Proton-Transfer Reactions of Photogenerated Radical Ion Pairs

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During the past decade it has become increasingly evident that single-electron transfer plays an important role in many bimolecular reactions.[1,2] This is particulary true for bimolecular photochemical reactions, owing to the decrease in molecular ionization potential and increase in electron affinity that occurs upon electronic excitation.

Interaction of an excited-electron acceptor (A*) with a ground-state donor (D) can result in either partial charge transfer (exciplex formation) or single-electron transfer (radical ion pair formation), depending upon on the nature of the donor and acceptor and the solvent polarity.[3] In general, single-electron transfer is expected to occur when calculated to be exergonic using Weller's equation (eq 1) where $^1E^*$ is the singlet energy

$$\Delta G_{ET} = {}^1E^* - (E_D^{ox} - E_A^{red}) - \frac{e_o^2}{\epsilon a} \quad (1)$$

of the electronically excited donor or acceptor, E_D^{ox} and E_A^{red} are the donor oxidation potential and acceptor reduction potential, and the last term is the free energy gained when separated radical ions are brought to the encounter distance, a, in a solvent of dielectric constant ϵ.[4] Exciplex formation can occur even when electron transfer is endergonic either by virtue of unfavorable redox potentials or low solvent dielectric constant.

A previous Account of research from this laboratory described the addition reactions of singlet (*E*)-stilbene with a number of alkenes, dienes, and aliphatic amines.[5,6] The [2 + 2] cycloaddition reactions of stilbene with electron-rich and electron-poor alkenes were shown to occur via singlet exciplex intermediates (eq 2), while the addition of tertiary amines was pro-

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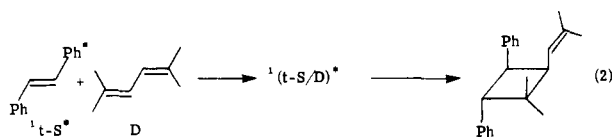
posed to occur via single-electron transfer followed by proton transfer from the amine cation radical to the stilbene anion radical, to yield a radical pair, which ultimately combines to yield the stilbene–amine adduct (eq 3). We and others have found that proton transfer

(3)
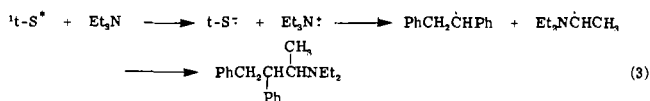
is one of the more common reactions of photogenerated radical ion pairs, having been observed for a variety of

excited electron acceptors with ground-electron-state donors including amines, methylarenes, alkenes, and dienes.[1,2] Since these donors and acceptors are very weak acids and bases in the ground state, a remarkable increase in kinetic acidity and basicity must occur upon single-electron transfer.

The limited evidence currently available indicates that organic cation radicals may be exceptionally strong acids and anion radicals strong bases. For example, Fessenden and Neta[7] have measured a p$K_{HA}{}^{\bullet+}$ of ca. 7 for $Me_2NH^{\bullet+}$ and Nicholas and Arnold[8] have estimated a value of −11 for $PhCH_3{}^{\bullet+}$ using a thermodynamic cycle. Bordwell and Bausch[9] recently reported that the pK_{HA}S of fluorene and its cation radical are 22.6 and −16, respectively, corresponding to an increase of 39 pK_a units upon oxidation. Rate constants of proton transfer from permethylbenzene cation radicals to pyridine bases as high as 2×10^7 M^{-1} s^{-1} have been reported by Schlesener, Amatore, and Kochi,[10] thus indicating that cation radical C–H acids possess high kinetic as well as equilibrium acidities. Rate constants as high as 6×10^5 M^{-1} s^{-1} have been reported for protonation of aromatic hydrocarbon anion radicals by 2-propanol.[11] Since amine and methylarene cation radicals are far more acidic than 2-propanol, significantly faster proton-transfer rates may be anticipated for radical ion pairs. In fact, Schaefer and Peters[12] report that proton transfer in the benzophenone–triethylamine radical ion pair occurs with a half-life of 15 ± 5 ps.

As part of a continuing study of the chemical behavior of exciplexes and radical ion pairs, the proton-transfer reactions of several classes of cation radicals have been investigated. We report here on the timing of the proton-transfer process and structure–activity relationships for several cation radical proton-transfer reactions.

