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Charge-transfer excitation of molecular complexes in organic and organometallic chemistry

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Abstract - Electron donor-acceptor or EDA complexes are common precursors leading to a variety of organic and organometallic reactions, as indicated by the ubiquitous appearance of characteristic charge-transfer absorption bands. Structural effects of HOMO-LUMO interactions extant in donor-acceptor pairs, established by X-ray crystallography, are critical to the charge-tranfer excitation of various types of weak molecular complexes in which time-resolved picosecond spectroscopy identifies the nature of CT ion pairs. Their relevance to the transition state description of electrophile/nucleophile interactions is underscored in the detailed study of electrophilic aromatic nitration.

INTRODUCTION

The color changes attendant upon the exposure of aromatic hydrocarbons to various halogens are attributed to the formation of weak complexes (ref. 1). The seminal idea that such colors derive directly from the charge transfer excitation of the 1:1 complex is due to Mulliken (ref.2). In a much more general context, charge-transfer absorption bands result whenever intermolecular complexes [D,A] are formed from the association of an electron donor (D) with an electron acceptor (A) (ref. 3). Indeed electron donors can also be characterized as reducing agents as well as nucleophiles (ref. 4). Furthermore, nucleophiles are often the most effective as negatively-charged anions, and they are also referred to sometimes as Brønsted and Lewis bases or in terms of their softness on the HSAB scale (ref. 5).Since each of these classifications relates in some way to a molecular property that is qualitatively considered in degrees of electron-richness (ref. 6), we prefer the more inclusive description of electron donors, as originally defined by Mulliken (ref. 7). The contrasting descriptions have also been applied to electrophiles and oxidants in reference to their electron-acceptor behavior, as the direct comparison below emphasizes.

Electron Donor (D)	Electron Acceptor (A)
reductant	oxidant
nucleophile	electrophile
base　　　(Brønsted, Lewis, HSAB)	acid
anion	cation
(electron-rich)	(electron-poor)

Electron donors and acceptors constitute reactant pairs that are traditionally considered with more specific connotations in mind-- such as nucleophiles and electrophiles in bond formation, reductants and oxidants in electron transfer, bases and acids in adduct production, anions and cations in ion-pair annihilation, etc. (ref. 8). As such, the preequilibrium formation of a non-bonded electron donor-acceptor (EDA) complex, i.e.

$$D \; + \; A \; \underset{}{\overset{K}{\rightleftharpoons}} \; [D, A] \tag{1}$$

has its counterparts that are variously described as an encounter complex, a precursor complex, a contact charge-transfer complex or a contact ion pair (ref. 9). Despite the limited values of the formation constant $K < 10$ M^{-1} in eq 1, a number of charge-transfer complexes have been isolated and structurally characterized by X-ray crystallography (ref. 10). Thus Fig. 1 depicts the myriad of crystallographic structures derived from the CT complexes of a simple (arene) donor with different electron acceptors selected from the list of common oxidants, electrophiles, acids and cations below (ref. 11).
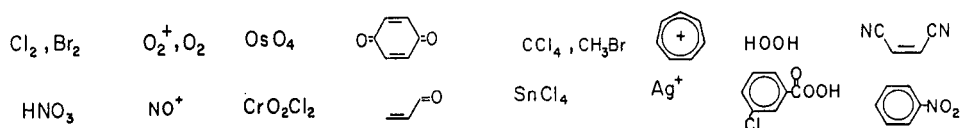
Although several structural types of arene complexes are included, the linear correlations in Fig. 2 typify the direct correspondence of the charge-transfer absorptions ($h\nu_{CT}$) with various types of acceptors, irrespective of whether they are involved in a η^2 or η^6 bonding relationship with the arene donor.
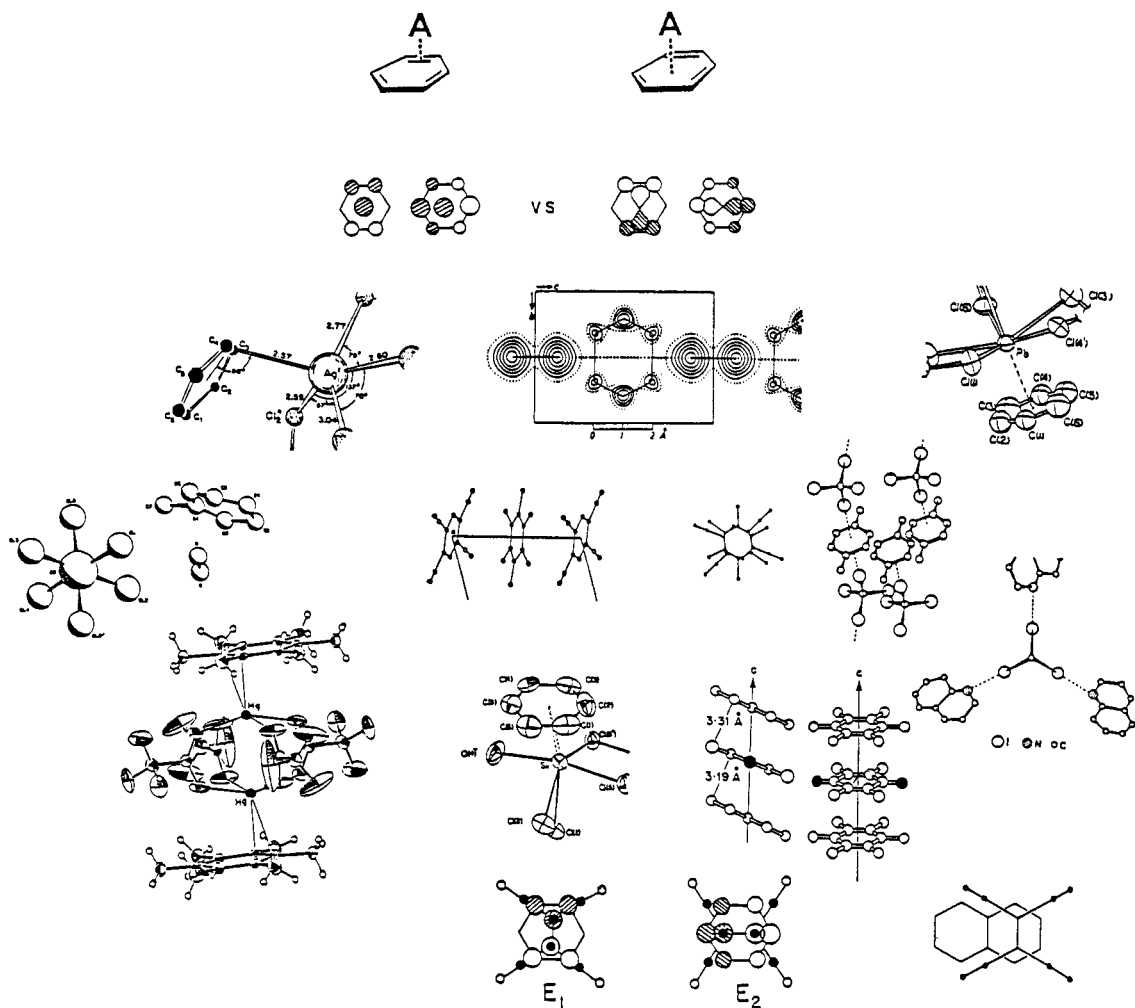
Fig. 1. Collage of X-ray crystallographic structures of aromatic EDA complexes showing η^2 and η^6 interactions to electron acceptors such as bromine, tetracyanobenzene, carbon tetrabromide, chloranil, tetracyanoethylene, together with nitrosonium, silver(I), alkyltin(IV) and lead(V) cations.
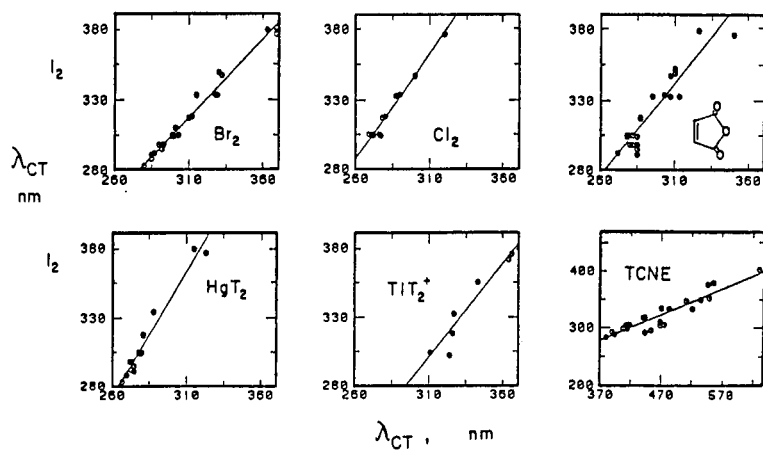

