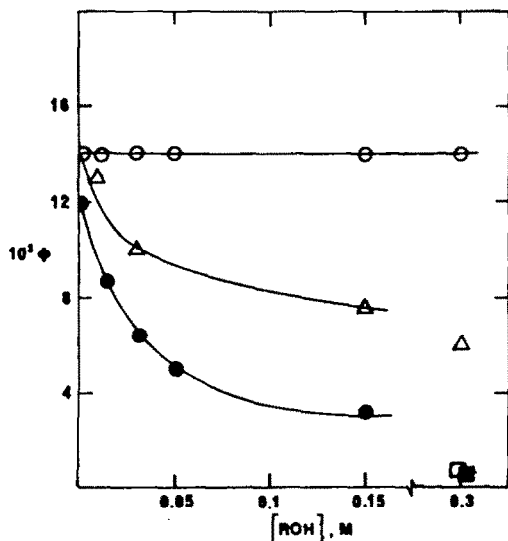


Fig. 5. Brønsted acid concentration dependence of the photosubstitution reaction of DCNB-xylene with H_2O (○), $\text{CF}_3\text{CH}_2\text{OH}$ (△), and $\text{CF}_3\text{CO}_2\text{H}$ (□) and biduryl formation from BN-durene with H_2O (●) and $\text{CF}_3\text{CO}_2\text{H}$ (■).

quantum yield for photosubstitution is independent of the concentration of water (≤ 0.3 M), decreases with increasing TFE concentration, and is largely quenched by 0.3 M TFA. Thus the quenching ability of the added acid appears to be determined by its acidity. The quantum yields for biduryl formation from the BN-durene system decrease with added water as well as TFA. The greater sensitivity of this system toward the weak acid water may reflect the greater base strength of the BN vs DCNB anion radical²⁰ which could result in its protonation by a weaker acid. Alternatively, the more localized BN anion radical may be more strongly solvated by water thus diminishing its reactivity as in the case of ion pairing with Na^+ .

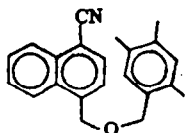
Addition of water has been found to increase the quantum yield of some radical ion pair proton transfer processes including the reaction of DCN with toluene.^{15b,38} The effect of water in these reactions is attributed to catalysis of the proton transfer process. The absence of catalysis by water of the present and related reactions¹⁰⁻¹³ is indicative of direct proton transfer from the cation radical to the anion radical.

Summary of proton transfer probes

In the preceding sections the effects of several chemical probes (solvent polarity, oxygen, NaClO_4 , and Brønsted acids) upon the quantum yields for product formation from cyanobenzene-methylbenzene systems are described. While no one of these probes provides definitive evidence for a specific ion pair intermediate in the proton transfer we believe that the bulk of the evidence favors the formation of products upon homogeneous reencounter of free radical ions rather than via the initially formed contact or solvent-separated radical ion pairs. Such a mechanism most economically accounts for (a) the parallel dependence of quantum yields for photosubstitution and ionic photodissociation upon donor oxidation potential (Fig. 1) and solvent polarity (Fig. 2), (b) total inhibition of product formation but not TCNB anion radical formation by O_2 , (c) the inverse but complementary effect of added NaClO_4 on photosubstitution and photooxygenation, and (d) the effects of Brønsted acids on product formation.

The proposal of proton transfer via homogeneous reencounter of free radical ions stands in marked contrast to our earlier proposals that proton transfer from aliphatic amine cation radicals to stilbene¹⁰ or 9-cyanophenanthrene¹¹ anion radicals occurs via the initially formed contact radical ion pairs. These reactions are significantly less sensitive to external perturbation (e.g. by O_2 , NaClO_4 , Brønsted acids) than are the reactions of cyanobenzenes with methylbenzenes. Proton transfer in the contact radical ion pair may be geometrically unfavorable due to the face-to-face geometry of the donor and acceptor. In accord with this proposal, Albini and Spreti^{15c} report that the linked donor-acceptor complex shown below forms a fluorescent exciplex, but fails to undergo photochemical reactions in acetonitrile solution. Diffusion apart allows reencounter of the donor cation radical methyl hydrogens with the face of the acceptor anion radical. The low probability of such an encounter may contribute to the lower quantum yields for photosubstitution vs ionic photodissocia-