Amine Cation Radicals. The original proposal of a sequential electron-transfer, proton-transfer mecha-

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(4) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968,** *72,* 257.

(5) Lewis, F. D. *Acc. Chem. Res.* **1979,** *12,* 152.

(6) For a recent review of the bimolecular photochemical reactions of stilbenes, see ref 2c.

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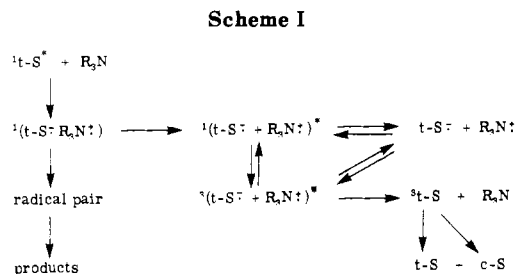(8) Nicholas, A. M. deP.; Arnold, D. R. *Can. J. Chem.* **1982,** *60,* 2165.

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Scheme I

^{1}t-S* + R$_3$N

↓

^{1}(t-S⁻ R$_3$N⁺) ⟶ ^{1}(t-S⁻ + R$_3$N⁺)* ⇌ t-S⁻ + R$_3$N⁺

↓   ↕

radical pair ^{3}(t-S⁻ + R$_3$N⁺)* ⟶ ^{3}t-S + R$_3$N

↓   ↓

products   t-S ⟶ c-S

Scheme II

PhCH=CHPh* + Me$_2$N̈CH$_2$R

↓ MeCN

PhCH=CHPh⁻• + Me$_2$N⁺CH$_2$R

↙ path a   ↘ path b

PhCH$_2$ĊHPh + ĊH$_2$NMeCH$_2$R   PhCH$_2$ĊHPh + Me$_2$NĊHR

↓   ↓

Ph Me
| |
PhCH$_2$CHCH$_2$NCH$_2$R   Ph
|
a   PhCH$_2$CHCHNMe$_2$
                                             |
                                             R

                                             b

nism for stilbene–amine addition (eq 2) was based upon the effect of solvent upon addition efficiency.[13] In nonpolar solvents, singlet *trans*-stilbene forms fluorescent, nonreactive exciplexes with tertiary amines.[14] As the solvent polarity is increased, the exciplex fluorescence intensity decreases and adduct formation efficiency increases. Conclusive evidence for the occurrence of single-electron transfer in polar solvent was provided by the observation of the stilbene anion radical by time-resolved resonance Raman spectroscopy.[15] Using a combination of steady-state and kinetic spectroscopy techniques, it was possible to establish that proton transfer occurs via the initially formed contact radical ion pair, ^{1}(t-S⁻·R$_3$N⁺)*. The longer lived solvent-separated radical ion pair, ^{1}(t-S⁻ + R$_3$N⁺)*, and free-radical ions do not undergo proton transfer reactions but rather decay via back electron transfer, yielding triplet *trans*-stilbene which decays to a mixture of *cis*- and *trans*-stilbene (Scheme I). Evidently, solvation decreases the kinetic acidity of the amine cation radical and prevents its deprotonation by either solvated stilbene anion radicals or neutral amine, which is present in high concentration. The occurrence of proton transfer within the short-lived contact radical ion pair explains the insensitivity of stilbene–amine addition reactions to radical ion scavengers such as oxygen or proton-transfer catalysts such as water (vide infra).

In accord with the sequential electron-transfer, proton-transfer mechanism, rate constants for quenching of singlet *trans*-stilbene by tertiary amines are dependent upon the amine ionization potential but not the nature of the α-C–H bond broken in the proton-transfer step.[13,16,17] As expected for electron-transfer quenching,[18] rate constants are diffusion controlled when electron transfer from the amine to singlet *trans*-stilbene is exergonic (eq 1) but decrease as electron transfer becomes increasingly endergonic.