Fig. 2. Direct relationship of the charge-transfer absorption bands of various arene-iodine complexes (ordinate) with those of the corresponding aromatic complexes with different acceptors (abscissa) as indicated (T = trifluoroacetate, TCNE = tetracyanoethylene).

DIRECT OBSERVATION OF TRANSIENT ION PAIRS BY CHARGE-TRANSFER ACTIVATION OF EDA COMPLEXES

According to Mulliken (ref. 7), the formation of the ion radical pair occurs upon the excitation of the charge-transfer band of the EDA complex, i.e.

$$[D,A] \quad \xrightleftharpoons{\quad h\upsilon_{CT} \quad} \quad [D^{+\cdot}, A^{-\cdot}] \qquad (2)$$
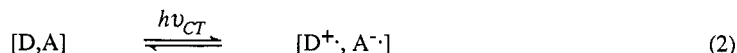
The experimental proof of Mulliken theory is established in the donor-acceptor complex of 9-cyanoanthracene (CNA) and tetracyanoethylene (TCNE) shown in Fig. 3A (ref. 12).Thus the deliberate excitation of the charge-transfer band at λ_{max} 630 nm with a 25-ps laser pulse leads to the series of time-resolved spectra in Fig. 3C taken shortly after the application of the 532-nm radiation from a Nd^{3+}: YAG laser. The transient absorption bands at λ 770 and 440 nm immediately following the 25-ps laser pulse clearly delineate the simultaneous appearance of the 9-cyanoanthracene cation radical (CNA$^{+\cdot}$) and the tetracyanoethylene anion radical (TCNE$^{-\cdot}$) as shown by
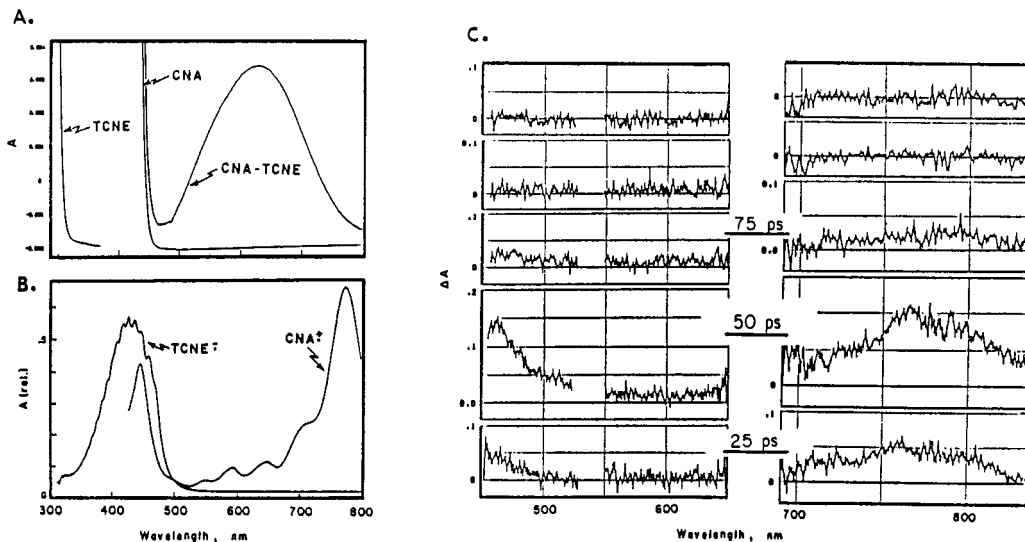

Fig. 3. Electronic absorption spectra of (A) the EDA complex of 9-cyanoanthracene (CNA) and tetracyanoethylene (TCNE) in comparison with the uncomplexed CNA and TCNE; (B) the donor cation CNA$^{+\cdot}$ and acceptor anion TCNE$^{-\cdot}$ generated spectroelectrochemically and (C) time-resolved ps absorption spectra taken at 25, 50, 75 and 100 ps following the CT excitation at 532 nm of [CNA, TCNE] with a 25 ps laser pulse.

comparison with the absorption spectra in Fig. 3B of these ion radicals generated spectroelectrochemically at a platinum-mesh anode and cathode, respectively. It is important to emphasize that the clean spectral separation in Fig. 3A ensures that the application of the 532-nm laser pulse leads specifically to the excitation of the charge-transfer band of the [D,A] complex, and not the local bands of either the uncomplexed CNA donor or TCNE acceptor. There is no evidence from the picosecond absorption data for either the existence of an excited state of the EDA complex or the formation of any intermediate states or species other than CNA$^{+\cdot}$ and TCNE$^{-\cdot}$. Electron transfer from the aromatic donor to TCNE thus effectively occurs in the EDA complex with the absorption of the ($h\upsilon_{CT}$) photon,i.e.