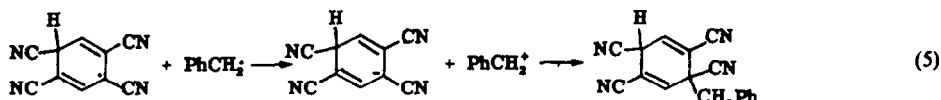
tion (Figs 1 and 2) or photooxygenation (Fig. 4). Spin statistics dictate that homogeneous reencounter of radical ions favors formation of the triplet radical ion pair which may react with greater efficiency than the initially formed singlet radical ion pair due to its slower rate of decay to ground state reactants.¹



Fate of the radical pair.

Irradiation of cyanobenzenes (Table 1) or naphthalenes¹⁵ with methylbenzenes results in the formation of substitution and/or bibenzyl type products (Table 1). In the preceding sections we have presented evidence that these two modes of reaction are mechanistically related, both arising from a radical pair which results from photostimulated electron transfer followed by proton transfer (Scheme 2). Assuming that this is in fact the case, the question remains as to why TCNB, *p*-DCNB, *o*-DCNB and dicyanonaphthalene^{15a} predominantly undergo photo-substitution and *m*-DCNB, BN, and 1- or 2-cyanonaphthalene^{15a} undergo bibenzyl formation. This divergence of chemical behavior indicates that the radical pairs formed in the former reactions undergo in-cage combination to the exclusion of cage escape, while the radical pairs formed in the latter reaction do not combine but undergo cage escape followed by benzyl radical coupling and hexadienyl radical disproportionation. (Eqs 1 and 2).

A possible clue to this divergence of chemical behavior is provided by a survey of the photochemical literature for other reactions of toluene which yield radical pairs. The radical pair intermediates and their chemical behavior for several such reactions are summarized in Table 4. These reactions are organized into two categories, those that yield predominantly radical pair combination products³⁹⁻⁴¹ and those that yield bibenzyl.^{14a,42,43} Those radical pairs in the former category all have one or more strongly electron-withdrawing cyano or carbonyl groups attached to the radical center of the second (nonbenzyl) radical, while those in the latter category have electron donating phenyl and hydroxy or amino groups. Evidently, benzyl radicals are more likely to combine with an electron-deficient than an electron-rich radical. This preference may reflect either a donor-acceptor interaction within the radical pair or full electron transfer to yield an ion pair which is held together by coulombic attraction, as shown in Eq. 5 for the TCNB-toluene system. In the absence of a strong donor-acceptor



interaction the radicals diffuse apart and benzyl radicals combine to form bibenzyls and cyclohexadienyl radicals disproportionate. Electron transfer between neutral radicals and biradicals to yield ion pair⁴⁴ and zwitterionic intermediates,⁴⁵ respectively, has previously been proposed; such mechanisms remain uncommon.

The occurrence of toluene photosubstitution with *o*- and *p*-DCNB but not *m*-DCNB finds precedent in the reactions of triethylamine⁴⁶ and 2,3-dimethyl-2-butene⁴⁷ with the dicyanobenzenes. The observation of bibenzyl and BN formation from *m*-DCNB-toluene suggests that radical ion pair formation followed by proton transfer occurs for *m*-DCNB as well as its isomers. A likely difference between the *o,p*- vs *m*-isomers lies in the locus of anion radical protonation. We assume that the anion radicals of *o*- and *p*-DCNB and TCNB (Scheme 2) are protonated at C₁, the position of highest π -spin density,⁴⁸ to yield cyclohexadienyl radicals stabilized by cyano substituents at the 1 or 3 positions. Radical coupling yields an adduct which can undergo thermal 1,2- or 1,4-elimination of HCN to yield the substitution product. In the case of *m*-DCNB or BN protonation of the anion radical at C₁ (Eq. 2) would not lead to the formation of a cyano-stabilized, electron-deficient radical and hence the radical pair might diffuse rather than couple. Alternatively, the *m*-DCNB and BN anion radicals may undergo protonation at C₄ (the position of highest π -spin density⁴⁸) or on the cyano nitrogen to yield radicals of substantially different character. Nitrile protonation has previously been suggested for the reactions of 1,3,5-tricyanobenzene with isobutyronitrile⁴⁹ and BN and 1-CN with diethylamine.⁵⁰ Unfortunately, the spontaneous loss of HCN from both addition and reduction products prevents experimental determination of the original locus of protonation.