While rate constants for fluorescence quenching of *trans*-stilbene by tertiary amines are determined primarily by the amine ionization potentials, product formation efficiency and selectivity is highly dependent upon the nature of the α-C–H bond being broken in the product-forming step. As shown in Scheme II for the
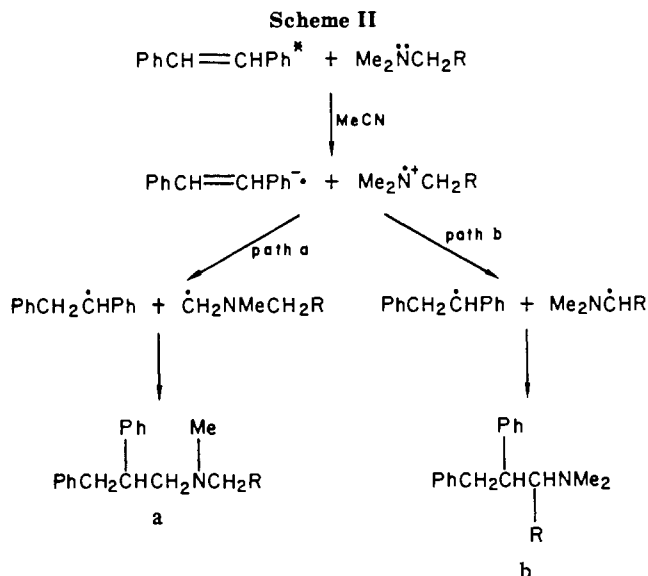
Table I.
**_trans_-Stilbene–Amine Adduct Yields and Ratios[a]**

amine	% a[b]	% b[b]	a/b[c] corrected
diisopropylmethyl	>95	<5	>20
isopropyldimethyl	>95	<5	>20
ethyldiisopropyl	92	8	12
diethylmethyl	63	37	2.3
n-butyldimethyl	86	14	2.0
ethyldimethyl	84	16	1.8
dimethylbenzyl	77	23	1.1
dimethylallyl	87	13	2.2
dimethylglycine ethyl ester	49	51	0.48
1-(dimethylamino)-2-butyne	13	87	0.05
dimethylpropargyl	<5	>95	<0.01

[a] Data from ref 16, 17. [b] See Scheme II for structures of products a and b. [c] Statistically corrected for the number of equivalent abstractable α-protons.

reaction of singlet stilbene with α-substituted trimethylamines, nonsymmetrically substituted tertiary amines are capable of yielding two stilbene–amine adducts.[16,17] Results obtained for a number of nonsymmetrically substituted amines are summarized in Table I, in which type *a* adducts correspond to addition of the less substituted α-C–H bond. For α-alkylated amines, the order of selectivity is Me > Et >> *i*-Pr, the opposite of that expected on the basis of alkyl radical stability, but in accord with product determining proton transfer.[16] The deprotonation of a planar amine cation radical bears analogy to the deprotonation of a carbocation in the second step of an El elimination reaction. The requirement of overlap between the half-vacant nitrogen p orbital and incipient carbon radical p orbital gives rise to a stereoelectronic effect on the deprotonation step. The Newman projections shown below for the cation radical of diisopropylmethylamine in the conformations required for deprotonation of methyl (a) vs. isopropyl (b) groups shows the higher ground-state
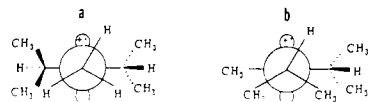
energy of the latter conformation. No stilbene–amine adducts are formed in cases where overlap of an α-C–H bond and the aminium radical p orbital is prevented either by steric congestion (e.g., triisopropylamine) or

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(17) Lewis, F. D.; Ho, T.-I.; Simpson, J. T. *J. Am. Chem. Soc.* **1982**, *104*, 1924.
(18) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

Scheme III

Scheme IV
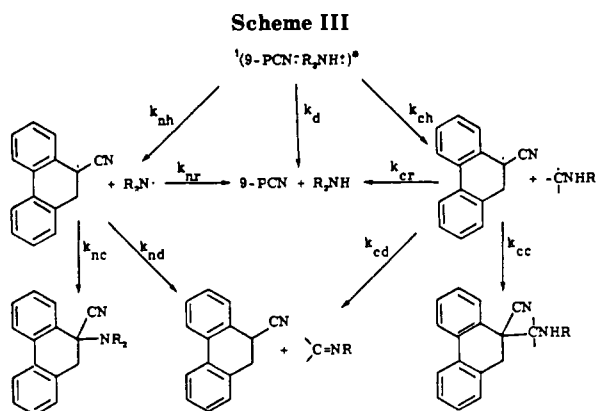
structural rigidity (e.g., 1-azabicyclo[2.2.2]octane).