$$[Ar, TCNE] \quad \xrightleftharpoons[k_{-1}]{\quad h\upsilon_{CT} \quad} \quad [Ar^{+\cdot}, TCNE^{-\cdot}] \qquad (3)$$
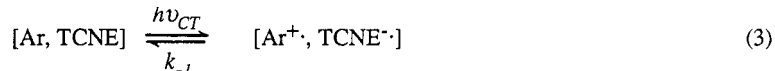
The transient existence of the ion pair with a lifetime of ~ 50 ps corresponds to the electronic relaxation of the ion pair by back electron transfer ($k_{-1} \simeq 2 \times 10^{10}$ s^{-1}). Such an experimental observation therefore represents the direct confirmation of Mulliken theory, in which the specific irradiation of the charge-transfer band of an EDA complex consisting of a relatively nonpolar ground state leads to the production of the ion radical pair [D$^{+\cdot}$, A$^{-\cdot}$]. Since this photo-induced electron transfer derives from an EDA complex [D,A] by a vertical transition, the interionic separation in the CT ion pair is considered to be akin to the contact or inner-sphere ion pair (ref. 4).

TIME-RESOLVED PICOSECOND SPECTROSCOPIC STUDIES OF CHARGE-TRANSFER COMPLEXES

In order to establish the generality of ion-radical pair formation by charge-transfer activation of EDA complexes, let us focus on a few diverse examples of acceptors interacting with arene donors pertinent to organic and organometallic chemistry.

Carbocations as electron acceptors in aromatic EDA complexes

Organic cations are electron acceptors by virtue of their electron-deficient centers on one or more carbon atoms. Indeed the coordinative unsaturation in such stable carbocations as tropylium (C$_7$H$_7^+$) and triphenylcarbenium (Ph$_3$C$^+$) is underscored by their well-known ability to form acid-base complexes with even such weak σ-donors as ethers, nitriles, etc. In a similar vein are the intermolecular interactions of tropylium ions with electron-rich anionic
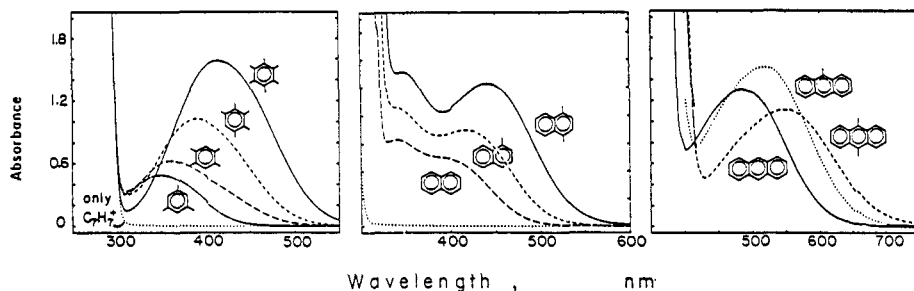
Fig. 4.   Charge-transfer absorption bands of the EDA complexes of tropylium cation with various benzene, naphthalene and anthracene donors.

donors to form charge-transfer salts that are manifested by the appearance of new absorption bands in the ultraviolet/visible region, both in solution and in the crystalline salt (ref. 13). Thus a colorless solution of tropylium salt in acetonitrile turns pale yellow instantaneously upon exposure to benzene (ref. 14). With naphthalene a bright lemon-yellow coloration develops; and a clear red solution results from anthracene. The quantitative effects of such dramatic color changes are illustrated in Fig. 4 by the appearance of distinctive charge-transfer bands. For the series of methylbenzene donors, the absorption maxima λ_{CT} are progressively red-shifted with increasing numbers of methyl substituents (Fig. 4A) to reflect the accompanying decrease in the ionization potentials IP. A similar bathochromic shift of the charge-transfer band is observed in the tropylium complexes with the series of methylnaphthalenes and methylanthracenes shown in Figs. 4B and 4C respectively. Such a progressive red shift of the new absorption bands with the ionization potentials of the aromatic donors accords with Mulliken charge-transfer theory (ref. 7). Indeed for weak EDA complexes the energy of the charge-transfer transition (i.e. $h\upsilon_{CT}$) relates directly to the ionization potential by the relationship: $h\upsilon_{CT} = IP - EA - w_p{}^*$, since the electron affinity EA of the tropylium acceptor is a common value, and the electrostatic work term $w_p{}^*$ is considered to be constant for related donors. The common CT behavior of the methylbenzenes, naphthalenes and anthracenes is underscored by the striking linear correlation expressed as: $h\upsilon_{CT} = 1.0\,IP - 4.8$ to encompass the energy span of almost 2 eV. Despite the limited magnitudes of the formation constant ($K \sim 1$ M^{-1}) of the tropylium-naphthalene complexes in solution, crystalline complexes can be isolated. Thus the X-ray diffraction pattern from the naphthalene complex with C$_7$H$_7{}^+$SbF$_6{}^-$ obtained as bright yellow orthorhombic crystals is solved as the 1:1 EDA complex in which the planar tropylium cation is poised centrosymmetrically over the naphthalene nucleus with an interannular separation of 3.36Å, as illustrated below (A).
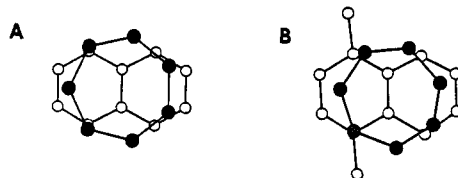
The related unsymmetrical donor 1,4-dimethylnaphthalene with the same tropylium salt C$_7$H$_7{}^+$SbF$_6{}^-$ affords orange monoclinic crystals of which the X-ray crystallographic determination established the same centrosymmetric structure for the donor-acceptor pair, as shown above (B). Moreover, the interplanar distance from the tropylium centroid to the naphthalene plane is 3.38 Å despite the presence of two sizeable methyl substituents to lower the symmetry of the donor. Otherwise the bond distance and bond angles in the crystalline EDA complexes are essentially the same as those established earlier for the separate, uncomplexed naphthalene donors and the tropylium salts. The pair of absorption bands illustrated in Fig. 4B can be accounted for by the charge-transfer transitions from the highest occupied molecular orbital (HOMO) and the subjacent HOMO-1 depicted below. As such, the centrosymmetric structures above accord with the optimum overlap of the naphthalene HOMO and HOMO-1 of a_u and b_{1u} symmetry, respectively, with the degenerate pair of tropylium e$_2{}''$ LUMOs of the same gross symmetry, i.e.