EXPERIMENTAL

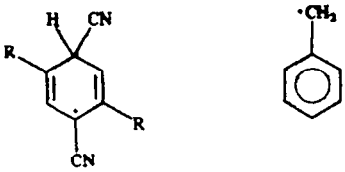
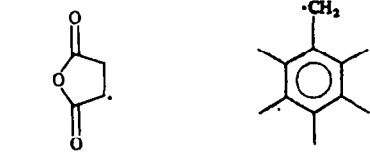
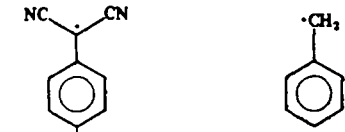
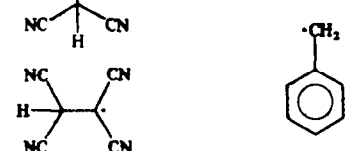
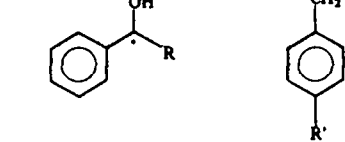
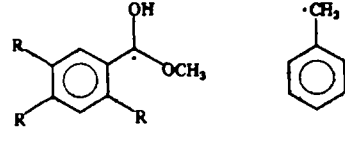
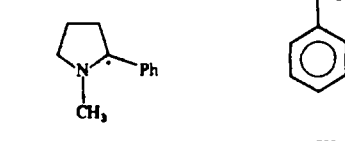
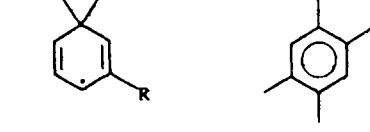
Materials. Arenecarbonitriles and methylarenes were commercial samples (Aldrich, Milwaukee, Wisconsin, or Pfaltz and Bauer, Stamford, Connecticut) and were purified by recrystallization or distillation prior to use. 1,2,3,5-Tetramethylbenzene was synthesized by the method of Baciocchi *et al.*⁵⁴ Solvents were spectrograde (Burdick and Jackson, Muskegon, Michigan, or Aldrich) and were dried by standard procedures and distilled under N₂ immediately prior to use. Trifluoroethanol and trifluoroacetic acid (Aldrich) were distilled prior to use.

General procedures. Quantum yield measurements were conducted on vacuum line degassed or N₂ purged solns of reactants and n-alkane internal standard contained in 13 mm o.d. Pyrex or quartz ampules. Samples were irradiated at 254 nm using a Rayonet PRP-100 Photochemical Reactor with dimethyluracil actinometry⁵¹ or at 313 nm with the potassium chromate-filtered output of a Hanovia 450 W medium pressure mercury lamp with *E*-stilbene actinometry.⁵² Irradiated samples were analyzed by gas chromatography using a 6 or 11 ft \times 1/8 in packed column containing 5% SF96 on Chromasorb G with a Varian 3700 flame ionization gas chromatograph interfaced with a Hewlett-Packard 3390A integrator-recorder. Product concentrations were deter-

mined by calibration of chromatograph response for authentic or isolated samples vs n-alkane internal standards.

Reaction products were isolated from preparative reactions by HPLC or flash chromatography on silica gel. Structures were assigned on the basis of spectroscopic data obtained using a Varian EM360 or CFT20 NMR spectrometer, a Perkin-Elmer R83 IR spectrometer, and a Hewlett-Packard 5985A gas chromatograph-mass spectrometer

Table 4. Behavior of radical pairs derived photochemically from toluene

Radical pair		Reaction	Reference
	R = CN or H	Combination	14 this work
		Combination	39
		Combination	40
		Combination	41
	R = CH ₃ or CF ₃ R = CH(CH ₃) ₂	Combination and bibenzyl	42
	R = CO ₂ CH ₃	Bibenzyl	14
		Combination and bibenzyl	43
	R = CN or H	Bibenzyl	this work

system using an ionizing voltage of 70 eV. Spectral properties of the substitution products of TCNB with toluene, xylene, and mesitylene are in agreement with those reported by Ohashi and co-workers.^{14b} Product purity was confirmed by elemental analysis.