The results obtained for several α-substituted trimethylamines (Table I) indicate that the amine cation radical kinetic acidity is subject to purely inductive as well as stereoelectronic effects.[17] This is particularly evident in the case of the α-acetylenic and methoxycarbonyl amines which yield predominantly type *b* adducts (Scheme II). Evidently, electron-withdrawing groups increase the α-C–H kinetic acidity of the amine cation radicals as they do for neutral carbon acids. The increased kinetic acidity of the cation radicals of these amines may account for their addition to singlet stilbene even in nonpolar solvents. Simple trialkylamines require polar nonhydroxylic solvents for addition to singlet stilbene and form nonreactive fluorescent exciplexes in nonpolar solvents.[13,14] These less acidic amines require the higher degree of excited-state charge separation possible in polar solvents in order for proton transfer to occur.

Secondary amines also add to singlet stilbenes in both polar and nonpolar solvents.[13] An interesting feature of this reaction is the formation of N–H rather than α-C–H adducts. Since the N–H bond dissociation energy is substantially higher than the α-C–H bond dissociation energy for dimethylamine (96 vs. 87 kcal/mol),[19] we suspected that the relative kinetic acidities (N–H ≫ α-C–H) of the amine cation radicals might be responsible for selective N–H addition. Plausible rationales for this proposal are provided by the higher kinetic acidity of neutral N–H vs. C–H acids of comparable equilibrium acidity[20] and by the proposal that singlet pyrene forms exciplexes with secondary and primary amines in which the amine N–H forms a hydrogen bond to pyrene.[21] Hydrogen bonding would lower the N–H vs. α-C–H bond energy and geometrically predispose the exciplex toward N–H transfer.

Further evidence concerning N–H vs. α-C–H proton transfer in photogenerated radical ion pairs was obtained by investigating the reactions of several singlet arenecarbonitriles with secondary and primary amines.[22] A general mechanism for the reaction of singlet 9-phenanthrenecarbonitrile (9-PCN) with secondary amines is shown in Scheme III. Analysis of the addition and reduction products formed with deuteriated
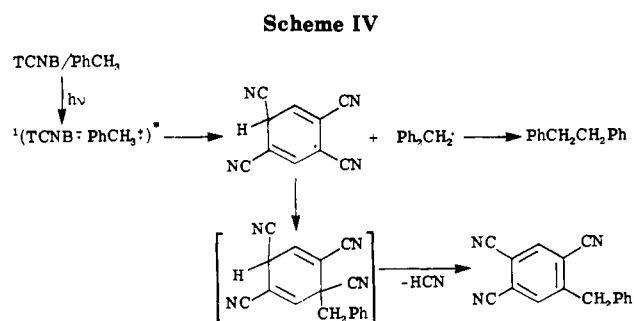
(N–D and α-C–D) amines indicates that $k_{nh}/k_{ch} > 10$ for dimethyl- and diethyl- and $k_{nh}/k_{ch} \sim 2$ for diisopropyl- and diallylamine in nonpolar solvent.[22c] These ratios are consistent with the expected decrease in the α-C–H bond strength due to alkylation or allylic stabilization. The k_{nh}/k_{ch} ratio is also observed to decrease with increasing solvent polarity. Moreover, N–H proton transfer is not observed to occur with strong electron acceptors such as the dicarbonitriles of benzene, phenanthrene, or anthracene even in nonpolar solvents.[22b] In short N–H transfer occurs under conditions in which the singlet arene and secondary amine form an exciplex intermediate which may be stabilized by amine cation radical N–H hydrogen bonding to the arene anion radical. Disruption of hydrogen bonding by increasing the solvent polarity or the singlet arene electron affinity results in decreased N–H reactivity.