HOMO a$_u$ HOMO-1 b$_{1u}$ Degenerate   LUMOs e$_2{}''$
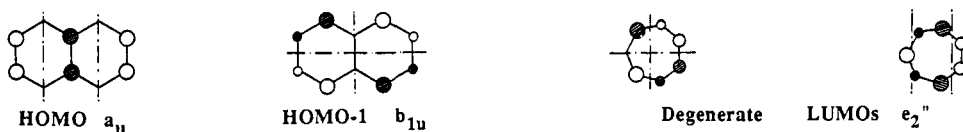
On the basis of similar considerations of orbital symmetry, the EDA complexes of tropylium with neither benzene nor anthracene donors would be centrosymmetric.

In order to ascertain the nature of the colored (visible) absorption bands of the tropylium EDA complexes in Fig. 4, the time-resolved spectra can be examined immediately following the application of a 30-ps pulse consisting of the second harmonic at 532 nm of a mode-locked Nd^{3+}: YAG laser (ref. 14). This wavelength coincides with the maxima of the CT absorption bands of the series of anthracene complexes with the tropylium acceptor in acetonitrile solutions (see Fig. 4C). Accordingly the time-resolved spectra obtained from the tropylium-anthracene system relate directly to the charge-transfer excitation since there is no ambiguity about the adventitious local excitation of complexed (or uncomplexed) chromophores. Indeed, intense transient absorptions are observed in the visible region between 500 and 750 nm immediately following the CT excitation of the tropylium EDA complexes. Comparison with the steady-state absorption spectra of the corresponding anthracene cation radicals that are independently generated by the spectroelectrochemical technique (vide supra), establish the identity of the
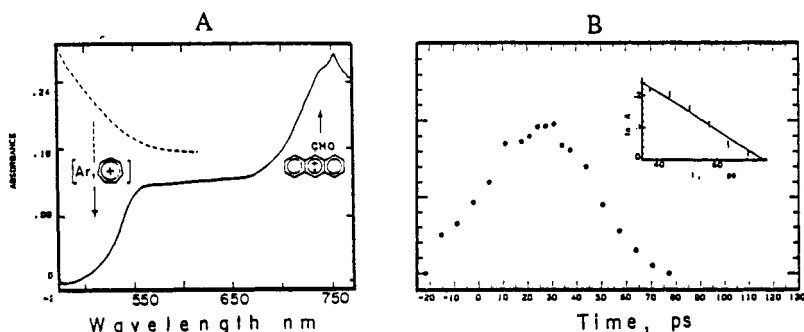
Fig. 5. (A) Typical time-resolved ps absorption spectrum following the charge-transfer excitation of tropylium EDA complexes with arenes (anthracene-9-carbaldehyde) showing the bleaching (negative absorbance) of the CT absorption band and the growth of the aromatic cation radical; (B) Temporal evolution of $ArH^{+\cdot}$ monitored at λ_{max}. Inset shows the first-order plot of the ion radical decay.

charge-transfer transients. The appearance of the absorption spectra of the anthracene cation radicals is also accompanied by the disappearance of the charge-transfer absorption bands. The simultaneity of these spectral changes is clearly delineated in those anthracene donors with 9-phenyl, bromo, acetoxy and formyl substituents owing to the well-defined absorption maxima of their charge-transfer bands. Fig. 5A typically illustrates the growth of the aromatic cation-radicals by the positive absorptions ($\Delta A \geq 0$) at wavelengths beyond 700 nm concomitant with the depletion of the ground-state EDA complexes by the negative CT absorptions ($\Delta A < 0$) at wavelengths less than 550 nm below the baseline. Such a photo-induced dismutation of the ground-state EDA complex readily identifies the charge-transfer excitation as

$$[Ar, \ \text{⊕} \ ] \quad \underset{k_{-1}}{\overset{h\nu_{CT}}{\rightleftharpoons}} \quad [Ar^{+\cdot}, \ \text{⊙} \ ] \qquad (4)$$
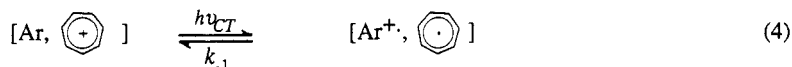
The accompanying changes in the absorption spectra of tropylium and the tropyl radical in eq 4 are obscured by their overlap with the dominant absorptions of the aromatic donors below 500 nm. The time-resolved spectroscopic observation of $Ar^{+\cdot}$ accompanying the excitation of the charge-transfer band of the EDA complex accords with the electron promotion from the filled HOMO (or HOMO-1) of the arene donor Ar to the empty LUMO of the tropylium acceptor. The formation of arene cation radicals occur within the risetime of the 30-ps laser pulse. We conclude that the electron transfer from the arene donor to the tropylium acceptor in the EDA complex effectively occurs with the absorption of the excitation photon ($h\nu_{CT}$) in accord with Mulliken's theory. In the absence of any discernible charge-transfer photochemistry, the subsequent decay of the cation-radical absorbance in Fig. 5B derives from a dark (adiabatic) process. Since the observed first-order rate constants k_{-1} are too fast to allow significant competition from diffusive separation, the annihilation of $Ar^{+\cdot}$ is ascribed to the reversal of the solvent-caged pair to regenerate the EDA complex. The magnitudes of the driving force $-\Delta G_{et}$ for the back electron transfer are evaluated from the redox potentials E^0 of the anthracenes and tropylium cation. In every case the driving force for the return of $Ar^{+\cdot}$ to the arene EDA complex is overwhelmingly large with $k_{-1} = 4 \times 10^{10} s^{-1}$. The rapidity of the back electron transfer underlies the singular absence of productive photochemistry accompanying the continuous irradiation of the tropylium EDA complexes of various anthracene, naphthalene, and benzene donors. Thus any photochemical transformation resulting from the CT excitation of the tropylium EDA complex is limited by the $Ar^{+\cdot}$ lifetime of $\tau \sim 15$ ps. Although these inextensible lifetimes discourage competition from any process involving the diffusive separation of the radical pair, the kinetics obstacle can be circumvented by a unimolecular process involving either the arene ion radical, the tropyl radical, or both in the solvent cage. Let us first consider the unimolecular fragmentation and rearrangement of $Ar^{+\cdot}$ as follows: The cycloreversion of dianthracene is a direct consequence of populating the charge-transfer excited state of the tropylium EDA complex (ref.14). The photo-efficiency of this charge-transfer cycloreversion is limited by the unimolecular rate of fragmentation (k_f) of the dianthracene cation radical relative to back electron transfer. The measured quantum yield of $\Phi_p = 0.02$ for the CT cycloreversion indicates that the rate constant k_{et} for back electron transfer is $\sim 10^{10} s^{-1}$ since the halflife of the diathracene cation radical was previously estimated to be $\sim 10^{-8}$ s (ref. 15). Indeed the magnitude of k_{et} for the back electron transfer evaluated by this indirect method is comparable to the values of k_{-1} obtained directly from the first-order decay of the arene cation radical. The isomerization of hexamethyl (Dewar benzene) HMDB, like that of the dianthracene *(vide supra)*, occurs as a direct consequence of the actinic activation of the tropylium EDA complex. Accordingly the charge-transfer mechanism for the aromatization of HMDB can be analogously attributed to the rapid isomerization of the transient cation radical ($HMDB^{+\cdot}$) (ref. 16). Other photochemical studies directed at the interception of such CT cation radicals by second-order processes have been unfruitful. For example, arene cation radicals are known to readily undergo both nucleophilic addition as well as deprotonation of methyl substituents (ref. 17). In particular, the cation radicals of 9-methyl- and 9,10-dimethylanthracene are particularly stable, and they persist in the time-resolved studies of the CT excitation of the corresponding tropylium EDA complexes for rather prolonged times *(vide supra)*. Attempts to intercept these methylarene cation radicals in the presence of added bases such as the hindered 2,6-di-tert-butylpyridine and 2,4,6-collidine lead to no change of the transient behavior; and the parent methylarenes are recovered intact even after prolonged CT irradiation. In order for effective CT photochemistry of arenes to occur via tropylium EDA complexes, a unimolecular process is required to effectively compete with $Ar^{+\cdot}$ lifetimes of ~ 15 ps. The latter largely precludes bimolecular quenching by second-order kinetics, except in those unusual cases in which leakage from the cage can be highly magnified by a subsequent chain process.