Irradiation of TCNB and isodurene. Isodurene (1.04 g, 0.044 M) and TCNB (1.26 g, 0.048 M) were added to 175 ml of acetonitrile in a preparative reaction well. The yellow mixture was degassed by bubbling with N₂ for 20 min before irradiation and throughout the entire irradiation period. The soln was irradiated with a 450 W Hanovia lamp through a Vycor lamp well. Total irradiation time was 65 min. The

photoreaction's progress was monitored by GC and the irradiation was stopped when the area of primary photo-products relative to the area of internal standard decreased. Relative yields of the three products with *m/e* = 285, based on integrated GC peak areas, are 68.3, 9.6, and 22.1%. These products were separated using HPLC (50% CH₂Cl₂-50% hexane). Fraction 1: 5-(2,4,6-trimethylbenzyl)-1,2,4-benzenetricarbonitrile, ¹H-NMR (CDCl₃, δ 2.12 (s, 6H), 2.32 (s, 3H), 4.26 (s, 2H), 6.95 (s, 2H), 7.12 (s, 1H), 8.06 (s, 1H); IR (CH₂Cl₂ soln) 2229, 1612, 1607, 1485, 853 cm⁻¹; *m/e* 285 (M⁺). (Found: C, 79.6; H, 14.79; N, 5.617. Calc for C₁₉H₁₅N₃: C, 80.01; H, 14.73; N, 5.26%.) Fraction 2: 5-

(2,3,5-trimethylbenzyl)-1,2,4-benzenetricarbonitrile, *m/e* 285 (M^+). Fraction 3: 5-(3,4,5-trimethylbenzyl)-1,2,4-benzenetricarbonitrile, $^1\text{H-NMR}$ (CDCl_3) δ 2.09 (s, 3H), 2.2 (s, 6H), 4.1 (s, 2H), 6.75 (s, 2H), 7.56 (s, 1H), 7.95 (s, 1H); IR (CH_2Cl_2 soln) 2241, 1618, 1603, 1466, 807 cm^{-1} ; *m/e* 285 (M^+).

Irradiation of p-DCNB and p-xylene. A soln of p-xylene (0.70 g, 0.038 M) and p-DCNB (8.85 g, 0.038 M) in 175 ml acetonitrile was irradiated for 50 min with a 450 W Hanovia lamp through a Vycor lamp well. The reaction was purged with prepurified N_2 for 20 min before irradiation and continually purged during irradiation. Removal of the volatile material followed by flash chromatography (separation on silica gel with 60% hexane-40% CH_2Cl_2) afforded a pure sample of 4-(4-methylbenzyl)benzonitrile, (0.1294 g, 9.5%, m.p. = 65°); $^1\text{H-NMR}$ (CDCl_3) δ 2.23 (s, 3H), 2.90 (s, 2H), 6.96 (s, 4H), 7.13 (d, J = 6 Hz, 2H), 7.43 (d, J = 8 Hz, 2H); IR (CH_2Cl_2 soln) 3020, 2950, 2220, 1600, 1440 cm^{-1} ; *m/e* 207 (M^+). (Found: C, 87.10; H, 6.5; N, 6.70; Calc for $\text{C}_{15}\text{H}_{13}\text{N}$: C, 86.97; H, 6.28; N, 6.75%.)

Irradiation of benzonitrile and durene. A soln of durene (1.00 g, 0.0427 M) and benzonitrile (0.77 g, 0.0428 M) in 175 ml acetonitrile was irradiated for 110 min with a 450 W Hanovia lamp through a Vycor well. The mixture was purged with prepurified N_2 for 20 min before irradiation and continually purged during irradiation. Removal of the volatile material followed by flash chromatography (separation on silica gel with 50% CH_2Cl_2 -50% hexane) afforded a pure sample of bis(2,4,5-trimethylphenyl)ethane (0.4578 g, 23%, m.p. = 136°); $^1\text{H-NMR}$ (CDCl_3) δ 2.19 (s, 18H), 2.7 (s, 4H), 6.9 (s, 4H); IR (CH_2Cl_2 soln) 3010, 2920, 1600, 1440, 880 cm^{-1} ; *m/e* 266 (M^+). (Found: C, 90.12; H, 9.58. Calc for $\text{C}_{20}\text{H}_{26}$: C, 90.23; H, 9.77%.)

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