Methylarene Cation Radicals. The photochemical reaction of tetracyanobenzene (TCNB) with toluene was initially investigated by Ohashi and co-workers,[23] who observed the formation of the substitution product 1-benzyl-2,4,5-tricyanobenzene and trace amounts of bibenzyl upon irradiation of the TCNB–toluene charge-transfer complex. On the basis of their mechanistic investigations, the photosubstitution reaction mechanism outlined in Scheme IV was proposed. The electron-transfer-initiated addition–elimination mechanism is identical with that for the reaction of 9-phenanthrenecarbonitrile with secondary amines, except that the addition product has not been detected. We have investigated the photochemical reactions of several cyanoaromatic and methylaromatic molecules with two objectives in mind: (a) to determine the timing of the proton transfer step and (b) to determine the influence of cation radical acidity and anion radical basicity upon the efficiency of the proton-transfer process.[24]

Unlike the reactions of the stilbene–amine radical ion pairs described in the preceding section, the substitution reaction described in Scheme IV does not occur via proton transfer in the initially-formed contact radical ion pair, but instead requires solvent separation of the radical ions prior to proton transfer. The initial evidence for the requirement of solvent separation was provided by the effect of oxygen upon the photosubstitution reaction. Unlike the stilbene-amine addition reactions which are insensitive to oxygen, irradiation of the TCNB–toluene system in air-saturated acetonitrile solution results in the formation of benzaldehyde

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(23) (a) Yoshino, A.; Ohashi, M.; Yonezawa, T. *Chem. Commun.* **1971**, 97. (b) Yoshino, M.; Yamasaki, K.; Yonezawa, T.; Ohashi, M. *J. Chem. Soc. Perkin Trans. 1* **1975**, 735. (c) Ohashi, M.; Nakayama, N. *Chem. Lett.* **1976**, 1143.
(24) Lewis, F. D.; Petisce, J. R. *Tetrahedron Symp. Print*, in press.

and total inhibition of photosubstitution. Benzaldehyde is plausibly formed by the electron-transfer-initiated photooxygenation mechanism proposed by Saito et al.[25] for the dicyanoanthracene-sensitized photooxygenation of methyl benzenes. Independent investigations of the TCNB–toluene system by Mataga et. al.[26] have established that the lifetime of the TCNB/toluene radical ion pair in acetonitrile solution is too short (ca. 0.3 ns) to allow quenching by dissolved oxygen and that the initial yield of TCNB•⁻ following pulsed laser excitation is the same in oxygenated vs. degassed solution. Since oxygen does not intercept the contact radical ion pair, but totally inhibits the photosubstitution process, we conclude that proton transfer must occur following solvent separation of the radical ions. Further evidence in support of this mechanism is provided by the inhibition of photosubstitution by Brønsted acids which are known to stabilize acidic aromatic cation radicals by preventing their deprotonation.[27]

The failure of proton transfer to occur in the TCNB–toluene contact radical ion pair stands in marked contrast to the behavior of arene–amine and ketone–amine radical ion pairs. One plausible explanation for the behavior of the TCNB–toluene system is that the face-to-face geometry of the ground-state complex and contact radical ion pair may be inappropriate for proton transfer. In accord with this proposal, Albini and Spreti[28] recently reported that a covalently linked durene–cyanonaphthalene forms a fluorescent exciplex, but fails to undergo photochemical reactions. Solvation of nonlinked radical ion pairs may allow reencounter of the donor cation radical methyl hydrogens with the face of the acceptor anion radical. The low probability of such an encounter may account for the lower quantum yield for photosubstitution vs. oxygenation.[23] Alternatively, solvation of the contact radical ion pair may allow deprotonation of the toluene cation radical by solvent to yield a benzyl radical. Benzyl radical displacement of cyanide from the TCNB anion radical has recently been observed by Mattes and Farid[29] and could account for the failure to detect the addition product in Ohashi's mechanism (Scheme IV).

The efficiency of the photosubstitution process shown in Scheme IV is dependent upon the cation radical acidity, quantum yields for the reaction of TCNB with methylbenzene decreasing with increasing methylation (toluene > xylene > mesitylene > durene > hexamethylbenzene). 1-Methylnaphthalene and 9-methylanthracene fail to react with TCNB as do p-methoxy- and p-aminotoluene. Lowering the methylarene oxidation potential either by ring substitution or extended conjugation stabilizes the cation radical more than the benzyl radical formed upon deprotonation, thus, decreasing the kinetic acidity of the cation radical.[9,10] The observed variation in photosubstitution efficiency with cation radical acidity is consistent with proton transfer to either the arene anion radical or to an external base.