Aromatic EDA complexes with nitrosonium ion

A nitrosonium salt like a nitronium salt can serve effectively either as an oxidant or as an electrophile toward different aromatic substrates. Thus the electron-rich polynuclear arenes suffer electron transfer with $NO^+ BF_4^-$ to afford stable arene cation radicals (ref. 18). Other activated aromatic compounds such as phenols, anilines and indoles undergo nuclear substitution with nitrosonium species that are usually generated in situ from the treatment of nitrites with acid. It is less well-known, but nonetheless experimentally established (ref. 19), that NO^+ forms intensely colored charge-transfer complexes with a wide variety of common arenes (ArH).

$$ArH + NO^+ \quad \overset{K}{\rightleftharpoons} \quad [ArH, NO^+] \qquad\qquad (5)$$
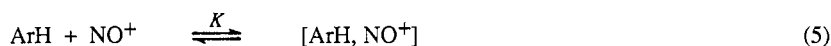
For example, benzene, toluene, xylenes and mesitylene generate yellow to orange vivid hues when added to colorless solutions of $NO^+PF_6^-$ in acetonitrile. Analogously, the more electron-rich durene, pentamethylbenzene, hexamethylbenzene and naphthalene afford dark red solutions when exposed to NO^+. These highly colored solutions upon standing at -20 °C, deposit crystals of the CT complexes. In this manner, the 1 : 1 arene complexes $[ArH, NO^+ PF_6^-]$ are isolated with ArH = mesitylene, durene, pentamethylbenzene and hexamethylbenzene, and the ORTEP diagram from the X-ray crystallography of the mesitylene complex is presented below (ref. 20).
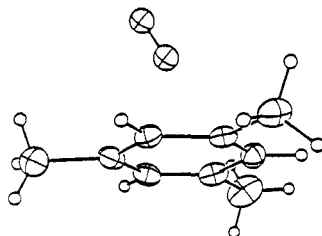
Indeed the relevant CT interaction clearly derives from the centrosymmetric (η^6) structure of the arene-NO^+ pair reminiscent of the other aromatic EDA structures presented in Fig. 1. However, the NO^+ complexes are unusual in two important ways. First, the formation constant K is strongly dependent on the donor strength (i.e., ionization potential) for the arene-increasing dramatically from 0.5 M^{-1} with benzene to 31,000 M^{-1} with hexamethylbenzene (HMB). Second, the frequency of the N-O stretching band in the infrared spectrum decreases markedly from υ_{NO} = 2037 cm^{-1} in the toluene complex to υ_{NO} = 1880 cm^{-1} in the hexamethylbenzene complex. Such a large change in υ_{NO} parallels the difference between the uncomplexed acceptor $[\upsilon(NO^+) = 2280$ cm$^{-1}]$ and free nitric oxide $[\upsilon(NO) = 1876$ cm$^{-1}]$. The unusually pronounced dependence of both the formation constant K and N-O stretching frequency of the aromatic EDA complexes with NO^+ with the aromatic donor strength (as evaluated by the ionization potential) point to a sizeable change in the charge-transfer component in the ground state of these complexes. In particular, the value of υ_{NO} in the hexamethylbenzene (HMB) complex which is essentially the same as that of free NO suggests complete electron transfer in the ground state. According to Mulliken theory (ref. 7), the ground state of weak EDA complexes (with K typically < 10 M^{-1}) can be described by $\psi = a\ \psi_{D,A} + b\ \psi_{D^+A^-}$ with the coefficients $a \gg b$ to denote a minor contribution from the charge-transfer state (ref. 3). The complete reversal upon CT excitation generates an excited state with a large (total) contribution from the charge-transfer state $\psi^* = b\ \psi_{D,A} - a\ \psi_{D^+A^-}$. Indeed, the time-resolved spectroscopy studies relate directly to the formation of ion radicals as CT transients from such weak EDA complexes. By an analogous reasoning, the ground state of strong EDA complexes such as HMB-$NO^+(K > 10^4$ M^{-1} and υ_{NO} the same as that of free NO) may be described essentially as an EDA complex of the cation radical with NO, i.e. $[HMB^+\cdot, NO]$. The slope of the linear correlation between $\ln K$ and IP indicates a sharp trend toward the benzene complex in which the ground state can be largely represented by the no-bond structure (with $a \gg b$).
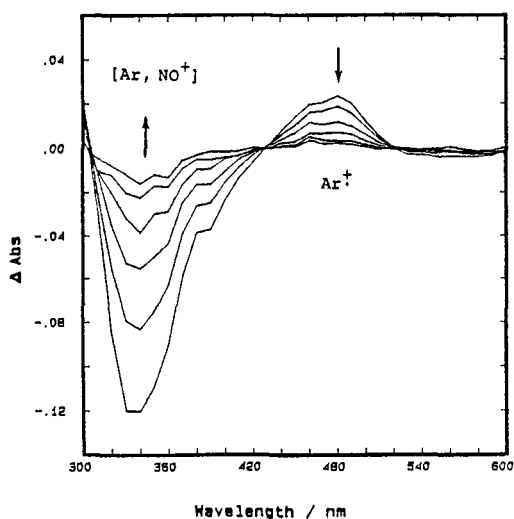

Fig. 6 Typical time-resolved absorption spectrum following the CT excitation of nitrosonium EDA complexes with arene (hexamethylbenzene) showing the bleaching of CT absorption and growth of the donor cation radical (HMB$^+\cdot$).