Methylaromatic–cyanoaromatic photochemistry is also dependent upon the nature of the anion radical.
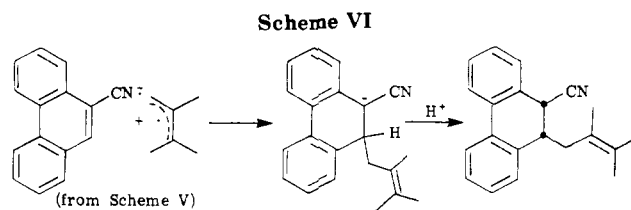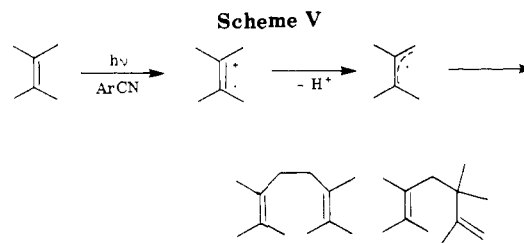
(25) Saito, I.; Tamoto, K.; Matsuura, T. *Tetrahedron Lett.* **1979**, 2889.
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(28) Albini, A.; Spreti, S. *Tetrahedron*, **1984**, *40*, 2975.
(29) Mattes, S. L.; Farid, S., unpublished results.

Scheme V

Scheme VI

(from Scheme V)

Cyanonaphthalenes yield complex mixtures of addition products[28] while mono- and dicyanoanthracenes or phenanthrenes fail to react. The stability of the anion radical is evidently important in these reactions; however, the details of the proton trnasfer process remain to be established.

Alkene and Diene Cation Radicals

Electron-rich alkenes and dienes undergo [2 + 2] and [4 + 4] cycloaddition reactions with singlet arenes via exciplex intermediates.[5,30] Alkene and diene cation radicals formed via photostimulated electron transfer undergo a variety of isomerization and addition reactions.[2b] Cation radical deprotonation has been observed to occur upon irradiation of 2,3-dimethyl-2-butene in the presence of several electron acceptors.[31,32] Arnold and co-workers[31] have calculated a pK_a of ca. –4 for deprotonation of its cation radical in acetonitrile; however, no information is available concerning its kinetic acidity. Both we[32] and Arnold et al.[31] have observed the formation of alkene dehydrodimers upon irradiation of 2,3-dimethyl-2-butene with cyanoaromatics in acetonitrile solution. Single-electron transfer followed by deprotonation of the alkene cation radical and allyl radical combination provides a plausible route to these dimers (Scheme V).

Irradiation of 2,3-dimethyl-2-butene with 9-cyanophenanthrene in acetonitrile solution yields a [2 + 2] cycloadduct, dehydrodimers, and an acyclic adduct. On the basis of the regio- and stereospecificity of adduct formation, attack of an allyl radical on the anion radical followed by stereospecific protonation of the resulting carbanion was proposed to occur (Scheme VI). Presumably, the alkene cation radical is deprotonated by solvent rather than the anion radical. Protonation of the arene anion radical can occur in protic solvents, as demonstrated by the formation of dihydrophenanthrene-9-carbonitrile with the incorporation of 2.0 equiv of deuterium upon irradiation in CH_3OD. Evidently, photoreduction occurs via two sequential electron-transfer, proton-transfer reactions as is the case in the electrochemical and alkali-metal reduction of phenanthrenes.[32] The second electron must come from a photogenerated anion radical, resulting in a pro-

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Scheme VII
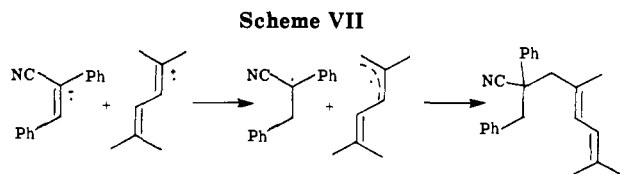
nounced light-intensity dependence for the photore-duction reaction.