The excitation of the charge-transfer band of the aromatic EDA complexes with NO^+ is carried out at $\lambda = 355$ nm using a 30-ns laser pulse (ref. 21). The time resolved spectrum in Fig.6 shows the typical bleaching of the CT absorption band and the appearance of the aromatic cation radical with $\lambda_{max} \sim 500$ nm
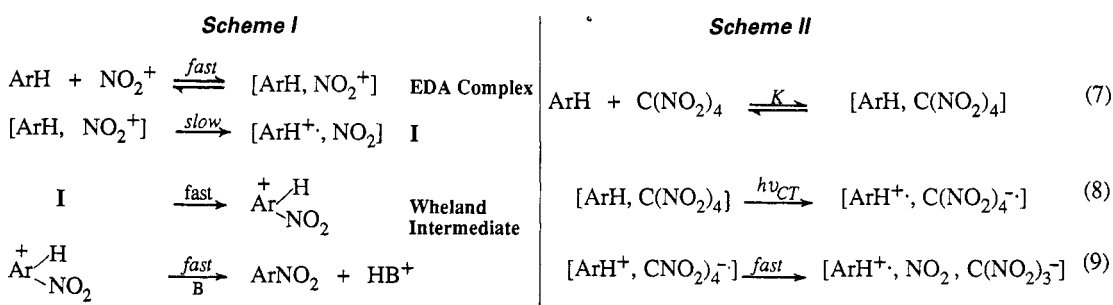
$$[ArH, NO^+] \quad \xrightleftharpoons[k_{-1}]{h\upsilon_{CT}} \quad [ArH^{+\cdot}, NO] \qquad (6)$$
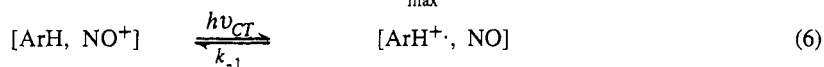
Since no photochemistry occurs upon the prolonged irradiation of the CT absorption band, the subsequent first-order decay of the $ArH^{+\cdot}$ absorption clearly relates to back electron transfer (k_{-1}). It is significant that the trend in k_{-1} accords with the expected increase in driving force for back electron transfer in proceeding from hexamethylbenzene $(IP = 7.71$ eV) to benzene $(IP = 9.23$ eV). Moreover, it is interesting to note that the magnitudes of these rate constants are in line with those found for the collapse of $[ArH^{+\cdot}, NO_2]$ in charge-transfer nitration (vide infra). The time-resolved spectral studies thus support the notion that ion radical pairs can be held together by CT interactions sufficient to retard their diffusive separation.

AROMATIC EDA COMPLEXES AS THE UNIFYING THEME IN ELECTROPHILIC AROMATIC SUBSTITUTION-CHARGE-TRANSFER ACTIVATION IN NITRATION

The idea that charge transfer may play a key role in aromatic nitration with nitronium ion was first suggested in 1945 by Kenner (ref. 22),who envisaged an initial step that "involves transference of a π-electron..." Later Brown (ref. 23) postulated charge-transfer complexes as intermediates, and Nagakura (ref. 24) provided further theoretical support for one-electron transfer between an aromatic donor (ArH) and an electrophile such as NO_2^+. Despite notable elaborations by Pederson, Perrin, Eberson and others (ref. 25), this formulation has not been widely accepted for nitration and related electrophilic aromatic substitutions. As broadly conceived, the seminal question focuses on the activation process(es) leading up to the well-established Wheland or σ-intermediate (ref. 26). In the electron transfer mechanism, the formation of the ion radical pair **I** is the distinctive feature, as summarized in Scheme I.

Accordingly, the properties and behavior of the intimate ion radical pair are crucial to establishing its relationship with the numerous facets of electrophilic aromatic nitration (ref. 27). For these reasons it is especially important to know whether the ion pair **I** will actually lead to the appropriate Wheland intermediate, and in the amounts necessary to establish the isomer distributions commonly observed in aromatic nitrations. However, the independent proof of the ion radical pair **I** has not been forthcoming owing to its expectedly transitory character.

Scheme I

$$ArH + NO_2^+ \quad \xrightleftharpoons{fast} \quad [ArH, NO_2^+] \quad \text{EDA Complex}$$

$$[ArH, NO_2^+] \quad \xrightarrow{slow} \quad [ArH^{+\cdot}, NO_2] \quad \textbf{I}$$

$$\textbf{I} \quad \xrightarrow{fast} \quad Ar\overset{+}{\underset{NO_2}{\diagup}}^{H} \quad \text{Wheland Intermediate}$$

$$Ar\overset{+}{\underset{NO_2}{\diagup}}^{H} \quad \xrightarrow[B]{fast} \quad ArNO_2 + HB^+$$

Scheme II

$$ArH + C(NO_2)_4 \quad \xrightleftharpoons{K} \quad [ArH, C(NO_2)_4] \qquad (7)$$

$$[ArH, C(NO_2)_4] \quad \xrightarrow{h\upsilon_{CT}} \quad [ArH^{+\cdot}, C(NO_2)_4^{-\cdot}] \qquad (8)$$

$$[ArH^+, C(NO_2)_4^{-\cdot}] \quad \xrightarrow{fast} \quad [ArH^{+\cdot}, NO_2, C(NO_2)_3^-] \qquad (9)$$

Charge-transfer nitration of aromatic donors

Picosecond time-resolved spectroscopy has defined the relevant photophysical and photochemical processes associated with the charge-transfer excitation of an arene complex such as anthracene with tetranitromethane (TNM ref. 28). As applied to benzenoid donors ArH, the formation of the pertinent ion radical pair by charge-transfer excitation is summarized below.

All the experimental observations with various benzenoid donors and tetranitromethane indeed coincide with the formulation in Scheme II. Thus the exposure of ArH to a nitrating agent such as TNM as in Fig. 7 leads immediately to the EDA complex in eq 7(ref. 29). It is singularly noteworthy that the charge-transfer spectrum of the aromatic EDA complex with TNM is not fundamentally distinguished from the CT spectra of other common nitrating agents shown in Fig. 7. Moreover all of these EDA binary complexes are present in low steady-state concentrations owing to the limited magnitude of K as measured by the Benesi-Hildebrand method. Activation of the EDA complex by the specific irradiation of the CT band results in a photo-induced electron transfer in accord with Mulliken theory. Thus the irreversible fragmentation following the electron attachment to TNM leads to the ion radical pair in eq 9. The measured quantum yield of $\Phi \approx 0.5$ is similar to that ($\Phi \approx 0.7$) obtained for anthracene. Such high quantum yields relate directly to the efficiency of ion radical pair production in eq 9 relative to energy wastage by back electron transfer of eq 8. Moreover the short lifetime (< 3 ps) of $C(NO_2)_4^{-\cdot}$ ensures that $ArH^{+\cdot}$ and $NO_2\cdot$ are born as an ion radical pair, initially trapped within the solvent cage, since this timescale obviates any competition from diffusional processes (ref. 28). Charge-transfer excitation thus provides the experimental means of generating the intimate ion radical pair $[ArH^{+\cdot}, NO_2]$ for Scheme I in sufficient concentrations and in a discrete electronic state as well as geometric configuration. Coupled with the observation of the fast kinetics allowed by the use of laser-flash photolytic techniques, we now focus on the pathways by which the ion radical pair collapses to nitration products with two series of aromatic ethers.
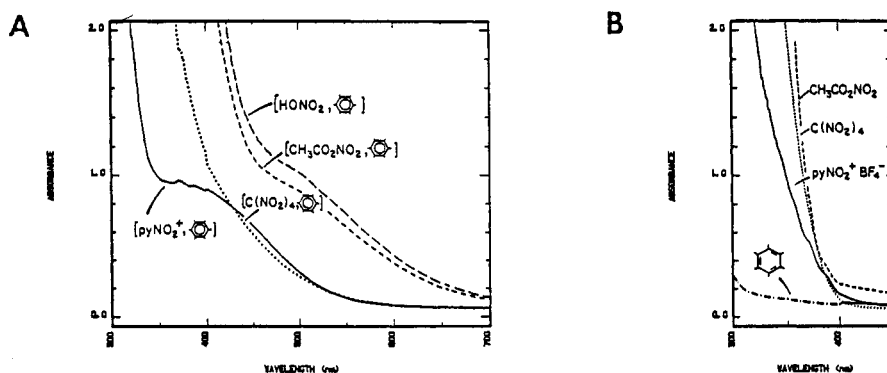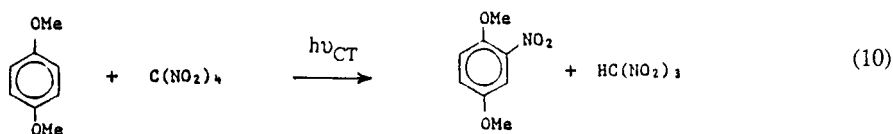
Fig. 7. (A) Comparative charge-transfer spectra of hexamethylbenzene-EDA complexes with various nitrating agents as indicated; (B) absorption spectra of the uncomplexed donor and acceptors.

p-Dimethoxybenzene (DMB) is the prototypical electron-rich aromatic donor owing to its reduced oxidation potential of only 1.30 V vs SCE. Charge-transfer excitation of the 1 : 1 DMB complex with TNM proceeds quantitatively according to the stoichiometry in eq 10. The photochemical process is hereafter referred to as *charge-transfer*

$$
\underset{\substack{OMe \\ | \\ OMe}}{\bigcirc} \; + \; C(NO_2)_4 \quad \xrightarrow{\; h\upsilon_{CT} \;} \quad \underset{OMe}{\overset{OMe}{\bigcirc}}^{NO_2} \; + \; HC(NO_2)_3 \tag{10}
$$

nitration . The excellent material balance obtained in charge-transfer nitration of DMB demands that the ion radical pair in eq 9 proceeds quantitatively to the nitration products according to the stoichiometry of eq 11 (ref. 29).

$$
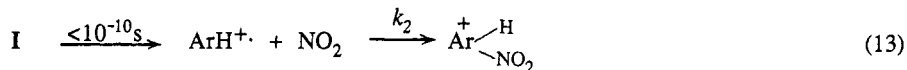[ArH^{+\cdot}, NO_2] \; \longrightarrow \; ArNO_2 \; + \; H^+ \tag{11}
$$
$$\mathbf{I}$$
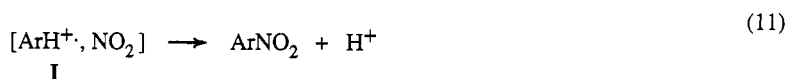
Indeed such cation radicals have been prepared from various arenes by other experimental methods, especially electrochemical oxidation (ref. 30). The arene cation radicals related to $DMB^{+\cdot}$ are weak Brønsted acids, but they are highly susceptible to nuclear addition, and the σ–adduct in eq 12 is the Wheland

$$
\mathbf{I} \; \longrightarrow \; Ar\overset{+}{\underset{NO_2}{\diagdown}}^{H} \; \xrightarrow{\; k_H \;} \; ArNO_2 \; + \; H^+ \tag{12}
$$
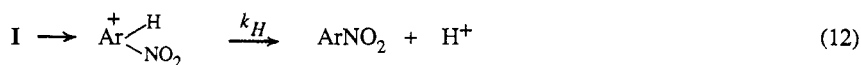
intermediate in electrophilic nitration, which is known to show no deuterium kinetic isotope effect for k_H upon deprotonation (ref. 31). Accordingly, the formation of the various isomeric Wheland intermediates will occur from the collapse of the ion radical pair in eq 12a. As such, the isomer distributions in the nitration products relate directly to the relative rates of addition to the various nuclear positions provided that it is irreversible and/or the adduct deprotonates rapidly. Thus the strong correlation observed between the spin densities at the various nuclear positions of $ArH^{+\cdot}$ and the isomeric product distribution in aromatic nitration bears directly on the mechanism of such an ion radical pair collapse to the Wheland intermediate (ref. 32) .

Although the Wheland intermediate in eq 12 has not been separately observed, the time-resolved spectral changes of the cation radical $ArH^{+\cdot}$ do provide insight as to how it is formed. Thus the relatively long lifetime of rather stable arene cation radical $DMB^{+\cdot}$ is sufficient to allow diffusive separation of the ion radical pair, $ArH^{+\cdot}$ and NO_2 , as essentially "free" species (ref. 29). The second-order process with the rate constant k_2 for the disappearance of $DMB^{+\cdot}$ then represents the "re"combination of these separated species to form the Wheland intermediate, i.e.

$$
\mathbf{I} \; \xrightarrow{\; \leq 10^{-10} s \;} \; ArH^{+\cdot} \; + \; NO_2 \; \xrightarrow{\; k_2 \;} \; Ar\overset{+}{\underset{NO_2}{\diagdown}}^{H} \tag{13}
$$

The strong solvent dependence of k_2 is largely attributed to the stabilization of $ArH^{+\cdot}$ by solvation, since it decreases with increasing solvent polarity in the order: hexane > benzene > dichloromethane. The slight negative salt effect of k_2 also accords with this conclusion. Since the common-ion salt tetrabutylammonium trinitromethanide (TBAT) has no effect on the charge-transfer nitration of DMB, the trinitromethanide is not a sufficiently strong nucleophile to intercept the associated cation radical $DMB^{+\cdot}$ in a process which would be tantamount to ion pair collapse. Aromatic nitration via the ion radical pair $\mathbf{I}$ thus proceeds with high efficiency when it is induced by the charge-transfer excitation of arene-TNM complexes. Furthermore the yields and isomeric distributions among the nitration products from various dialkoxybenzenes are strikingly akin to those obtained under the more conventional electrophilic conditions (ref. 33).   One can conclude from these observations that intermediates leading to the conventional electrophilic nitration are similar to, if not the same as, those derived by charge-transfer nitration.