Arnold et al.[31b] have suggested that the photosub-stitution reactions of 2,3-dimethyl-2-butene with di-cyanobenzenes occur via allylic radical–radical anion coupling followed by loss of cyanide and/or via covalent bond formation in the radical ion pair to yield a zwit-terion intermediate, followed by the loss of HCN. Mazzocchi and Klinger[33] favor the zwitterion mecha-nism for addition of 2,3-dimethyl-2-butene to *N*-methylphthalimide. The absence of products arising from radical ion pair proton transfer presumably re-flects the slow rate of proton transfer from the alkene cation radical to the delocalized cyanoaromatic anion radicals.

Formation of an acyclic adduct is also observed to occur upon irradiation of α-phenylcinnamonitrile with 2,5-dimethyl-2,4-hexadiene in acetonitrile solution.[34] In this case the regiochemistry of addition is consistent with proton transfer within the radical ion pair, followed by radical combination (Scheme VII). Greater charge localization for the anion radical of α-phenyl-cinnamonitrile vs. the cyanoaromatics may account for its protonation by the diene cation radical.

The quantum yields for the addition reactions such as those outlined in Schemes VI and VII are quite low (<0.01),[31-34] plausibly reflecting the low kinetic acidity of alkene and diene cation radicals. Addition of small amounts of methanol results in nucleophilic trapping of the alkene or diene cation radical and the formation of products derived from the resulting methoxyalkyl or allyl radicals and quenching of the reactions shown in Schemes VI and VII. Evidently deprotonation of the cation radicals is slower than nucleophilic addition of methanol.

Concluding Remarks

All of the reactions described in this Account are believed to occur via photostimulated single-electron transfer from a ground-state electron donor to an ex-cited-state electron acceptor followed by deprotonation of the donor cation radical, either by the acceptor anion radical or an external base. Deprotonation of the donor cation radical yields resonance stabilized radicals (e.g., α-aminoalkyl, benzyl, and allyl radicals), which could also be formed in one step by hydrogen atom transfer, a process thermodynamically equivalent to sequential electron transfer, proton transfer. Clearly, the prefer-ence for the electron transfer mechanism must be based

on kinetics rather than thermodynamics. Exergonic electron transfer is sufficiently rapid to occur within the lifetime of the excited-state acceptor, whereas hydrogen atom transfer evidently is not.

Briefly reviewing the experimental evidence for the electron-transfer mechanisms outlined in Schemes I–VII, the formation of free radical ions has been directly observed by transient absorption and Raman spec-troscopy; reactivities within donor families are deter-mined by relative cation radical kinetic acidities and not by product radical stabilities; and solvent polarity has a pronounced effect on product quantum yields. Of course, the observation of radical ions by transient spectroscopy does not require that they be intermedi-ates in the photochemical reactions. In fact the quan-tum yields for the reactions of methylarene and alkene and diene cation radicals are sufficiently low (≤ 0.01) to discourage attempts to study the proton transfer process by kinetic spectroscopy. Thus structure–re-activity relationships, solvent effects, and the effect of various additives (acid or base catalysts, salts, oxygen) provide the principal evidence about cation radical deprotonation.

As expected for reactions involving ionic intermedi-ates, solvation has a pronounced effect on the reactions described in this Account. In most cases, quantum yields for product formation increase with increasing solvent polarity, reflecting the dependence of ΔG_{ET} upon solvent polarity (eq 1). However, the highest quantum yields for product formation are observed for reactions such as that of singlet stilbene with amines in which proton transfer occurs in the contact radical ion pair, prior to solvation of the radical ions. Once the cation radical is fully solvated, proton transfer evidently occurs more slowly. Using the Marcus formalism, slow proton transfer is consistent with the observation of large work terms for proton-transfer reactions which require a specific orientation of the encounter complex in order for proton transfer to occur.[35] If the contact ion pair has the correct geometry for proton transfer, then the work term for proton transfer will be negligible and the free energy of activation for exergonic proton transfer may be very small, resulting in fast proton transfer. This is clearly the case for the benzo-phenone–amine systems investigated by Schaefer and Peters.[12] If proton transfer requires reorientation of the contact radical ion pair formed either upon initial electron transfer or reencounter of the donor and ac-ceptor radical ions, exergonic proton transfer may be slow due to the Marcus work term. In such cases, proton transfer will not compete effectively with ex-ergonic electron transfer, resulting in low quantum yields for product formation.

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