Indeed, the parallel behavior extends even to those arenes in which significant amounts of byproducts are formed. For example, the direct nitration of *m*-dimethoxybenzene is reported to produce 2,4-dimethoxynitrobenzene in only poor yields (~ 30 %) (ref. 34). In addition, an unusual blue coloration develops rapidly during the electrophilic nitration of *m*-dimethoxybenzene. The same intense blue color occurs with *m*-dimethoxybenzene and TNM, but only upon the deliberate exposure of the EDA complex to CT irradiation. Among the dimethoxybenzenes, the *meta* isomer is unique in that it is the only one to develop an intense (blue) coloration upon electrophilic and/or charge-transfer nitration. The subsequent chromatography of the highly colored reaction mixture from electrophilic nitration yields significant amounts of dimethoxyphenyl dimers which are known to derive from the cation radical by arene coupling, and similar results are observed with 2,6-dimethoxytoluene and 1,3,5-trimethoxybenzene.
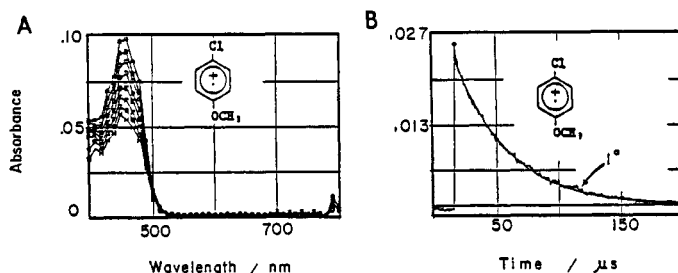

Fig. 8 (A) Time-resolved absorption spectrum of the donor cation radical following the CT excitation of the tetranitromethane complex with arene (p-chloroanisole). (B) first-order decay of the donor cation radical to the Wheland intermediate in aromatic nitration.

The anisoles (XA) with 4-fluoro, chloro and bromo substituents are substantially poorer electron donors as evidenced by their oxidation potentials E^0_{ox} that are ~500 mV more positive than that of DMB (*vide supra*). As a result, the corresponding cation radicals $XA^{+\cdot}$ are significantly more susceptible than $DMB^{+\cdot}$ to nucleophilic addition. The latter can be circumvented in the CT nitration of haloanisoles by either the addition of neutral salt in dichloromethane or the use of acetonitrile as a polar medium. Most importantly the decay of the transient cation radical $XA^{+\cdot}$ formed by the CT excitation of the EDA consistently followed *first-order* kinetics (ref.29). The clean first-order rate processes are applicable to the complete disappearance of $XA^{+\cdot}$ as established by the return of the absorbance to the baseline in Figure 8 for X = Cl. Since only CT nitration of XA occurs under these experimental conditions, the experimental first-order rate constant k_2 relates solely to the nuclear collapse of the ion radical pair in eq 14. Indeed,the regiospecificity of such an ion radical pair collapse yields the isomeric mixture of nuclear nitration

$$[, NO_2] \xrightarrow{k_1} , etc. \tag{14}$$
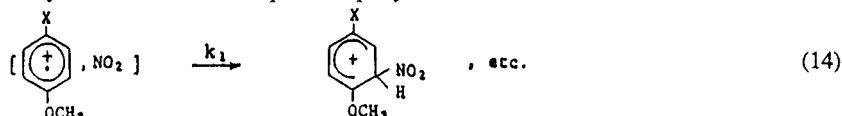
products that is essentially indistinguishable from that obtained under conventional electrophilic conditions. It is also worth noting that the byproducts from CT nitration are strongly reminiscent of the byproducts reported in electrophilic nitration of the anisoles with nitric acid. In particular, the demethylation of the methoxy group to afford nitrophenols, and the trans-bromination of 4-bromoanisole to afford a mixture of 4-nitroanisole and 2,4-dibromoanisole are both symptomatic of radical-pair collapse at the *ipso* positions. These produce the σ-adducts which are akin to the Wheland intermediates known to undergo such transformations as those in eqs 15 and 16

$$\xrightarrow{[-CH_3^+]} \longrightarrow \tag{15}$$

$$+ \longrightarrow + + H^+ \tag{16}$$
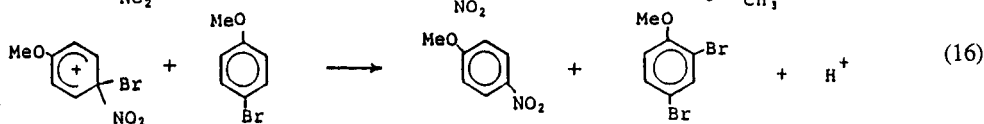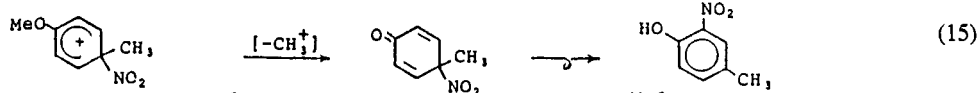
(ref. 35). The kinetics of the collapse of the ion radical pair $[ArH^{+\cdot}, NO_2^{\cdot}]$ from the representative arenes show that the decay of the spectral transients for nitration in eq 12 is a reflection of the stability of the aromatic cation radical. For example, the cation radical from *p*-methylanisole decays by second-order kinetics similar to the kinetic behavior of the long-lived cation radical from *p*-methoxyanisole. The large difference in the rates of diffusive combination with NO_2 corresponds to their relative stabilities as measured by $\Delta E^0 = 8.5$ kcal mol^{-1} of the parent arenes. There is a further, larger gap of $\Delta E^0 = 10.4$ kcal mol^{-1} which separates the stabilities of the cation radicals of *p*-methylanisole and *p*-fluoroanisole, the least reactive haloanisole. Strikingly, every member of the family of *p*-haloanisole cation radicals reacts with NO_2 by first-order kinetics. This decay pattern strongly suggests that the CT nitration occurs by the cage collapse of the geminate radical pair $[ArH^{+\cdot}, NO_2]$ prior to diffusive separation, except when the anisole cation is a relatively stabilized species such as those with the *p*-methyl and *p*-methoxy substituents.

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